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DEPARTAMENTO DE INGENIERÍA QUÍMICA

PROGRAMA DE DOCTORADO EN QUÍMICA

**Preparación de materiales adsorbentes obtenidos a partir
del char de pirólisis de residuos plásticos y biomásicos
para su aplicación en la depuración de efluentes líquidos
y gaseosos**

**Production of adsorbent materials from pyrolytic char of
biomass and plastic wastes and their application in
liquid and gas effluents treatment**

TESIS DOCTORAL

Presentada por

Ledicia Pereira Gómez

Directores

María Ángeles Martín Lara y Rafael Rodríguez Solís

Granada, 2025



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Ledicia Pereira Gómez

Departamento de Ingeniería Química

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Abstract

This doctoral thesis has been developed within the activities of the VALORCAT research group, which is part of the Department of Chemical Engineering at the University of Granada. It has received funding from the CARBOPLASTIC (TED2021-130157B-I00), AGROMITCAR (CPP2021-008551), and ADSORCHAR (PDC2022-133808-I00) projects, granted by the Ministry of Science and Innovation, Next Generation EU, the Transformation and Resilience Plan, and the State Research Agency.

The primary objective of this work is the development of adsorbent materials derived from the pyrolytic char of various types of waste. The obtained chars were activated and modified using different techniques to test their effectiveness and applicability in the adsorption of diverse contaminants in both liquid and gaseous effluents. All chars were thoroughly characterized in terms of their chemical and textural properties. Additionally, extra characteristics of some of the developed materials were analyzed to better understand their industrial viability, such as process scaling studies, techno-economic analysis, and Life Cycle Assessment (LCA).

The following is a summary of each chapter of this doctoral thesis:

Chapter 1: Introduction & Objectives

This chapter outlines the current state of waste management and regulations at both national and European levels. It highlights the need for research and innovation in waste treatment technologies, particularly for hard-to-manage waste, technologies such as pyrolysis and its variants. This chapter further details the different types of pyrolysis and emphasizes the necessity of investigating the applications of the char produced in pyrolysis, which is the main focus of this work. A general perspective on the use as an adsorbent is provided. The wastes used as precursors to develop the adsorbent in this thesis, i.e. post-consumer plastic waste, Solid Recovered Fuel (SRF), olive stone, pine and acacia splinters, and cellulose casings, were described. Furthermore, the target contaminants considered for adsorption were heavy metals and contaminants of emerging concern in the liquid phase and carbon dioxide in the gas phase. Finally, the specific objectives of this doctoral thesis are outlined.

Chapter 2: Materials & Methods

This chapter provides a detailed description of the materials, analytical techniques, and experimental methods employed. The analytical techniques used for characterizing the developed materials are first described, followed by experimental setups for producing char by pyrolysis and the techniques used for activating and

modifying the pyrolysis-derived chars. The setups for liquid and gas phase adsorption experiments are also described. Finally, the analytical techniques employed for measuring contaminants in liquid and gas phases are detailed.

Chapter 3: Char Produced from the Rejected Fraction of Post-consumer Plastic Waste

This chapter focuses on char produced from laboratory-scale pyrolysis of a representative mixture of plastics that simulates the rejected fraction of post-consumer plastics that are landfilled. The chapter is divided into two sections: application in liquid and gaseous effluents.

For liquid effluents, the char was activated with four different activating agents (Na_2CO_3 , KOH, NaOH, and K_2CO_3), then characterized and tested for heavy metal adsorption in synthetic liquid streams and real industrial wastewater. Both batch and continuous experiments were conducted. This work is presented in **Paper 1: Conversion of char from pyrolysis of plastic wastes into alternative carbons for heavy metal removal**. The results showed that the char activated with Na_2CO_3 exhibited the highest adsorption of heavy metals in batch mode, due to a higher presence of oxygenated surface groups and larger mesoporosity, which favors the adsorption of these elements. The highest adsorption capacity was obtained for lead, with a value of 40 mg g^{-1} . This material was then used in a continuous column mode with industrial wastewater from an agrochemical industry. The results indicated that under a wastewater flow rate of 2 mL min^{-1} and 0.935 g of activated char, the column effluent remained below the discharge limits for 15 minutes. The surface of the Na_2CO_3 -activated material was then modified with citric acid to increase the content of oxygenated functional groups on the surface, work studied in **Paper 2: Plastic waste to carbon adsorbent: activation with sodium carbonate and functionalization with citric acid**. Although an improvement in lead adsorption ($\sim 37 \text{ mg g}^{-1}$ to $\sim 52 \text{ mg g}^{-1}$) was observed, a techno-economic analysis concluded that the improvement was not sufficient to offset the additional treatment costs. Moreover, a life cycle analysis showed that citric acid post-modification increased the environmental impact, thus making questionable the applicability of this procedure.

For gaseous effluents, seven different chemical agents were used to activate a plastic char, followed by characterization and CO_2 adsorption tests both in static and continuous modes, work included in **Paper 3: Transforming a mixture of real post-consumer plastic waste into activated carbon for biogas upgrading**. The textural characteristics of the different activating agents were found to be $\text{K}_2\text{CO}_3 \sim \text{KOH} > \text{Na}_2\text{CO}_3 > \text{NaOH} > \text{ZnCl}_2 > \text{FeCl}_3$. Carbon dioxide adsorption isotherms also showed that the char activated with K_2CO_3 performed the highest adsorption capacity (130.2 mg g^{-1} at 273 K), followed by KOH (125.0 mg g^{-1} at 273 K), which

was confirmed in column tests. This behavior correlated with the volume of ultramicropores and oxygenated functional groups that enhance CO₂ adsorption. The material showed promising characteristics for biogas upgrading applications. Regeneration tests demonstrated that, after five cycles, the material maintained its adsorption capacity.

Chapter 4: Char Produced from Biomass and Landfill Waste at an Industrial Scale

This chapter deals with char obtained from the pyrolysis of industrial-scale waste, specifically SRF, olive stone, pine and acacia splinters, and cellulose casings. These wastes were chemically activated using KOH and physically activated using CO₂. The materials were tested for adsorption in both liquid and gaseous effluents.

Chemical activation with KOH, presented in **Paper 4: Promoting the circular economy: valorization of a residue from industrial char to activated carbon with potential environmental applications as adsorbents**, resulted in excellent porosities, with BET surface areas ranging from 776 to 1186 m² g⁻¹ and pore volumes from 0.37 to 0.59 cm³ g⁻¹, with 70-90 % micropore contribution. The materials were tested for CO₂ adsorption, with capacities ranging from 90 to 130 mg g⁻¹ at 273 K. A good correlation was found between CO₂ adsorption, microporosity, and the oxygenated functional groups developed in the samples. The adsorption capacity for heavy metals was moderate due to the limited presence of mesopores, with lead being the best adsorbed metal (~20 mg g⁻¹). Better results were obtained for contaminants of emerging concern, such as acetaminophen, caffeine, and diclofenac, with adsorption capacities ranging from 200 to 500 mg g⁻¹, making these materials attractive for final applications.

Physical activation with CO₂, considered a simpler and more environmentally friendly method, is presented in **Paper 5: On the physical activation of biomass and urban waste chars for water treatment and CO₂ adsorption**. It resulted in materials with moderate porosity between 340 and 370 m² g⁻¹, except for the SRF material (136 m² g⁻¹), and a high contribution of microporosity (up to 83 % with olive stone). Carbon dioxide adsorption was good, with the highest value being 121 mg g⁻¹ at 273 K and 100 kPa, correlated with the micropore distribution. In regeneration cycles, the materials were stable. For liquid effluent contaminants, the highest lead adsorption was obtained with the SRF material (~25 mg g⁻¹), and the activation of the pine char showed the highest caffeine adsorption (~17 mg g⁻¹). Column studies for lead and caffeine adsorption showed stable regeneration cycles after the first cycle.

Chapter 5: Scaling Up the Production of Activated Char

This chapter presents a scaling study of the activation process using K_2CO_3 for SRF material, comparing laboratory-scale activation with a pilot-scale process, which had 20 times the capacity. This work is included in ***Paper 6: Unraveling the lab-scaling up production of activated carbon from plastic-enriched waste***. The Characterization of the obtained materials revealed slight improvements in textural properties for the larger-scale materials, probably due to the agitation of the sample prepared at a rotary drum. The optimal activation temperature was found to be 750 °C, with a char: activating agent ratio of 1:0.5. A positive effect was observed from the rotary drum function provided by the pilot-scale furnace.

Chapter 6: Conclusions and Future Work

This chapter summarizes the general and most relevant conclusions of the work. The main conclusion is the demonstration of the potential use of waste materials for producing adsorbent materials for effluent decontamination, using environmentally friendly activation methodologies such as the use of carbonates as activating agents.

Resumen

Esta tesis doctoral se ha desarrollado dentro la actividad del grupo de investigación VALORCAT, perteneciente al Departamento de Ingeniería Química de la Universidad de Granada. Ha recibido financiación de los proyectos CARBOPLASTIC (TED2021-130157B-I00), AGROMITCAR (CPP2021-008551) y ADSORCHAR (PDC2022-133808-I00), concedidos por el Ministerio de Ciencia e Innovación, Next Generation EU, Plan de Transformación y Resiliencia y Agencia Estatal de Investigación.

El principal objetivo de este trabajo es el desarrollo de materiales adsorbentes a partir de char de pirólisis de diferentes tipos de residuos. Los char obtenidos fueron activados y modificados usando diferentes técnicas para probar su eficacia y aplicabilidad en la adsorción de varios tipos de contaminantes, tanto en efluentes líquidos como gaseosos. Todos los char fueron caracterizados en profundidad en cuanto a sus propiedades químicas y texturales. Además, se analizaron características extra de algunos de los materiales desarrollados que permiten conocer más en detalle la viabilidad de los materiales para su uso industrial, como son un estudio de escalado del proceso de activación, estudio tecno-económico y Análisis de Ciclo de Vida (ACV).

A continuación, se realiza un resumen de cada uno de los capítulos que componen esta tesis doctoral:

Capítulo 1: Introducción y Objetivos

Este capítulo enmarca el estado actual de la gestión de residuos y su normativa, tanto a nivel nacional como europeo. Esto permite entender la necesidad de investigación e innovación en tecnologías de tratamiento de residuos de difícil gestión, tecnologías como puede ser la pirólisis y sus variantes. A continuación, se describen los diferentes tipos de pirólisis y se indica la necesidad de investigar sobre las aplicaciones del char producido en la pirólisis, objetivo principal de este trabajo. A partir de aquí se ofrece una perspectiva general de la aplicación del char como material adsorbente. Asimismo, se describen los precursores o residuos empleados para desarrollar los materiales adsorbentes de este trabajo: fracción rechazo de residuos plásticos post-consumo, Combustible Sólido Recuperado (CSR), hueso de aceituna, astilla de pino y acacia y tripa de celulosa. Además, los contaminantes considerados para la adsorción fueron metales pesados y contaminantes emergentes en fase líquida, y dióxido de carbono en fase gas. Finalmente, se enumeran los objetivos específicos de esta tesis doctoral.

Capítulo 2: Materiales y Métodos

En este capítulo se describen en detalle los materiales, técnicas analíticas y experimentales empleadas. En primer lugar, se describen las técnicas analíticas empleadas para la caracterización de los materiales desarrollados. A continuación, se describen los montajes experimentales para la producción del char (pirólisis) y las técnicas empleadas para la activación y modificación de los char obtenidos en la pirólisis. Los montajes para realizar los procesos de adsorción en fase líquida y gaseosa también son descritos. Por último, se describen las técnicas analíticas utilizadas para la medición de los contaminantes en fase líquida y gaseosa.

Capítulo 3: Char Producido a partir de la Fracción Rechazo de Residuos Plásticos Post-consumo

En este capítulo se emplea char producido a partir de pirólisis a escala de laboratorio. El residuo precursor se trata de una mezcla representativa de plástico que se asimila a la fracción rechazo del plástico post-consumo que llega a los vertederos. Este capítulo se subdivide en dos secciones: aplicación en efluentes líquidos y aplicación en efluentes gaseosos.

Para estudiar la adsorción en efluentes líquidos, el char obtenido se activó con cuatro agentes activantes (Na_2CO_3 , KOH , NaOH , and K_2CO_3), para después caracterizarlos y probar su eficacia en adsorción de metales pesados en corrientes líquidas sintéticas y agua residual industrial real. Se realizaron experimentos tanto en modo discontinuo como en continuo. Este trabajo se presenta en el **Artículo 1: Conversion of char from pyrolysis of plastic wastes into alternative carbons for heavy metal removal**. Los resultados arrojaron que el carbón activado con Na_2CO_3 presentaba una mayor adsorción de metales pesados en modo discontinuo debido a la mayor presencia de grupos oxigenados en superficie y una mayor mesoporosidad que favorece la adsorción de estos elementos. La mayor capacidad de adsorción se obtuvo para el plomo con un valor de 40 mg g^{-1} . Este material se empleó para hacer ensayos en continuo en columna de relleno con aguas industriales procedentes de la industria agroquímica. Los resultados obtenidos indican que con un caudal de agua residual de 2 mL min^{-1} y una masa de char activado de $0,935 \text{ g}$, el efluente de la columna se mantendría por debajo de los límites establecidos de vertido durante 15 minutos. A continuación, se modificó la superficie del material activado con Na_2CO_3 con ácido cítrico para tratar de incrementar el contenido de grupos funcionales oxigenados en la superficie, trabajo estudiado en el **Artículo 2: Plastic waste to carbon adsorbent: activation with sodium carbonate and functionalization with citric acid**. Aunque se observó una mejoría en la adsorción de plomo de $\sim 37 \text{ mg g}^{-1}$ a $\sim 52 \text{ mg g}^{-1}$, tras realizar un análisis tecno-económico se concluyó que esta mejoría no es suficiente para compensar el coste de los tratamientos adicionales. Además, a través de un análisis de ciclo de vida se observó

que se incrementa el impacto medioambiental de la post-modificación con ácido cítrico, por lo que la aplicabilidad de este procedimiento es cuestionable.

En cuanto a la aplicación en efluentes gaseosos, se utilizaron siete agentes químicos diferentes para la activación del char de plástico, realizando después una caracterización además de las pruebas de adsorción de dióxido de carbono tanto en estático como en continuo, trabajo incluido en el **Artículo 3: Transforming a mixture of real post-consumer plastic waste into activated carbon for biogas upgrading**. Las características texturales empleando los diferentes agentes activantes resultaron ser $K_2CO_3 \sim KOH > Na_2CO_3 > NaOH > ZnCl_2 > FeCl_3$. Además, las isotermas de adsorción de CO_2 también muestran que el material activado con K_2CO_3 tiene una mayor capacidad de adsorción ($130,2 \text{ mg g}^{-1}$ a 273 K), seguido por KOH ($125,0 \text{ mg g}^{-1}$ a 273 K), confirmado también en ensayos de columna. Este comportamiento está correlacionado con el volumen de ultramicroporos y los grupos funcionales oxigenados que favorecen la adsorción de CO_2 . El material presenta características interesantes para su uso en enriquecimiento de biogás. Pruebas de regeneración demuestran que, tras 5 ciclos, el material mantiene constante su capacidad de adsorción.

Capítulo 4: Char Producido a Escala Industrial a partir de Biomasa y Residuos de Vertedero

En el Capítulo 4 se emplea char obtenido de pirólisis de residuos a nivel industrial, específicamente de los residuos Combustible Sólido Recuperado (CSR), hueso de aceituna, astilla de pino y acacia y tripa de celulosa. Estos residuos fueron activados de forma química usando KOH y de forma física usando CO_2 . Los materiales fueron probados tanto en adsorción en efluentes líquidos como gaseosos.

En cuanto a la activación química con KOH , presentada en el **Artículo 4: Promoting the circular economy: valorization of a residue from industrial char to activated carbon with potential environmental applications as adsorbents**, se obtuvieron excelentes porosidades, S_{BET} , entre $776\text{-}1186 \text{ m}^2 \text{ g}^{-1}$ y volumen de poros de $0.37\text{-}0.59 \text{ cm}^3 \text{ g}^{-1}$ con $70\text{-}90 \%$ de contribución de microporos. Los materiales obtenidos se probaron para adsorción de CO_2 , obteniéndose capacidades de adsorción de $90\text{-}130 \text{ mg g}^{-1}$ a 273 K . Se obtuvo una buena correlación entre la adsorción de CO_2 con la microporosidad y los grupos funcionales oxigenados desarrollados en las muestras. También se estudió la capacidad de adsorción de contaminantes en efluentes líquidos. En cuando a metales pesados, se observó una capacidad de adsorción moderada debido a la presencia limitada de mesoporos. El metal mejor adsorbido resultó ser el plomo, con una capacidad de adsorción $\sim 20 \text{ mg g}^{-1}$. Mejores resultados se obtuvieron en la adsorción de contaminantes orgánicos emergentes como acetaminofeno, cafeína y diclofenaco.

Las capacidades de adsorción obtenidas se encontraron entre 200-500 mg g⁻¹, haciendo estos materiales atractivos para su aplicación final.

La activación física con CO₂, considerado un método de activación más sencillo y respetuoso con el medioambiente, se presenta en el **Artículo 5: On the physical activation of biomass and urban waste chars for water treatment and CO₂ adsorption**. Se obtuvieron materiales con una porosidad moderada entre 340-370 m² g⁻¹, excepto para el material CSR (136 m² g⁻¹), y una alta contribución de microporosidad (hasta 83 % con hueso de aceituna). La adsorción de CO₂ fue buena, siendo la más alta de 121 mg g⁻¹ a 273 K y 100 kPa, correlacionada con la distribución de microporos. En ciclos de regeneración los materiales se mostraron estables. En cuanto a la adsorción de contaminantes en efluentes líquidos, la mayor adsorción de plomo se obtuvo con el material de CSR (~25 mg g⁻¹) y con el material de pino para la cafeína (~17 mg g⁻¹). Estudios en columna de adsorción de plomo y cafeína resultaron en ciclos de regeneración que se hacen estables después del primer ciclo.

Capítulo 5: Escalado de la Producción de Char Activado

En este capítulo se realiza un estudio de escalado del proceso de activación con K₂CO₃ del material CSR, comparando el proceso de activación realizado a escala laboratorio con el proceso realizado en un horno piloto, con una capacidad 20 veces mayor. Este trabajo se incluye en el **Artículo 6: Unraveling the lab-scaling up production of activated carbon from plastic-enriched waste**. A partir de la caracterización de los materiales obtenidos se determinó que en los materiales preparados a mayor escala se observaba una ligera mejoría en las propiedades texturales, probablemente debido al efecto de mezclado con el tambor rotativo. La temperatura óptima de activación resultó ser 750°C y el ratio char:agente activante 1:0,5. Además se observó un efecto positivo en la función de tambor rotativo que ofrecía el horno a escala piloto.

Capítulo 6: Conclusiones y Trabajo Futuro

En este capítulo se resumen las conclusiones generales y más relevantes de este trabajo. La principal conclusión es la demostración del potencial de uso de residuos para producir materiales adsorbentes para la descontaminación de efluentes empleando metodologías de activación más respetuosas con el medioambiente.

Chapter 1. Introduction and Objectives

1.1. Status of solid waste management in Europe and Spain

The European Union (EU) is undergoing a process to put the region at the front line of environmental action and green transition, setting example by becoming the first climate-neutral region in the world.

For this purpose, several policies are in development to reinforce the environmental legislative framework. ‘The European Green Deal’ represents Europe’s core strategy to ensure, by 2050, a climate-neutral, clean, and circular economy, optimizing the use, reuse, and management of resources, minimising pollution, and protecting the health and well-being of citizens from environment-related risks and impacts.

The Waste Framework Directive (WFD) is the EU’s legal framework for treating and managing waste. It introduces an order of preference for waste management called the “waste hierarchy”, shown in **Figure 1.1**, according to which, landfilling is the least preferable option, prioritising waste prevention. Two specific plans, framed within the European Green Deal, cover the topic of solid waste management to some degree, updating the WFD and setting specific targets. These are the Zero Pollution Action Plan and the Circular Economy Action Plan.

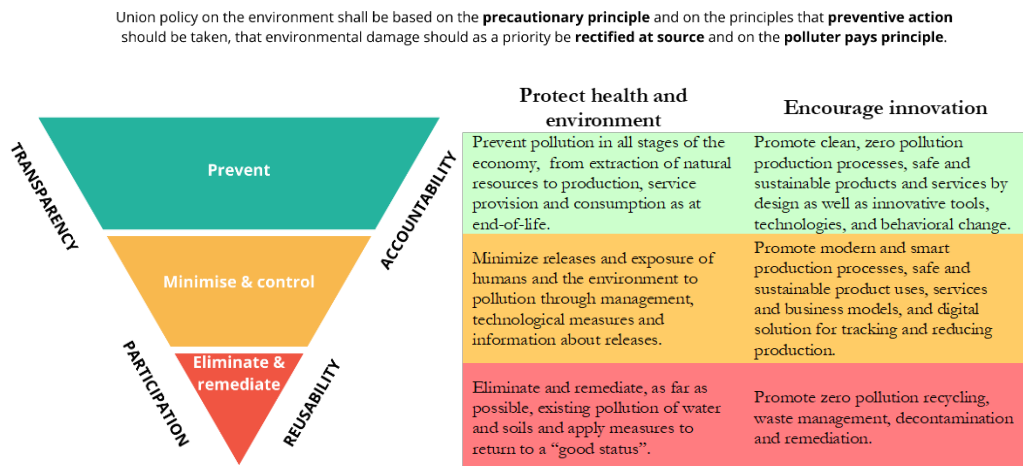


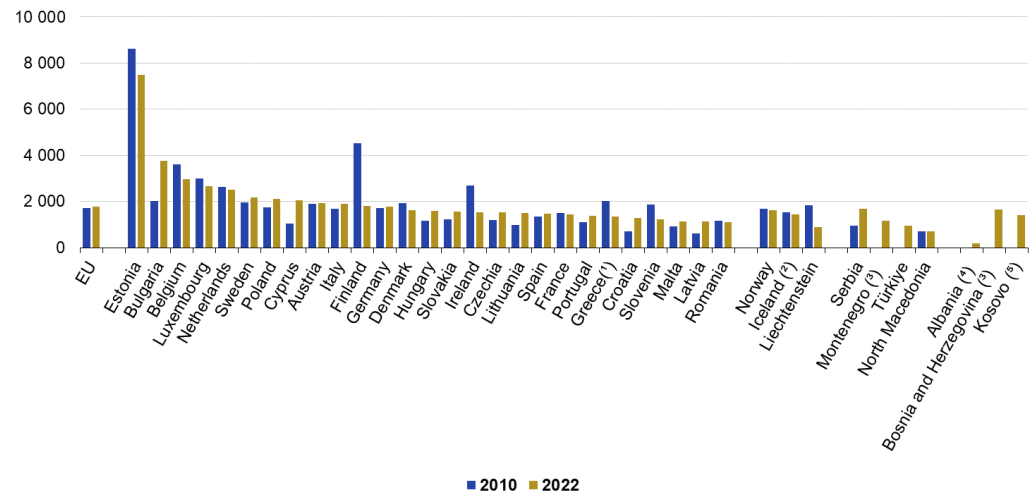
Figure 1.1. The zero-pollution hierarchy (adapted from The Zero Pollution Action Plan, EU)

The Zero Pollution Action Plan target 6 establishes that, by 2030, the EU should reduce significantly total waste generation, and by 50 % residual municipal waste.

This target considers as a baseline the data collected from the Eurostat database on waste.

In the EU, 795 million tonnes of waste were generated in 2022, including manufacturing, energy, wastewater, construction and demolition, households, and other economic activities, excluding major mineral waste. When expressed in relation to population size, the EU generated, on average, 1.8 tonnes per inhabitant of waste excluding major mineral waste in 2022.

Figure 1.2 shows the waste generation per capita during 2010 compared to 2022. It is necessary to note that the large quantity of waste generated in Estonia is related to energy production based on oil shale. Analysing **Figure 1.2**, the waste generation trend with time comparing 2010 and 2022 is, in general terms, steady or increasing; showing that the reduction targets for 2030 of reducing waste generation by 50 % will be difficult to meet. Target seems unrealistic, but with the new law enforcement, efforts in research and new technologies, it could be achievable.

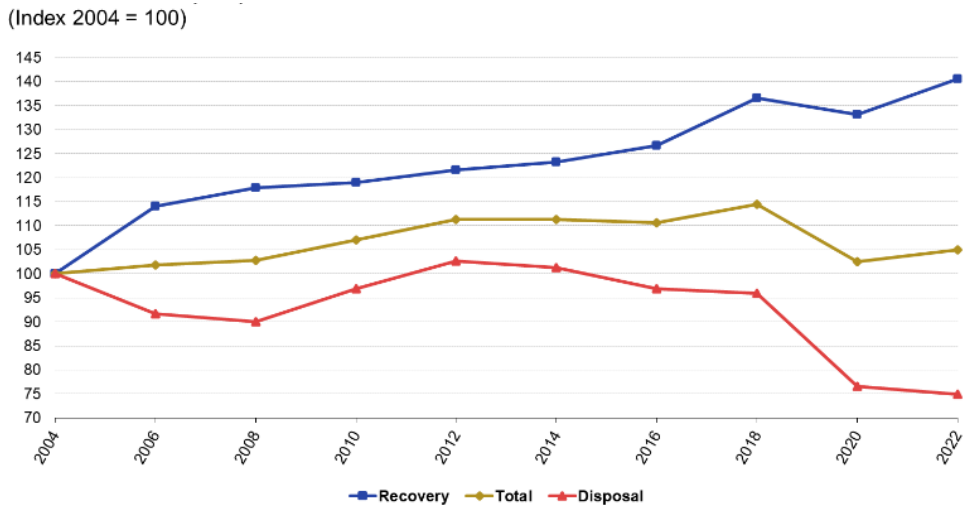


(*) provisional data. (**) data 2020. (**) 2010: not available. (**) data 2021.
(*) This designation is without prejudice to positions on status, and is in line with UNSCR 1244/1999 and the ICJ Opinion on the Kosovo Declaration of Independence.
Source: Eurostat (online data code: env_wasgen)

Figure 1.2. Waste generation in EU, excluding major mineral waste, 2010 and 2022 (kg per capita) [1]

In 2022, approximately, 1992 million tonnes of waste were treated in the EU [1]. This value does not include exported waste but includes the treatment of waste imported into the EU, meaning that treated amounts are not directly comparable with those on waste generation.

Generated waste can be recovered for different purposes such as recycling, and backfilling which refers to the use of waste in excavated areas for the purpose of slope reclamation or safety or for engineering purposes in landscaping or used as raw material in valorisation methods. On the other hand, waste can be disposed of in landfills. As seen in **Figure 1.3**, during the period 2004-2022, the quantity of waste recovered increased by 40.6 %, from 870 million tonnes in 2004 to 1223 million tonnes in 2022. On the contrary, the quantity of waste subject to disposal decreased by 25.1 %, from 1027 million tonnes in 2004 to 769 million tonnes in 2022. This reduction was achieved in a period of 18 years.



Source: Eurostat (online data code: env_wastrt)

eurostat 

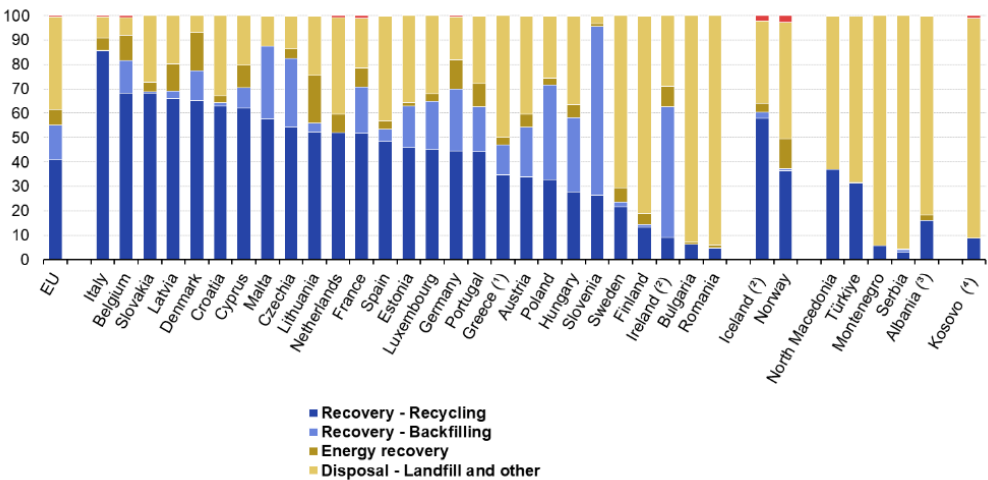
Figure 1.3. Waste treatment, EU, 2004-2022 [1]

Figure 1.4 shows the waste treatment type of recovery and disposal in percentage and by country. Spain remains in a good position in terms of recycling but there is room for improvement when it comes to waste sent to landfill.

The Circular Economy Action Plan sets specific policy areas related to chemicals, circular economy, industry (including textiles), plastics, sustainable development, and waste and recycling. In particular, the waste and recycling policy develops policies for batteries and accumulators, biodegradable waste, construction and demolition waste, end-of-life vehicles, landfill waste, mining waste, packaging waste, sewage sludge, ships, waste oil, and others. According to the EU's waste hierarchy, landfilling is the least preferable option. This policy introduces restrictions on the landfilling of all waste that is suitable for recycling or other material or energy recovery from 2030. It also limits the share of municipal waste landfilled to 10 % by 2035 and introduces rules on calculating the attainment of municipal waste targets,

requiring EU countries to put in place an effective quality control and traceability system for municipal waste landfilled.

In Spain, as seen in **Figure 1.4**, the percentage of landfilling in 2022 stands at 45 %, far from the 10 % required for 2035. The Spanish regulation, “Ley 7/2022, de 8 de abril, de residuos y suelos contaminados para una economía circular”, endeavor is to adapt EU requirements to the Spanish escenario. This regulation introduces two new taxes at the national level: a special tax on non-reusable plastic packaging and a tax on landfilling and incineration. The marketing of single-use plastics such as straws, cotton buds and expanded polystyrene cups is forbidden. New rules on packaging design are enforced: bottle caps must remain attached to the bottle during the consumption stage and all PET bottles must contain, at least, 25 % of recycled plastic. From 2030, all bottles must contain, at least, 30 % of recycled plastic. The landfilling of excess unsold non-perishable products, such as textiles, toys, and electric devices, is forbidden. These products will be managed through regular reutilisation channels including donations. If this is not possible, the following option must comply with the waste hierarchy. Apart from existing separate collection streams, it is mandatory to implement new separate collection streams such as organic urban waste, textiles, cooking oil, hazardous domestic waste, and bulk waste.



(*) provisional data. (**) 2020 value. (**) data 2021.

(*) This designation is without prejudice to positions on status, and is in line with UNSCR 1244/1999 and the ICJ Opinion on the Kosovo Declaration of Independence.

Source: Eurostat (online data code: env_wastrt)

eurostat

Figure 1.4. Waste treatment by type of recovery and disposal, 2022 (% of total treatment)[1]

In this scenario, innovation in new waste valorisation techniques is needed to achieve the proposed waste management goals.

1.2. Pyrolysis as a waste valorisation technology

Pyrolysis is a thermochemical process that converts waste into valuable products such as gases (syngas), organic vapours (liquid oil), and a solid product (char), at moderately high temperatures ($> 400\text{ }^{\circ}\text{C}$) in a deoxygenated environment [2–4]. Pyrolysis breaks down the feedstocks into basic organic molecules. The condensable part of the produced gas is named oil and is considered the most valuable product obtained in the process, indeed, most research is focused on the maximization of oil production and its purification and upgrading [5]. Common organic molecules obtained are volatile acids, alcohols, ketones, aldehydes, phenols, esters, sugars, furans, hydrocarbons, multifunctional compounds, as well as large molecular oligomers [6]. The oil can be used as fuel or as building blocks to obtain other products in the chemical industry.

Pyrolysis is among the most promising methods for handling low-grade waste [7]. Low-grade waste attends to the type of waste which is difficult to valorise through other traditional methods due to its poor quality and/or heterogeneity. Pyrolysis feedstocks might have a natural origin, namely biomass, such as wood, animal waste, agricultural residues, sewage sludge or algae. In this case, pyrolysis products will be branded as “bio”. Alternatively, other feedstocks such as plastics or landfill waste, can be used, although their products are not classified as “bio”. Compared to other waste management methods such as gasification, incineration, and landfilling, pyrolysis is less harmful to the environment [8].

Landfill sites occupy large areas of land, which also come with high taxes and a substantial risk of harmful plastic additives leakage, e.g., dimethyl phthalate in PVC, bisphenol A in polycarbonates, into soils and groundwater [9]. Energy recovery techniques such as incineration and gasification break down plastics and significantly reduce their volume. The by-products, e.g., heat and gases, can be used as sources of energy. However, incineration is environmentally unfriendly, as it requires high amounts of energy to generate enough heat for breaking down the plastics [10] and produces large quantities of atmospheric carbon dioxide (CO_2) and particulate emissions containing polycyclic aromatic hydrocarbons (PAHs) [11].

Having said that pyrolysis is among the most promising methods for handling low-grade waste, shortcomings exist when implementing pyrolysis at full scale, explaining why pyrolysis is not widely used as a waste valorisation industrial process in the current development state.

The feeds of the pyrolysis process tend to be varied and heterogeneous, leading to variations in the end-product quality. Wax, toxins, and contaminants need to be removed, and the obtained oils must be refined to obtain products with similar chain lengths. Nonetheless, this is a two-fold topic, being also seen as a benefit since the

technology allows to treat heterogeneous waste streams that would otherwise be discarded in landfill sites. Another issue is the acidic and oxygen-sensitive nature of pyrolysis oils which can damage the process equipment. In terms of environmental impact, the process is energy intensive and can emit carbon monoxide, nitrogen oxides, and sulphur dioxide. It is necessary to find cost-effective equipment and processes to make pyrolysis competitive against other valorisation techniques. New advances in pyrolysis techniques are enlightening the path to approach a fully scalable technology.

1.2.1. Pyrolysis techniques

The different types of pyrolysis processes can be divided into three main groups: conventional approaches, advanced approaches, and emerging approaches. The parameters that are used to characterise each type of pyrolysis include pyrolysis heating rate, temperature and time, residence time of volatiles, and feedstock size [12].

The yield of each pyrolysis product can be increased depending on the process conditions: (i) char—low temperatures and heating rates; (ii) liquid products—average temperatures, high heating rates, and short gas residence time; and (iii) gas—high temperatures, low heating rate, and long gas residence time [13].

1.2.1.1. *Conventional approaches*

Slow pyrolysis

The objective of slow pyrolysis is the production of char, the oil and syngas being considered as by-products. The operation conditions are defined as moderate temperatures (300 – 700 °C), heating rate below 1 °C s⁻¹ and long residence time (>5 min). Usually, batch processes and drum reactors are used. When biomass is used as feedstock, cellulose and hemicellulose are destructured at high temperatures, decreasing the char yield. For this reason, it is recommended to use a particle size from 5 to 50 mm [12].

Intermediate pyrolysis

The advantage of using intermediate pyrolysis is the generation of oil with reduced viscosity, and low tar concentrations [14]. The operation conditions vary between residence time of 2 – 4 s and process temperature < 500 °C [15]. The liquid fraction (40 – 60 %) is the main product, followed by gases (20–30 %) and solid char (16 – 25 %) [12].

Fast pyrolysis

The typical operational conditions are temperatures from 450 to 800 °C, and short residence time, from 0.5 to 10 s [16]. These high process temperatures and short holding times prevent volatiles from taking part in the secondary reactions and inhibit the primary products from the cracking reactions enhancing oil yields. Fixed and fluidized beds are the most used equipment at large scale. Fast pyrolysis requires a high rate of heat transfer, which can be maximised by using a fine particle size feedstock (< 1 mm) [17].

Flash pyrolysis

Flash pyrolysis uses greater heating rates compared to fast pyrolysis. Typical operational parameters are process temperatures from 800 to 1200 °C, particle size < 0.1 mm, heating rates > 1000 °C s⁻¹ and residence times < 2 s [14]. The size of the particle needs to be small (<0.1 mm). Flash pyrolysis eliminates the formation of char.

1.2.1.2. *Advanced approaches*

Catalytic pyrolysis

Catalysis is used to encourage certain types of reactions in the process being the principal objective to deoxygenate pyrolytic vapours and synthesise aromatic hydrocarbons. Depending on how the catalyst is placed in the process, two types of processes can be defined. The first is an in-situ catalytic process, where the feedstock is blended with the catalyst material by using wet or dry mixing [18]. In-situ catalytic pyrolysis promotes the formation of liquid and gas products and inhibits tar formation [19]. An important drawback is the loss of catalytic activity due to coke formation [20]. Ex-situ catalytic pyrolysis relies on a divided reactor. The feedstock is placed at one location and the catalyst is placed downstream of the reactor. The feedstock is initially converted into vapour, which then passes by the catalyst and is transformed into oil. Common catalysts are alkali and alkaline earth metals, zeolites, iron, and quartz sand. Catalytic pyrolysis advantages include lower process temperatures and energy requirements, and the obtention of oil with fewer impurities.

Co-pyrolysis

Synergistic interactions among feedstocks can enhance pyrolysis performance since the physical and chemical properties vary considerably [21]. Existing equipment with no modification can be used for co-pyrolysis. The selection of suitable co-feedstocks must consider the H/C ratio. A H/C ratio improves the production of hydrocarbons and the formation of stable intermediates. The major

disadvantage of the co-pyrolysis process is the requirement of an additional pre-treatment unit.

Microwave-assisted pyrolysis

The heat transfer in conventional pyrolysis occurs first via convection from high-temperature gas to the feedstock particles. Then, the heat is transmitted via conduction from the surface of the particles to the core. Feedstocks usually have low thermal conductivity, therefore, a temperature gradient is created. On the contrary, microwaves penetrate the feedstock, and the microwave energy transforms into thermal energy inside the particles.

Hydropyrolysis

This process uses pressurized hydrogen (>10 MPa) to convert feedstocks into pyrolytic oil with high-quality [22]. Hydropyrolysis advantages include inhibition of char formation, oil with low oxygen content and introduction of additional hydrogen in the oil [17]. In addition, unsaturated hydrocarbon production is reduced.

Autothermal pyrolysis

Conventional pyrolysis is an endothermic process with high requirements of heat and an effective heat flux. This is considered the most important issue in process scale-up [23]. The heat demand is usually calculated in volumetric terms, but heat transfer is a surface phenomenon, and this is the limiting step, resulting in heat demand exceeding the heat supply for larger reactors [24]. The autothermal pyrolysis process has been developed to overcome the heat transfer limitation during scale-up. To balance the heat demand, some of the heat from the feedstock or pyrolysis products is consumed. Another option is to supply the reaction zone with limited oxygen, allowing the organic matter to react with oxygen and release the heat required for the primary and secondary processes. Process scale-up is made easier in autothermal processes because the chemical reactions, not the available heat, govern the process. The reactions involving oxygen can change the pyrolysis products, but the main goal of adding a small amount of oxygen to the system is to encourage the oxidative oxygen-char and oxygen-volatile interactions. In order to achieve the process's heat needs, vapour products typically burn [25].

1.2.1.3. Emerging approaches leading to sustainable integrated systems

The integration of various technologies promotes the circular economy and improves resource recovery by eliminating the drawbacks of each individual process [26].

Integration of pyrolysis with anaerobic digestion

Recalcitrant compounds, such as lignin, in biomass are difficult to break down by anaerobic microorganisms leaving energy-containing compounds in the digestate [27]. The remaining digestate after the anaerobic digestion can be subjected to pyrolysis, reducing the cost of waste management, and allowing optimal use of digested residues to produce energy and products [27]. In addition, organic pollutants present in the digestate are destroyed.

Bifunctional catalyst-sorbent materials in pyrolysis

One drawback of pyrolysis processes is the CO₂ emissions. Newly developed materials can integrate CO₂ sorption and catalytic functionalities. Incorporating a bifunctional material in the system minimises mass transfer issues and reduces the cost of the material [28]. Bifunctional materials can help the gas diffusion, bringing the catalyst site, where the product is formed, close to the sorbent side, where CO₂ is adsorbed.

1.2.2. Industrial pyrolysis plants currently operating worldwide

Although chemical recycling is an interesting option to convert waste into a resource, the reality is that it is not widely used at present. The number of chemical recycling plants in Spain and Europe is very limited, both in terms of number and production capacity. It is estimated that currently only 0.2 % of post-consumer plastic waste collected in Europe is recovered through chemical recycling processes [29].

Table 1.1 shows industrial pyrolysis plants currently working worldwide. The Empyro plant located in Hengelo, Netherlands, started its operation in 2015 and currently treats 5 tons per hour of wood residues. The plant is looking into using other feedstock types.

The Red Arrow Facilities are a series of 5 commercial pyrolysis units in Rhinelander, Wisconsin. The company was a specialty chemical company purchased by the Kerry Group in 2015. The plant processes 40 tons of wood per day. These plants are used by Kerry Group to produce chemicals for the food industry and heating fuels. Liquid smoke, generated by the controlled pyrolysis of hardwood sawdust, is used to flavour, and give anti-microbial benefits across a range of applications, from beverages to desserts.

Battelle's catalytic pyrolysis technology is an ex-situ pilot scale system that can treat pine and corn stover. The pyrolysis vapour is directed to a catalytic reactor before it is condensed to form a bio-oil. Battelle's expertise is in developing innovative processes and catalysts. They have developed several types of vapour phase catalysis reactors, including (moving and fixed) packed bed reactors, catalyst-

coated ceramic monolith type reactors, catalyst-coated ceramic foam type reactors and a novel moving bed reactor. The latter mechanically move the granular catalyst and contacts it with the pyrolysis vapour.

Table 1.1. Worldwide operating pyrolysis plants (adapted from [30])

Plant name	Location	Units	Capacity kg h ⁻¹
Red arrow, WI	USA	Circulating fluidised bed	1700
Dyna Motive	Canada	Bubbling fluidised bed	400
Bio-alternative	USA	Fixed bed	2000
Batelle	USA	Catalytic pyrolysis technology	1000
Empyro	Netherlands	Flash pyrolysis	5000
Bioliq	Germany	Fast pyrolysis	500
BEST Energy	Australia	Bubbling fluidised bed	300
Fortum	Finland	-	350
IRR Manufacturing	South Africa	-	1000

Focusing on the Spanish scenario, existing pyrolysis plants are listed in **Table 1.2**. Plastic Energy operates two plants in Seville and Almeria since 2016 using the same TACTM patented technology which treats end-of-life plastics [31]. Plastic Energy has also announced the construction of a second pyrolysis plastic recycling plant in Seville in cooperation with Total Energies. It will be operational by 2025 with a treatment capacity of 33000 tonnes of end-of-life plastic waste per year. The recycled material obtained will be used for food packaging [32]. Although Plastic Energy leads the sector, other plants are in operation such as Ecoparque in Toledo which employs flash pyrolysis of solid recovered fuel (SRF) or Hintes Oil Europa in Almería which treats SRF and other agricultural and industrial residues.

Table 1.2. Pyrolysis plants operating in Spain (adapted from [29])

Plant name	Location	Capacity tonnes year ⁻¹
Plastic Energy	Seville	5500 (*)
Plastic Energy	Almería	5500 (*)
Ecoparque	Toledo	2300 (*)
Hintes Oil Europa	Almería	3600 (*)

*Tonnes of pyrolysis oil produced per year

1.3. Char applications

1.3.1. Turning pyrolytic char into a valuable resource

The char yield in a pyrolysis process varies from 10 to 35 %. Depending on the composition and physical properties of char, it can be used in different industrial processes [13]. Char is considered as a subproduct of pyrolysis since the main objective is the production of valuable oils. However, it is necessary to find applications for this material in order to avoid environmental impacts and improve the economic viability of pyrolysis.

1.3.2. Fuel

Biomass-derived chars show energy density values similar to those of fossil fuels, being good candidates in electricity or heat production plants with only minor drawbacks compared to fossil fuels due to present impurities.

Biomass-based char can be used in boilers to produce direct heat and/or steam to generate electricity; but co-firing with more conventional fuels often presents higher efficiency, than when used alone. In addition, this solution often decreases the initial investment, since already existing facilities are applied [33].

1.3.3. Soil remediation

This application has been widely studied for biomass-derived chars or biochars. For plastic or urban waste-derived char, the development of this application has been slower due to the potential presence of hazardous chemicals. Despite these challenges, the interest in demonstrating the efficacy of these materials in soil remediation has increased [34].

Biochar helps to improve soil fertility, nutrient retention, and soil structure, promoting plant growth and productivity. Its porous structure and high surface area provide habitat for beneficial microorganisms and facilitate water retention, reducing soil erosion. Moreover, biochar acts as a carbon sink, sequestering carbon in the soil and mitigating greenhouse gas emissions. It also can immobilize heavy metals and organic pollutants through adsorption, reducing their bioavailability and preventing leaching into groundwater. In addition, biochar-amended soils present enhanced cation exchange capacity, buffering capacity, and pH regulation, making them more resilient to environmental stressors and fluctuations [34].

1.3.4. Engineered materials

The properties of char materials have been exploited in many sectors of science and technology due to their excellent properties and surface modifications to get the specific properties, which make them effective in different fields, such as

supercapacitor electrode materials, batteries, solar cells, catalyst supports, drug delivery, bioimaging, aerospace, and medicinal biology.

In the medical field, research has been developed on the substitution of commercially employed fluorescence tags in bacteria sensing, by carbon materials named carbon quantum dots, acting as sensors for microbiological control [35].

Activated carbon is widely used in energy storage and as an electrode in capacitors because of its large specific surface area, large pore volume, moderate cost, and appropriate electrical properties with high capacitance values [36].

Another notable application for char is in solar membrane separation processes. Due to its hydrophobicity nature, gas permeability, and high interfacial evaporation rate, char materials can be used as a separation device, for example in seawater desalination [37].

Activated carbon can be also used as support for metal catalysts. Its use facilitates the dispersion and stabilization of small metal particles on its surface. Compared to bulk metal catalysts, activated carbon-supported systems offer several advantages, including a higher surface area of catalytically active atoms. Additionally, the inert carbon surface allows adjustment of the pore size distribution and the surface chemical properties in terms of polarity and hydrophobicity. Metal particles can even be recovered by burning the carbon support. However, less than 1 % of the worldwide produced activated carbon is used as catalyst support, possibly because activated carbon particles are difficult to reproduce due to inconsistent carbon precursor compositions [38].

1.3.5. Adsorbent materials

The prime application of char is as an adsorbent and has gained attention due to the laudable textural properties these carbonaceous materials may reach after a convenient activation [39].

The properties of the char can be improved for adsorption purposes by enhancing its surface area and porosity, using chemical or physical activation. Several literature reviews examining advancements in chemical and physical activation and providing a comprehensive and up-to-date theoretical framework on this subject are found in various works [39–43]. The surface of the char can also be functionalised by adding special functional groups that may have special interactions with the target pollutant. This is named surface modification or functionalisation.

1.3.5.1. Chemical activation

For chemical activation, the char is impregnated or mixed with chemical agents which react with the carbon and oxygen contained in the char. Common chemical activation substances found in the literature include alkalis like NaOH and KOH.

When using KOH, the following reactions occur (R1.1-R1.5) [44]. The KOH reacts with carbon leading to potassium metal salts, potassium carbonate, and gases and vapours (H_2O , H_2 , and CO_2) (R1.1 and R1.2). Potassium carbonate further oxidates and reacts with carbon producing extra gases (CO and CO_2) (R1.3, R1.4, and R1.5). Both the reactions with carbon and the gas formation are responsible for the formation of a highly porous structure in the char. The generated vapour and gases act as a physical activation while the reaction with carbon directly creates cavities.



For NaOH, the reactions follow the same pattern and can be summarised in the following reaction (R6) [40]:



Also, chemicals like potassium carbonate (K_2CO_3) zinc chloride (ZnCl_2), phosphoric acid (H_3PO_4), and sulphuric acid (H_2SO_4), among others, have been used in the preparation of activated carbons.

If using K_2CO_3 , the reactions are the same intermediate reactions as when using KOH (R3, R4 and R5). The difference between the K_2CO_3 and KOH lies in the moment when the oxidation of the carbon material happens, which starts at over 600-700 °C for K_2CO_3 [45], whereas the reaction of KOH with the carbon precursor starts at lower temperatures (~ 400 °C) [46].

Concerning the use of chlorides (neutral activating agents), the main mechanisms for pore formation are oxidation, template, and gasification [47].

1.3.5.2. Physical activation

Physical activation is considered a greener and simpler method compared to chemical activation. There is no need for chemicals handling and there are fewer parameters to be controlled in the process [48].

The most frequently used activating agents are CO₂ and steam. The porosity formation is formed when CO₂ and/or steam react endothermically with the carbon species according to the following oxidation reactions [49]:



Steam is a more reactive agent than carbon dioxide, causing a faster reaction (higher reaction rate) with the carbon species [50]. However, activated carbons prepared by carbon dioxide exhibit larger micropore volume and narrower micropore size distribution than those prepared by steam activation [51].

1.3.5.3. Surface modification or functionalisation

The tailoring of the surface in terms of chemical interactions, i.e. with oxygenated groups, has been reported to boost the adsorption performance as a result of specific interaction between acidic centres of the carbon and the basic point of the adsorbate molecule, the latter enhancing the ability to retain pollutants such as organic molecules and, therefore, the overall performance of the material. However, in the case of heavy metals, the nature of the metal defines their preference for certain groups. For example, Pb²⁺ tends to be adsorbed on the π -electron cloud in the basal planes of the graphitic surface of carbon materials whereas other cations such as Ni²⁺ and Zn²⁺ are adsorbed on oxygen functional groups [52]. Additionally, a high impregnation ratio of activated carbon with a specific metal-chelating agent can enhance the selectivity of the carbon towards that metal. This allows for efficient removal of the targeted pollutant while minimizing interference from other contaminants present in the wastewater. However, there is a limit to the impregnation ratio beyond which the adsorption capacity starts to decrease. This is because an excessive impregnation ratio can lead to pore blockage and hinder the accessibility of the pollutants to the functional groups on the carbon surface [39].

Examples of substances used for surface modification include acids such as nitric, sulphuric, or citric acid, ammonium persulphate, or hydrogen peroxide. Acidic functional groups are highly favourable for heavy metal removal from water since metal ions tend to create metal complexes with the negatively charged acid groups [53].

Physical methods also exist for surface modification, being the most popular microwave treatment. This method leads to homogeneous and quick thermal reactions. Other advantages include: the energy flows from the inside out, there is no need for direct contact between the microwave source and the material, or, in other words, no heat convection is needed leading to energy and time savings [53]. The major outcome of microwave modification is pore enlargement.

1.3.5.4. Effect of process parameters on activation

Numerous studies demonstrate the impact of activation temperature on the textural properties of activated carbons during the synthesis process both in chemical and physical activation. The activation temperature significantly impacts surface properties like BET surface area, pore volume, etc., with an increase in temperature boosting these characteristic parameters. However, a rise in the activation temperature generally results in a solid yield reduction [54].

In chemical activation, the porosity is influenced more by the activation temperature than its duration. In contrast to chemical activation, the porosity of the physically activated carbons is greatly influenced by the activation time. The higher the activation temperature or the longer the activation time, the greater the porosity depending on the strategy followed [40].

The ratio of activating agent vs char is an important factor to consider. In general terms, if this ratio is too high, the tendency is that the porosity and surface area decrease due to the formation of macropores instead of micropores, which might be detrimental to the adsorption process [55]. Best results are obtained with moderated ratios activated agent vs char such as 1:1 or 2:1 [40].

1.4. Raw Materials

The following section describes the main features of the raw materials or feedstocks used in the pyrolysis process where the char materials object of this thesis was obtained.

1.4.1. Rejected fraction of post-consumer plastic

Post-consumer plastics represent an abundant reservoir of carbon that can be effectively converted into useful materials through pyrolytic techniques [56]. Plastics are essential in modern life, offering outstanding properties for applications in packaging, construction, motoring, electronics, or agriculture sectors. Every year, 381 million tons of plastic waste are generated worldwide, which is expected to double by 2034 [2]. It is necessary to develop efficient reduction, reuse, and recycling strategies to reduce waste production, which will directly impact carbon dioxide emissions, and tackle climate change and ecological problems [57,58].

According to Plastics Europe’s biennial “Circular Economy for Plastics – A European Analysis” report, published in March 2024, it is estimated that 32.3 Mt of post-consumer plastic waste was collected in 2022 in Europe, as seen in **Figure 1.5**. The report shows that the share of post-consumer plastics waste collected separately is higher compared to mixed collection streams. Recycling rates for separately collected plastics are 13 times higher than those collected via mixed streams. In the case of plastic packaging, post-consumer waste is currently almost only recycled if collected separately.

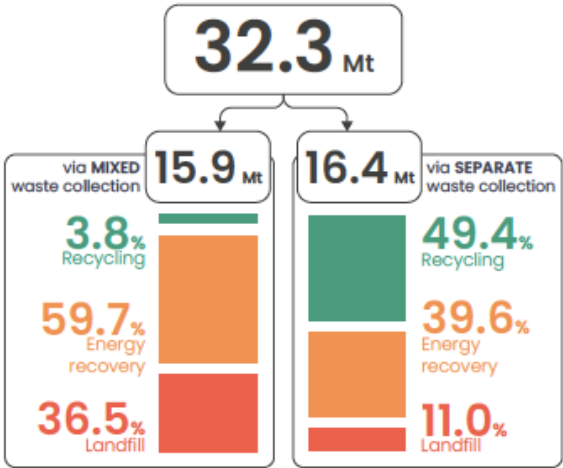


Figure 1.5. Post-consumer plastic waste collection and treatment in Europe during 2022 [59]

According to **Figure 1.6**, although the recycling rate of plastics is higher than the rate sent to landfilling, still 23.5 % is not recycled.

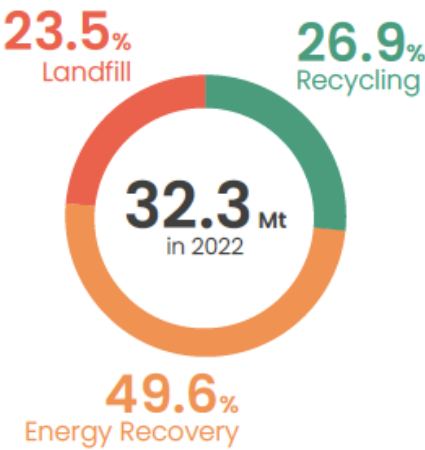


Figure 1.6. Post-consumer plastics waste treatment in Europe in 2022 (EU27+3) [59]

Ideally, plastic materials should remain longer in use following the circular plastics economy model shown in **Figure 1.7**, and this is where chemical recycling and pyrolysis enter.

Circular plastics economy

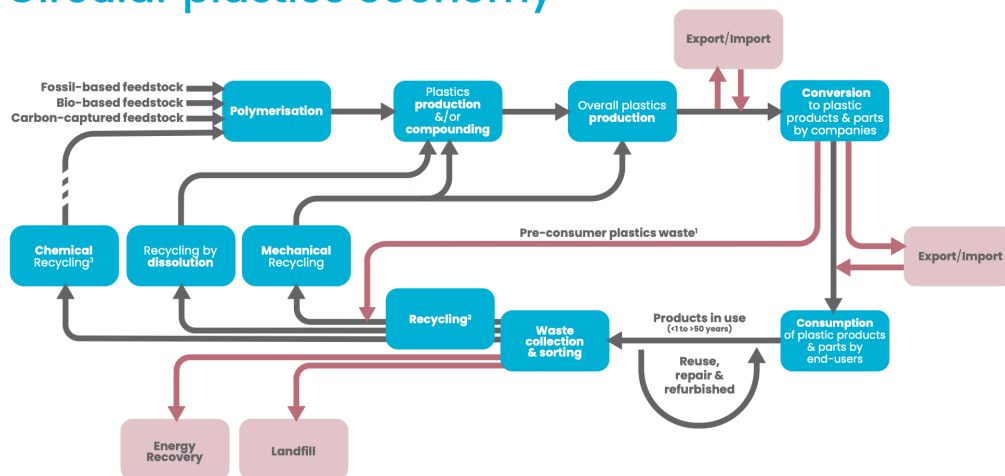


Figure 1.7. Pathway to a circular plastics economy [59]

The post-consumer mixed plastic streams that end up in municipal solid waste (MSW) treatment plants are initially subjected to intensive sorting based on plastic type before further reprocessing. The separated plastics are usually mechanically recycled, but the rejection stream of the sorting process, which possesses low quality for mechanical recycling, currently ends up in landfilling or incineration.

A characterization of the rejected fraction of mixed plastic waste from the MSW treatment plant of Granada was thoroughly performed within previous research projects developed by the VALORCAT research group, resulting, on average, percentages of 55 % of polypropylene (PP), 8.6 % of polystyrene (PS), 10.1 % of expanded PS (EPS), and 27.2 % of film [56,60]. To obtain homogeneous and reproducible samples, the mixture was replicated at a laboratory scale.

1.4.2. Solid Recovered Fuel (SRF)

The MSW usually undergoes several selection processes using different mechanical means in a treatment plant, where recovered materials (metals, plastics, glass, etc.) have enough quality to be recycled. However, a rejected stream has historically been used as fuel for energy recovery by direct combustion [61]. Therefore, this stream has been branded as solid recovered fuel. This stream is characterised for being highly heterogeneous and it might also be subjected to alternative uses rather than combustion. Following the efforts of the European Union to properly manage waste streams, a European standard was developed in

2021 (EN ISO 21640:2021) aiming to classify and specify the properties of this sort of waste. This document facilitates efficient trading and safe use of this material.

According to this standard, SRF is classified into five groups based on limit values for three characteristics: an economic characteristic (net calorific value), a technical characteristic (chlorine content) and an environmental characteristic (mercury content). The classes also impose limitations on what can be called SRF restricting it with a minimum net calorific value as well as maximum values of chlorine and mercury.

The permitted origins of this waste are also specified in the document, being a mandatory rule that the material is not suitable for recycling. The main origins are non-hazardous industrial waste (manure from agriculture or rejected fibre from the paper industry), non-hazardous construction and demolition waste, non-hazardous from waste management facilities, non-hazardous wastes from recycling facilities, non-hazardous municipal solid waste and similar non-hazardous commercial waste and non-hazardous waste not otherwise specified in the list. The origin of the SRF material studied in this thesis is municipal solid waste. **Figure 1.8** shows a sample of the SRF material received from the industrial pyrolysis plant.



Figure 1.8. Image of the SRF feedstock

1.4.3. Olive stone

One of the most significant industries in the world is the olive oil sector. Around 11×10^6 ha of land are used for olive tree agriculture worldwide, yielding more than 20×10^6 t of olives annually. Most of these olives will be used to make olive oils. Olive stones, various pomaces, and debris from olive pruning are the primary by-products of the olive oil industry. One hectare of olive groves produces more than five tons of these by-products per year in cultures with traditional and intense typologies. Environmental issues may arise from the field's disposal of these by-products. Still, there is a lot of potential for these by-products (biomasses) to be used as a source of energy and high-value goods. Every year, the olive industry produces about 30000 t of olive stones [62]. **Figure 1.9** shows an image of olive stones used in this work.



Figure 1.9. Image of the olive stone feedstock

1.4.4. Pine and acacia splinter

Regarding the ideas of the bio-economy and circular economy, wood offers several benefits. It is a biodegradable, naturally occurring, renewable material with exceptional mechanical and thermal properties. Compared to materials made from inorganic or fossil resources, wood products typically have far less of an impact on the environment throughout the manufacturing and end-of-life phases. Furthermore, wood does not compete with food like resources of agricultural origin do. As a result, since the start of the twenty-first century, wood has been used more for new purposes like energy generation, construction materials, chemicals, etc [63].

Although wood is a natural material, waste wood generally contains additives (glues, varnishes, and paints), various pollutants (wood treatment products and heavy metals), and contaminating materials (glass, plastics, metals, etc.). This heterogeneity greatly complicates recycling processes. Pyrolysis represents a great option for these types of waste. **Figure 1.10** shows an image of the splinter feedstock received from the industrial pyrolysis plant.



Figure 1.10. Image of the splinter feedstock

1.4.5. Cellulose casings

The traditional intestinal casings are more costly than the artificial ones in developed countries. As a result, only luxury meat products may still employ natural casings. In addition to causing financial loss, sausage degradation poses a major risk to consumer health. Because of their consistent layer thickness, rigidity, and shape,

the artificial casings are less likely to break and are, therefore, more suited for filling. Because they are inexpensive, readily available, and have advantageous functional qualities like good tensile and tear strength, good barrier qualities to O₂, aroma compounds, and heat seal ability, petrochemical-based plastics like polyolefins, polyesters, and polyamides have become more and more popular as packaging materials [64].

On the contrary, they have an impoverished water vapour transfer rate, and most significantly, they are fully nonbiodegradable and, hence, contribute to environmental degradation, which poses major ecological difficulties. However, there are bio-based substitutes made of cellulose and collagen. Even these edible coatings can shield food items from oxidation of nutrients, light-induced alterations, microbial development on the surface, and moisture migration. In addition to serving as transporters of active ingredients (antioxidants, antimicrobials, colours, and flavours), edible coatings can serve as barriers against oils, gases, or vapours [64]. **Figure 1.11** shows an image of the cellulose casings feedstock received from the industrial pyrolysis plant.



Figure 1.11. Image of the cellulose casings feedstock

1.5. Target pollutants for environmental remediation

1.5.1. Heavy metals

Among the most dangerous components within industrial wastewater, heavy metals stand out as a significant concern owing to their pronounced toxicity, bioaccumulation potential, and persistent nature in natural environments. Unlike organic contaminants that may degrade over time, heavy metals resist natural breakdown processes, posing substantial and long-term health risks to humans and ecosystems alike [65,66].

Lead, for instance, is one of the most encountered heavy metals in contaminated water sources, often introduced through activities such as metal mining, corrosive lead batteries, paper and glass production, and cleaning processes [67]. The presence

of lead in water bodies is associated with severe health risks, including cardiovascular diseases, kidney failure, liver cirrhosis, intestinal disorders, mental retardation, and increased susceptibility to kidney and liver cancers [68].

Another significant contaminant is cadmium, which, despite its lack of any known physiological role in the human body [69], is extremely hazardous. Sources of cadmium pollution include battery electroplating, photovoltaic cell production, metallurgical operations, and textile manufacturing [70]. Its high toxicity and tendency to bioaccumulate make cadmium a formidable threat, with health effects ranging from bone marrow damage, calcium depletion, hypertension, and kidney failure to sensory loss and central nervous system damage, even at low concentrations [71,72].

Copper, the third most consumed metal globally [73], also poses serious environmental and health challenges. Widely used as an algicide in ornamental ponds, water reservoirs, and industrial applications [74], copper often finds its way into aquatic ecosystems through wastewater discharge, threatening water quality [75,76]. High copper concentrations in drinking water have been linked to a wide spectrum of adverse health effects, including but not limited to abdominal pain, vomiting, diarrhoea, nausea, liver and kidney damage, calf cramps, and gastrointestinal irritation [75].

To safeguard public health, the World Health Organization (WHO) has established stringent permissible limits for these metals in drinking water, with lead, cadmium, and copper having allowable concentrations of 10, 3, and 2000 $\mu\text{g/L}$, respectively [77]. These regulatory standards highlight the critical importance of effective water treatment strategies and continuous monitoring to ensure compliance with established safety thresholds.

1.5.2. Contaminants of emerging concern

Organic dyes, pharmaceuticals, and personal care products, among other organic substances of anthropogenic origin related to modern life which have been labelled as contaminants of emerging concern, are prevalent in wastewater as a result of human activities and their low biodegradability [78].

For instance, caffeine, a widely consumed stimulant, has been found in Italian and German natural waters at varying concentrations, with reported maximum levels of 124 ng L^{-1} in Italian water sources [79] and 640 $\mu\text{g L}^{-1}$ in Germany [80].

Among pharmaceuticals, diclofenac, a widely spread anti-inflammatory pharmaceutical, stands out as a critical environmental contaminant. With an estimated annual global consumption of approximately 1000 tons, diclofenac has been detected in surface, ground, and drinking water sources at concentrations

ranging from ng L^{-1} to $\mu\text{g L}^{-1}$. Its prevalence is especially notable in regions like Switzerland, Spain, Sweden, and the Baltic region [81].

Another pharmaceutical frequently reported in water bodies is acetaminophen, also known as paracetamol, a widely used painkiller, fever reducer, and analgesic. It is one of the most abundantly produced pharmaceuticals in the world, valued at ~130 million USD in 2022 (~8000 USD/ metric ton) with an annual global consumption of ~16250 metric tons [82]. Due to its excessive usage, acetaminophen has been found up to contents of $0.1\text{--}300 \text{ mg L}^{-1}$ in effluents of many countries such as Spain, France, UK, China, and USA [83].

The low biodegradability and the increasing rate of detection in waterbodies of this type of contaminants makes the traditional treatments insufficient to tackle their presence in urban and industrial wastewater, raising the need for additional specific steps to remove them [84].

1.5.3. Carbon dioxide

The worldwide energy-related CO_2 emissions were reported to have stayed constant at 36.1 Gt [85] but had a significant impact on the global annual average of atmospheric CO_2 concentration, leading to a rise of approximately 2.6 parts per million in 2020 [86]. Strategies for reducing atmospheric CO_2 concentrations include the use of renewable energy sources [87], energy optimization growing [88], natural forests [89], and sequestration by diverse processes, in which absorption using amine-based solvents is currently the most used technique [90]. However, the adsorption technique is emerging as an economical and greener alternative for capturing and storing the emitted CO_2 from industrial activity [90,91].

Biogas is one of the most promising options on the market for sustainable energy. Nevertheless, a considerable quantity of CO_2 and other gases are present in the raw gas, which restricts its use. Many commercial biogas upgrading technologies, including membrane separation, chemical scrubbing, water scrubbing, organic solvent scrubbing, pressure swing adsorption, and cryogenic separation, are now used in industry to remove CO_2 from biogas [92]. While these methods are effective, they are often associated with significant challenges. High energy consumption, risk of corrosion, high capital and operational costs, and considerable methane loss render these techniques less economically viable compared to natural gas derived from fossil fuels.

In recent years, the use of solid porous adsorbents for CO_2 removal from biogas has recently emerged as a viable and biogas-attractive alternative. These materials, including activated carbons, zeolites, and MOFs, offer several advantages, such as low energy consumption and small economic investment [40].

1.6. Specific objectives

The main purpose of the thesis is to develop adsorbent carbon materials from biomass and plastic wastes, specifically designed for contaminant adsorption in liquid and gas effluents. Specific objectives are described below:

- 1 – Valorize low-value char produced from the pyrolysis of waste into valuable adsorbent materials, contributing to research into the waste management challenge.
- 2 – Employ different types of waste to prove the ability of each material as an adsorbent material, i.e., rejected fraction of post-consumer plastic, Solid Recovered Fuel (SRF), olive stone, pine and acacia splinter, and cellulose casings.
- 3 – Modify the surface properties of each material to improve the adsorption capability, using different types of activation and modification techniques.
- 4 – Test the materials in adsorption applications: removal of heavy metals, contaminants of emerging concern in ultrapure water and real wastewater in liquid effluents; and adsorption of carbon dioxide in gas effluent aimed at biogas upgrading.
- 5 – Check the industrial application of some of the developed materials through techniques such as scaling-up or life cycle assessment.

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Chapter 2. Materials and Methods

2.1. Characterisation of materials

2.1.1. Thermogravimetric Analysis (TGA)

The Thermogravimetric analysis (TGA) is an experimental method that measures the mass change of a sample subjected to programmed temperature modifications and controlled atmosphere. This method gives information on different physical and chemical properties and phenomena. Physical examples are the crystalline transition, fusion, vaporisation, sublimation, absorption, adsorption and desorption, whereas chemical examples are chemisorption, desolvation, decomposition, oxidative degradation, solid state reactions and solid-gas reactions [1].

Specifically in this work, TGA has been used to conduct the proximate analysis. The proximate analysis quantifies the percentages of moisture, volatiles, fixed carbon, and ash on a solid sample. The device used was a Perkin-Elmer STA 6000 thermobalance (RSD < 5 %). The sample was first kept at 30 °C under N₂ (20 mL min⁻¹). Next, the temperature was risen to 110 °C (heating rate, 40 °C min⁻¹) and maintained for 10 min at this temperature. Then, the temperature was raised to 875 °C (heating rate, 40 °C min⁻¹) and kept at this temperature for 10 min. Finally, the N₂ was changed into O₂ (20 mL min⁻¹) at 875 °C for another 10 min. The determination of each of the constituents was completed by quantifying the weight loss in each step, and the fixed carbon by the difference.

2.1.2. Elemental analysis

The elemental analysis typically measures the elemental composition of a sample in terms of carbon, hydrogen, and nitrogen.

This analysis is based on controlled, dynamic combustion of samples in a reactor and measurement of the amount of the corresponding oxides. The samples are combusted in the column filled with an oxidizing-reducing catalytic bed with an electronically controlled temperature. The produced gases are usually directed to the analyser, which is usually a gas chromatograph. All gases (H₂O, CO, CO₂ and N_xO_y) are separated by chromatographic columns and then detected on a thermally conductive detector (TCD).

In this work, this analysis was performed in an Thermo Scientific Flash 2000 device (RSD values, 0.5 % for C, 1 % for H, and 0.6 % for N). Oxygen was estimated by the difference with the other elements after the removal of the ash content from the proximate analysis.

2.1.3. Nitrogen and carbon dioxide adsorption isotherms

Gas adsorption is used to characterize a wide range of porous materials. These materials have an irregular surface structure, making direct measurement of surface area difficult. One technique commonly used to characterize such solids is physical adsorption, which involves the physical adsorption of gas molecules, typically N_2 , on the solid surface through Van der Waals forces, as a function of the relative pressure of the contacting gas, at a constant temperature, i.e. the boiling point of the adsorbate in the case of N_2 physisorption [2].

Nitrogen physisorption occurs on the pore wall, which adsorbs gas molecules in successive layers until the pore is filled, reaching equilibrium between the adsorbed and gas-phase molecules. If the relative pressure increases, the pore adsorbs a new layer until filling. If the pore diameter is larger, more nitrogen layers will be needed, resulting in a higher P/P_0 .

Adsorption isotherms are represented by curves that provide insight into the behavior of an adsorbed particle during the adsorption process, i.e. the interaction between the particles and the surface characteristics. If the adsorbed particles correspond to those of a gas, their pressure is considered. The isotherm can be used to determine multiple characteristics of a porous solid material.

The calculation of the surface area of an adsorbent is commonly performed by the Brunauer, Emmett, and Teller (BET) method, which is a technique applicable in the equilibrium of gas-solid systems. The method depends on the vapor saturation pressure and equilibrium pressure to obtain the monolayer volume and the adsorbed volume at equilibrium pressure [3]. The BET method is the most extended method and accepted within the scientific community to enable the comparison of surface area of different materials.

The t-plot method allows to estimate the volume and surface of micropores. The t-plot method attempts to relate the adsorption on a material with an ideal curve which describes the thickness of the adsorbed layer on a surface. A plot is constructed, where the isotherm loading data is plotted versus thickness values obtained through the model [4].

The Horvath-Kawazoe method allows to obtain the micropore size distribution [5]. It uses potential functions to describe the interaction between the adsorbent and the adsorbate. The potential energy is defined as a function of the pore width, the distance between a gas atom and the surface at zero interaction energy, the Avogadro's constant, the minimum of the potential energy, and the distance between molecule and wall [6].

The adsorption-desorption isotherms with N₂ at -196 °C were obtained in a Sync 200 device from 3P Instruments©. The samples were degassed overnight at 100 — 150 °C under a vacuum in a J4 prep degasser station of 3P Instruments©. The specific surface area was obtained by the Brunauer-Emmett-Teller method (S_{BET} , relative standard deviation RSD < 1 %), and the total specific pore volume (V_{T}) was calculated from the N₂ uptake at $p/p_0 \sim 0.99$. The t-plot method was used for the estimation of the specific surface of micropores (S_{MP}) and the micropore volume (V_{MP}). The micropore size distribution was obtained by CO₂ adsorption isotherms carried out at 0 °C, considering the Horvath–Kawazoe (HK) method for the calculation.

2.1.4. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a sensitive quantitative spectroscopic technique that analyzes the surface chemistry of a material. The technique consists of hitting the surface of the solid material with high-energy photons such as X-rays. The X-ray sources that are most commonly used in a laboratory are monochromatic Al ($K\alpha$, 1486.7 eV), non-monochromatic Mg ($K\alpha$, 1253.6 eV), and monochromatic Ag ($L\alpha$, 2984.3 eV) with wavelengths 8.34, 9.89 and 4.15 Å, respectively [7]. As a result, photoelectrons are emitted from the first few layers of the surface. The kinetic energy of the emitted photoelectrons, E_k , is measured following the equation based on Einstein's law [8]:

$$E_k = h\nu - E_b \quad (2.1)$$

where $h\nu$ is the energy of the incident photon and E_b represents the binding energy of the electron at a particular level. In XPS, the penetration depth of X-rays (~ 1 -3 keV) in solid materials is on the order of several microns and varies significantly (~ 1 -100 μm) depending on the material, the energy of the X-ray used, and the incident angle. However, the surface sensitivity of XPS is due to the photoelectrons generated only within the top ~ 10 nm thickness of the material surface as they have a considerable probability of being emitted from the surface without inelastic scattering and, therefore, of being detected [9].

The photoelectron peaks are named after the element and the orbital from which they originated. For instance, the C_{1s} refers to the emitted electrons from the 1s orbital. This technique delivers both qualitative and quantitative information about the chemical state, elemental composition, overall electronic structure, and density of electronic states of various solid samples.

In this work, XPS was used to study the type of functional groups related to carbon and oxygen, present in the surface of the studied materials. The chemical nature of the elements at the surface was assessed by deconvolution of the high-

resolution XPS spectra. Regarding the C_{1s} spectrum, the following contributions were considered for deconvolution: C=C (284.6 eV), C-C (285.3 eV), C-O (286.6 eV), C=O (288.0 eV), and O=C-OR (289.9 eV) [10]. The O_{1s} region was fitted to quinone (530.7 eV), C=O (531.5–532.0 eV), and C-O (~533 eV) [11].

The XPS data was obtained using a Kratos AXIS Ultra-DLD device using an X-ray source from Al $K\alpha$. All the spectra were corrected to the C_{1s} peak of adventitious carbon to 284.6 eV. The software XPSpeak 4.1® was applied for the processing and deconvolution of the peaks, considering a Shirley background correction.

2.1.5. Thermal Programmed Desorption (TPD)

In a TPD analysis, the sample is subjected to a constant heating rate under an inert atmosphere (typically, He or Ar) up to high temperatures (usually above 1100 °C or until the limit of the thermal stability of the sample). The desorbed gas mixture is monitored as a function of the temperature by gas chromatography-mass spectrometry or other suitable technique. In this sense, TPD is not a desorption technique, but a decomposition technique. The nature of the oxygenated groups can be assessed by their decomposition temperature and the nature of the gases released in a qualitative manner [12].

In this work, a deconvolution was conducted based on the temperature at which the oxygenated functional groups decompose. According to the literature [12], carboxylic acids decompose below 400 °C; the carboxylic anhydrides decompose between 350 and 600 °C; the lactones reveal a peak above 600 °C. Phenol groups are registered in a middle-temperature range of 500–750 °C, while carbonyl/quinone groups release CO above 700 °C. Finally, pyrone-like groups, if present, are released at 950 °C.

Thermal Programmed Desorption (TPD) with NH_3 was conducted on an AMI-300Lite chemisorption station from Altamira Instruments® equipped with a Thermal Conductivity Detector (TCD). Briefly, 100 mg of sample was loaded and submitted to adsorption with NH_3 (10 % NH_3 in He) under 100 °C and a temperature program from 100 °C to 1000 °C was applied.

2.1.6. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a technique used to obtain high-resolution images and surface information of samples. An electron beam with acceleration voltages of up to 30 kV is focused on the specimen [13]. The interactions between the electron beam and the surface of the specimen emit signals from the specimen, and detectors collect them. The recorded signals are combined to form an image of the surface.

The equipment used for this work was a FEI Quanta 400 device (30 kV, 3.5 nm resolution).

2.1.7. Transmission Electron Microscopy (TEM)

TEM uses electrons that are passing through the sample to create an image. As a result, TEM offers valuable information on the inner structure of the sample, such as crystal structure, morphology, and stress state information, while SEM provides information on the sample's surface and its composition.

The instrument used for this work was a TALOS F200C G2 device (200 kV, 0.3 nm resolution) coupled to an EDX detector Bruker X-flash 6T-30.

2.1.8. X-ray Diffraction (XRD)

X-rays constitute the part of the electromagnetic spectrum with wavelengths between 0.01 and 10 nm (0.1–100 keV), which is between gamma radiation at the short-wavelength/high-energy side and the vacuum ultraviolet region at the long-wavelength/ low-energy side.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample.

The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's law:

$$n\lambda = 2d \sin(\theta) \quad (2.2)$$

where n is an integer, λ is the wavelength of the X-rays, d is the interplanar spacing generating the diffraction, and θ is the diffraction angle [14].

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed, and counted. By scanning the sample through a range of 2 θ angles, all possible diffraction directions of the lattice should be attained. Conversion of the diffraction peaks to d -spacings allows identification of the compound because each compound has a set of unique d -spacings [14]. Therefore, XRD is also capable of producing chemical composition information apart from information on the crystalline structure.

In this work, it is not expected to achieve crystalline structure, but the opposite. Nevertheless, XRD can help to corroborate chemical composition data if crystalline impurities are present.

The disorder degree of carbon and the presence of crystalline impurities were analyzed by XRD in a Bruker D8 Discover device equipped with a detector Pilatus3R 100 K-A, working with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The diffractograms were registered between the 2θ ranges of $10\text{--}85^\circ$.

2.2. Experimental set-up

2.2.1. Pyrolysis

2.2.1.1. Laboratory scale

The pyrolysis was carried out in a fixed horizontal laboratory-scale reactor Nabertherm R 50/250/12 Model furnace, shown in **Figure 2.1**, at 500°C for 90 min, with a $10^\circ\text{C min}^{-1}$ heating rate under a N_2 atmosphere (800 mL min^{-1}). The conditions have been chosen in accordance with previous work of the authors [15–17]. The resulting char was ground, sieved below $500 \mu\text{m}$, and named as native char. The native char was stabilized using a 1 M HCl solution in a proportion of 1:20 (wt./v.) to remove ash and leachable components, followed by ultrapure water washing until neutral pH and a drying step at 120°C for 24 h. This char was named washed char.



Figure 2.1. Laboratory scale pyrolysis and activation oven model Nabertherm R 50/250/12

2.2.1.2. Industrial scale

The setup at the industrial scale consisted of a fluidized bed multiple reactor system working at temperatures between 500 and 600°C for the processing of municipal, industrial, and agroforestry residues.

2.2.2. Chemical activation

2.2.2.1. Laboratory scale

The activation of the char started with the mixing of the chemical agent in a defined ratio which was introduced in the reactor. The thermal treatment consisted of several steps. Firstly, the mixture was heated from room temperature to 300°C at a rate of $10^\circ\text{C min}^{-1}$ and held for 1 h to ensure the melting of the activating agent.

Next, the temperature was raised from 300 °C to 800 °C at a rate of 10 °C min⁻¹ and kept for 1 h. All the steps were carried out under inert N₂, with a flow rate of 200 mL min⁻¹. The activated char was stabilized using an HCl solution 1 M in a proportion of 1:20 (wt./v.) to remove ash, leachable components, and non-reacted activation agent, followed by ultrapure water washing until neutral pH and a drying step at 120 °C for 24 h, see a scheme of the procedure in **Figure 2.2**.

For laboratory experiments, the reactor used was a fixed horizontal laboratory-scale reactor Nabertherm R 50/250/12 Model furnace. The sample was introduced in the oven using a cylindrical steel container with dimensions of 250 mm length and 25 mm diameter.

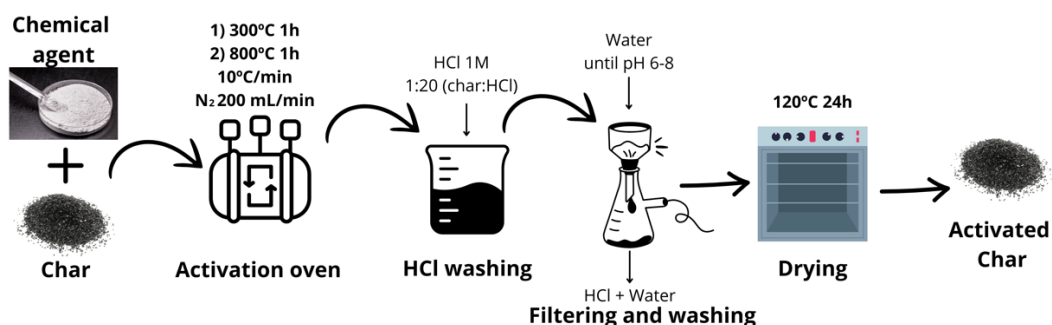


Figure 2.2. Diagram of char chemical activation method

2.2.2.2. Pilot scale

For scaling-up experiments, a hinged rotary tube kiln from Carbolite® Gero was used, model TS03 11/1000, represented in **Figure 2.3**. The samples were introduced in a quartz tube with dimensions of 1000 mm length and 125 mm diameter. The procedure of sample preparation followed was the same as the procedure explained in the previous section. The amount of sample introduced in the oven resulted in a scaling-up factor of 1:20. The reactor was tested both in static and rotatory mode.

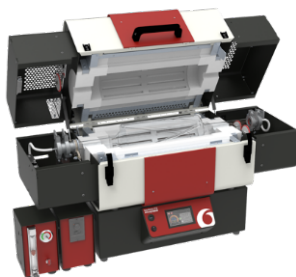


Figure 2.3. Pilot scale activation oven model Carbolite® Gero TS03 11/1000

2.2.3. Citric acid surface modification

For the preparation of citric acid-modified activated char, the activated char was placed in a beaker and mixed with the citric acid solution in different concentrations at a ratio of 4 g of char to 25 g of citric acid solution, see **Figure 2.4**. The mixture was stirred in a magnetic stirrer for 30 min to ensure complete wetting of the material. The mixture was then placed in an oven at 50°C for 24 h to ensure the dehydration reaction and then subjected to another 24 h at 100°C. The mixture was washed until neutral pH was reached and in an oven at 105°C for 24h.

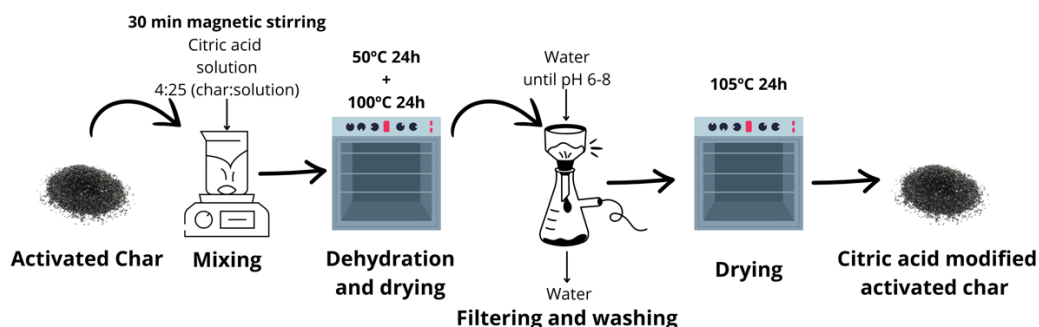


Figure 2.4. Diagram of citric acid-modified activated char method

2.2.4. Physical activation

For physical activation, N_2 (200 mL min^{-1}) was fed until reached 750°C (heating rate, $10^\circ\text{C min}^{-1}$). Next, the gas was switched to CO_2 (200 mL min^{-1}), and the temperature was kept for 1 h. Then the gas was switched to N_2 again to let the sample cool to room temperature. The washing procedure was the same as for chemical activation except that the quantity of HCl used is lower since the sample does not contain extra chemicals, see **Figure 2.6**.

The equipment and container used were the same as the one used for chemical activation at the lab scale, with the precaution of not filling the container at an excessive height, to ensure the CO_2 penetration into the core of the sample.

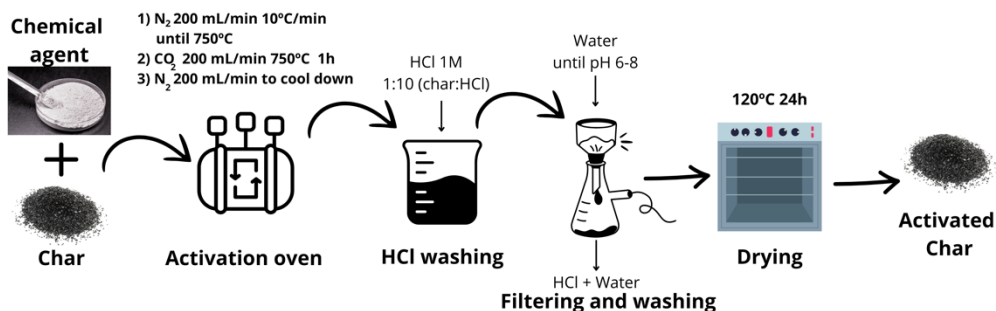


Figure 2.6. Diagram of char physical activation method

2.2.5. Liquid phase batch experiments

The solutions of the different contaminants were placed in 100 mL Erlenmeyer flasks at room temperature (25 °C) with an adsorbent dose of 2 g L⁻¹. The flasks were agitated in an orbital stirring device at 160 rpm until equilibrium was reached, as depicted in **Figure 2.5**. The samples were filtered with syringe filters (Millipore Millex-GV PVDF, 0.45 µm), and the concentration of the contaminant was analyzed. All the experiments were carried out at a free pH, ranging from 4 to 6.

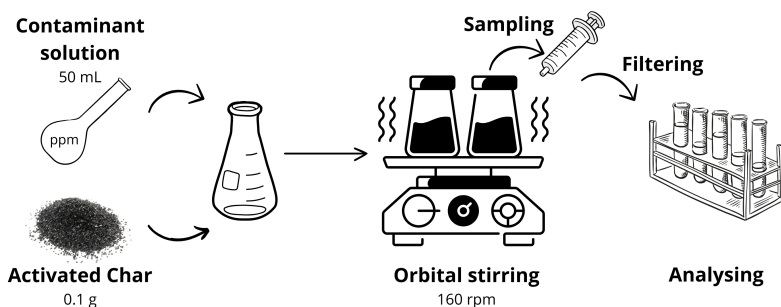


Figure 2.5. Diagram for liquid phase batch experiments

The results were adjusted to different adsorption models which provide valuable information about activated carbon properties and adsorbate-adsorbent interactions [18]. The Freundlich model [19] assumes that the attraction between the metal ions and the surface of the adsorbent is based on physical forces, such as electrostatic or Van der Waals forces, and describes the equilibrium on heterogeneous surfaces having different affinities for the adsorption sites. Homogeneous surfaces will present $n_F = 1$. The expression of the model is as follows:

$$q_e = K_F C_e^{n_F} \quad (2.3)$$

where q_e (mg g^{-1}) is the adsorbed amount in the equilibria; K_F ($\text{mg g}^{-1}/(\text{mg L}^{-1})^{n_F}$) is the Freundlich's constant; n_F (dimensionless) is the Freundlich's exponent; and C_e (mg L^{-1}) is the equilibrium concentration of the ion in the liquid phase.

The Langmuir model [20] also assumes that the interactions are only physical; however, the following assumptions are considered: i) sorption occurs at specific sites on the adsorbent surface; ii) each site can hold only one ion (monolayer); iii) the surfaces are homogeneous; iv) all adsorption sites have equal energy and affinity to adsorbates; and v) there are no interactions between adsorbate ions at adjacent sites. The Langmuir isotherm is described by the following expression:

$$q_e = \frac{q_L K_L C_e}{1 + K_L C_e} \quad (2.4)$$

where q_e (mg g^{-1}) and q_s (mg g^{-1}) are the adsorbed amount in the equilibria and the maximum, respectively; K_L ($\text{mg}^{-1} \text{L}$) is the Langmuir's constant; and C_e (mg L^{-1}) is the equilibrium concentration of the ion in the liquid phase.

The Sips three-parameter model [21] combines the Langmuir and Freundlich models and serves to describe heterogeneous surfaces. The model will behave as the Langmuir and Freundlich models at high and low concentrations, respectively. The expression reads as follows:

$$q_e = \frac{q_s (K_s C_e)^{n_s}}{1 + (K_s C_e)^{n_s}} \quad (2.5)$$

where q_e (mg g^{-1}) and q_s (mg g^{-1}) are the adsorbed amount in the equilibria and the maximum, respectively; K_s ($\text{mg}^{-1} \text{L}$) is the Sips's constant; n_s (dimensionless) is the Sips's exponent; and C_e (mg L^{-1}) is the equilibrium concentration of the ion in the liquid phase.

2.2.6. Liquid phase continuous experiments

The dynamic behavior was tested in a fixed-bed column as shown in **Figure 2.7**. The set-up consisted of a jacketed column (11 cm height, 1.5 cm internal diameter), thermostated at 25 °C. The column was loaded with 0.5 g of activated carbon, sieved at 355–500 μm to avoid bed compaction, and retained with glass spheres and wool. The test was operated in continuous pumping of the contaminant in up-flow mode, at an average rate of 2 mL min^{-1} . Samples were collected from the top of the column and analyzed to obtain the breakthrough curves. For the desorption experiments, a solution consisting of aqueous HCl 1 M, in the case of desorption of Pb^{2+} and methanol in the case of caffeine, was fed at the same flow rate.

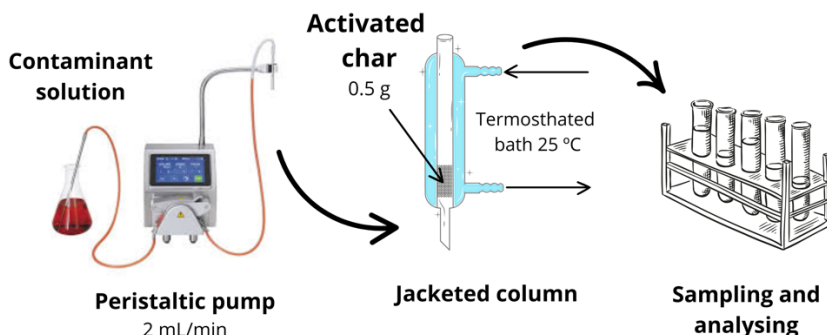


Figure 2.7. Diagram for liquid phase continuous experiments

The breakthrough curves were fitted to different models. The Thomas model [22] assumes that the plug flow takes place in the fixed bed, with negligible diffusion restrictions and, second-order reaction kinetics. The equation of Thomas describes the temporal evolution of the normalized concentration as follows:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(K_T C_0 \left(\frac{q_0 m}{v C_0}\right) - t\right)} \quad (2.6)$$

where K_T ($L \text{ mg}^{-1} \text{ min}^{-1}$) is the Thomas rate constant; q_0 (mg g^{-1}) is the equilibrium adsorption capacity; m (g) is the mass of the adsorbent in the column; v (mL min^{-1}) the inlet flow rate; C_0 (mg L^{-1}) is the initial concentration and, C_t (mg L^{-1}) is the concentration at a given time.

The Yoon–Nelson model [23] assumes that the decrease in the probability of adsorption for each ion is proportional to the probability of adsorption and the probability of breakthrough:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp(K_{YN}(\tau - t))} \quad (2.7)$$

where K_{YN} (s^{-1}) is the Yoon-Nelson rate constant and τ (min) is the time required to reach 50 % of breakthrough.

The Bohart-Adams model [24] proposes that the adsorption process is not instantaneous and that the rate is proportional to the residual adsorption capacity of the adsorbent and the concentration of the adsorbate:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(K_{BA} C_0 \left(\frac{a_0 x}{u C_0}\right) - t\right)} \quad (2.8)$$

where K_{BA} ($L\ mg^{-1}\ min^{-1}$) is the Bohart-Adams rate constant; a_0 ($mg\ L^{-1}$) the initially available adsorption capacity of the adsorbent; x (cm) is the bed height; and u ($cm\ min^{-1}$) is the linear flow velocity.

The dose-response model [25] is a simplified model that better fits the breakthrough curves at low and high times as it provides an asymmetric prediction.

$$\frac{C_t}{C_0} = 1 - \frac{1}{1+(K_{DR}t)^\alpha} \quad (2.9)$$

where α (dimensionless) and K_{DR} (min^{-1}) are the dose-response parameters.

2.2.7. Gas phase static experiments

The adsorption of CO_2 and CH_4 was carried out under static mode in a physisorption device (Sync 200 device from 3P Instruments©), obtaining the isotherms at 273 and 298 K up to 100 kPa. The gas uptake, either CO_2 or CH_4 , uptake (q , $mg\ g^{-1}$) was adjusted to the Freundlich model [19]:

$$q = K_F p^{1/n_F} \quad (2.10)$$

where p is the equilibrium pressure of the gaseous adsorbate, and the K_F ($mg\ g^{-1}\ kPa^{-n_F}$) and n_F stand for, respectively, the Freundlich constant and exponent.

2.2.8. Gas phase continuous experiments

Dynamic adsorption tests of CO_2 , CH_4 , and their mixtures using N_2 as a gas carrier were conducted in a fixed-bed column, leading to the obtention of the breakthrough curves as shown in **Figure 2.8**. The plastic-based activated carbon (1 g) was placed in a thermostatic column, 10 cm height and 1 cm internal diameter equipped with a porous ceramic porous at the base, operating at 30 °C and atmospheric pressure. Glass balls were inserted in the top of the column to prevent possible dragging of the solid. Different adsorption assays feeding 100 mL min^{-1} of gas stream composed of CO_2/N_2 or CH_4/N_2 mixtures from 20/80 to 80/20 (v/v) were conducted to define the breakthrough curves. The adsorption of CO_2/CH_4 mixtures was also assessed ranging from 50/50 to 80/20 (v/v). Furthermore, the adsorption behavior with simulated landfill biogas composed of 55 % (v/v) CH_4 , 39 % CO_2 , 6 % N_2 , and trace amounts of O_2 and H_2S , was also evaluated. The concentration of gases in the gas streams was monitored with an INFRA.sens® AK5 device from Wi.tec-Sensorik, based on non-dispersive infrared (NDIR) analysis in a dual beam to analyze both CO_2 and CH_4 . The evolution over time of the concentration of gases at the outlet was used to depict the breakthrough curves. The gas adsorption uptake, either for CO_2 or CH_4 , was quantified as the area below the adsorbed gas, which means the $1-C_t/C_{inlet}$ curve, being C_t and C_{inlet} the concentration of the gas at a certain time and the inlet value respectively. The area

was computed from the initial time until the saturation time (t_{sat}), defined as the time in which $C_{\text{tsat}}/C_{\text{inlet}}=0.95$ [26]:

$$q = \frac{\vartheta C_0 \int_0^{t_{\text{sat}}} \left(1 - \frac{C_t}{C_0}\right) dt}{m_{\text{AD}}} \quad (2.11)$$

where ϑ means the volumetric flow rate (100 L min^{-1}), C_0 (mol L^{-1}) is the inlet CO_2 or CH_4 concentration, and m_{AD} (g) means the mass of adsorbent loaded in the column.

The removal capacity (R) was calculated as the amount of CO_2 retained in the column concerning the total fed CO_2 :

$$R = \frac{q_{\text{CO}_2} m_{\text{AC}}}{\vartheta C_0 t_{\text{sat}}} = \frac{\int_0^{t_{\text{sat}}} \left(1 - \frac{C_t}{C_0}\right) dt}{t_{\text{sat}}} \quad (2.12)$$

To assess the performance of the CH_4 upgrading, certain key parameters were estimated: productivity, CH_4 purity, and CH_4 recovery. The molar yield of CH_4 (Y_{CH_4} , $\text{mol g}^{-1} \text{ s}^{-1}$) with a selected purity level (90 %) was determined from the integration of the molar flowrate profile of CH_4 leaving the gas outlet between the time interval of t_1 to t_2 , defined as the time where CH_4 reaches the purity selected as 90 % [27,28]:

$$Y_{\text{CH}_4} = \frac{1}{m_{\text{AD}} t_{\text{cycle}}} \int_{t_1}^{t_2} F_{\text{CH}_4}(t) dt \quad (2.13)$$

where $F_{\text{CH}_4}(t)$ is the molar flow of CH_4 in the outlet stream, and t_{cycle} means the necessary time to reach the inlet conditions. Besides, the CH_4 purity was calculated as the percentage of the CH_4 in the outlet gas as follows:

$$\text{CH}_4 \text{ purity} = \frac{\int_{t_1}^{t_2} F_{\text{CH}_4}(t) dt}{\int_{t_1}^{t_2} F_{\text{CH}_4}(t) dt + \int_{t_1}^{t_2} F_{\text{CO}_2}(t) dt} \quad (2.14)$$

The CH_4 recovery was estimated as the CH_4 extracted in the raffinate during the interval t_1 - t_2 concerning the amount fed during the cycle:

$$\text{CH}_4 \text{ recovery} = \frac{\int_{t_1}^{t_2} F_{\text{CH}_4}(t) dt}{\int_0^{t_{\text{cycle}}} F_{\text{CH}_4}(t) dt} \quad (2.15)$$

The adsorption-desorption cycles of reusing with a CO_2 - CH_4 mixture were carried out by swapping the inlet with pure N_2 at the same flow rate, i.e. 100 mL min^{-1} . The desorption cycle was finalized when the monitored CO_2 and CH_4 concentrations were negligible.

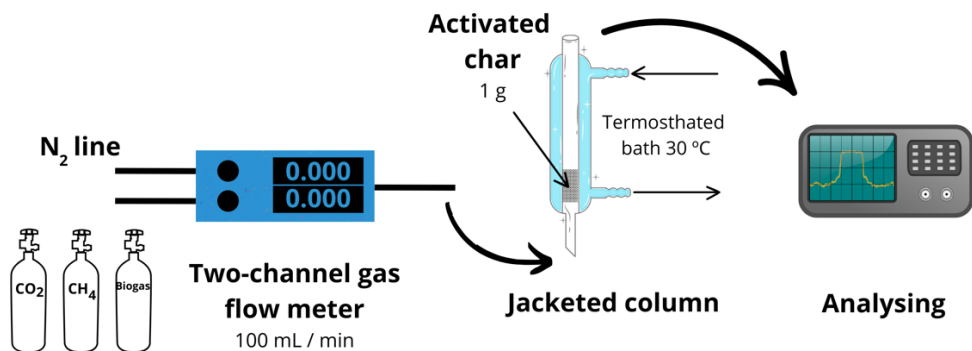


Figure 2.8. Diagram for gas phase continuous experiments

2.3. Quantification of pollutant concentrations

2.3.1. Heavy metals

2.3.1.1. Flame Atomic Absorbance Spectrometry (AAS)

Atomic Absorbance Spectrometry (AAS) employs the principle that atoms absorb light at a specific wavelength. When this specific wavelength of light is provided, the energy (light) is absorbed by the atom. Electrons in the atom move from the ground state to an excited state. The amount of light absorbed is measured and the concentration of the element in the sample can be calculated.

The experimental procedure starts when a solution containing the analyte is introduced into a flame. The flame turns the sample into free ground-state atoms that can be excited. A lamp emitting light at a wavelength specific to the atoms is passed through the flame, and as the light energy is absorbed, the electrons in the atoms are elevated to an excited state.

The Beer-Lambert Law describes the relationship between light absorption and concentration of the element. According to the law, the amount of light absorbed is proportional to the number of atoms excited from the ground state in the flame:

$$A = \epsilon l C \quad (2.16)$$

where A is the absorption of light by a solution to the path length of travel through that solution (l), C is the concentration of absorbing substance in the solution, and ϵ represents the extinction coefficient of the molar absorptivity of the substance in the solution.

The absorbance is related to transmittance (T), calculated in terms of light intensity (which can be measured), and can be related to absorbance by the following equation:

$$T = \frac{I}{I_0} = 10^{\epsilon l C} = 10^A \quad (2.17)$$

where I_0 is the intensity of the incident light, and I is the intensity of the transmitted light. Since intensity can be measured easily using photometry, equations 2.16 and 2.17 can be used to determine the concentration of an unknown sample given the scaling factor ϵ (the path length is generally kept constant and falls out of the equation). To obtain this constant, standard solutions of the analyte in question must be prepared, and the extinction coefficient ϵ can be found as the slope of the line relating concentration and absorption between these samples. It is worth noting that the linear trend between concentration and absorption only holds for a specific concentration range, and the extinction coefficient, as well as unknown concentration, can only be found by interpolation within this area [29].

The radiation is generally produced by a highly monochromatic hollow-cathode lamp, specifically chosen to (mostly) only produce wavelengths of light corresponding to the analyte being looked for.

This technique was used to determine the concentration of a specific heavy metal individually and decide in advance which one was the target, in particular lead, cadmium, copper, nickel, or zinc. The equipment used for AAS measurements was a PerkinElmer® PinAAcle 500 Flame device.

2.3.1.2. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is one of the most used methods for elemental analysis since it is capable of simultaneously measuring multiple elements. This technique utilizes inductively coupled plasma to generate excited atoms and ions that emit characteristic electromagnetic radiation. The plasma is an ionized gas containing free electrons and cations at high temperatures and low pressures and it is powered usually by a free-running radio frequency generator. Induction plasma, or “inductively coupled plasma,” refers to the utilization of a flowing gas under specific pressure and temperature conditions as a plasma source [30].

The characteristic electromagnetic radiation is then transformed into interpretable data by optical emission spectroscopy. OES analyzers consist of two main parts: the first is an electrical source that causes atoms in a metallic sample to emit distinctive light lines, also known as optical emission lines, by heating a tiny

portion of the material to thousands of Celsius degrees. An electrical high-voltage source in the spectrometer via an electrode is used to accomplish this. The material at the sample's surface heats up and vaporizes as a result of an electrical discharge created by the electrode and the sample's different electrical potentials. The element-characteristic emission lines are then released as a result of the material's atoms becoming stimulated. The second part is an optical system. The vaporized sample, known as plasma, emits light in the form of several optical emission lines that enter the spectrometer. A diffraction grating in the spectrometer separates the incoming light into wavelengths appropriate to each element, and a matching detector measures the light intensity for each element. The observed intensity is proportional to the sample's concentration of each element.

In this work, the ICP-OES was used to assess the content of elements when the composition of the sample was unknown. The equipment used was a PerkinElmer® OPTIMA 8300 device.

2.3.1.3. Inductively Coupled Plasma coupled to Mass Spectrometry (ICP-MS)

In this technique, the means to produce excited atoms are the same as the one explained in the previous section, but the ions produced are measured using mass spectrometry. Several different types of mass analyzers have been used for ICP-MS; usually quadrupoles. By sorting ions according to their m/z ratio, which is the mass of an ion divided by its charge, a quadrupole functions as a kind of mass filter. Four parallel hyperbolic or cylindrical metallic rods, typically 15–20 cm long, arranged in a square array, constitute a quadrupole. Ions flow via a time-varying electric field created in the center of the rods by applying radio frequency alternating current and direct current potentials. Only certain combinations of AC and DC potentials provide a stable ion flight trajectory through the quadrupole for an ion with a given m/z ratio [31].

The equipment used in this work consisted of a PerkinElmer® NexION 300D using an ion filter plasma torch as the ionization source.

2.3.2. Contaminants of Emerging Concern

2.3.2.1. High-performance Liquid Chromatography (HPLC)

This technique was used to analyse target contaminants of emerging concern in the liquid phase.

This technique consists of a mobile or eluent phase, and a stationary phase, usually a column consisting of solid particles based on silica, coated silica, or polymers that improve surface area and retention time. The sample enters the system and mixes with the mobile phase, then passes through the stationary phase under

pressure produced by the pump. As the mixture moves through the column, each component interacts differently with the stationary and mobile phases. The interaction of the sample with the stationary phase is defined by the nature of the stationary phase, by adsorption, partition, ion exchange, and size exclusion chromatography. When the sample leaves the column, it is directed to the detection system aiding the quantification. Commonly used detectors are based on techniques such as UV-vis, fluorescence, refractive index, or mass spectrometry, which send a signal and translate it graphically into a chromatogram. The chromatogram represents the different compounds in the sample with different peaks, known by their retention times. These peaks have different areas which are related to their concentration in the sample, making it a quantitative analysis technique that allows the determination of the concentration of a specific compound dissolved in a sample using a previously defined calibration curve [32].

Ultraviolet-based detection is widely used in high-performance liquid chromatography due to its ease of operation, relative sensitivity, and cost-effectiveness compared to other methods. This detector measures the absorbance of UV-vis light at multiple wavelengths simultaneously. Diode array detectors (UV-vis DADs), also known as photodiode array detectors (UV-vis PADs), measure the absorbance of UV-vis light at multiple wavelengths simultaneously and are very sensitive, allowing the detection of compounds at low concentrations [33].

The concentration of the organic compound was quantified by High-Pressure Liquid Chromatography (HPLC) in an Alliance e2695 HPLC device from WatersTM coupled to a 2998 photodiode array UV-visible detector. The stationary phase used for the separation was a Zorbax Bonus-RP column (4.6×150 mm, 5 µm). For the analysis of caffeine and diclofenac, isocratic methods were carried out. A mixture of acetonitrile (A) and acidified water with 0.1 % (vol.) of trifluoroacetic acid (B) was pumped at a rate of 1 mL min⁻¹ with an A:B ratio of 15:85 for caffeine and 65:35 for diclofenac. In the case of acetaminophen, a gradient method was applied from 20:80 to 60:40 in 7 min. The quantification was conducted at 275 nm for caffeine, 247 nm for diclofenac, and acetaminophen.

2.3.3. Carbon dioxide and methane

2.3.3.1. *Non-Dispersive InfraRed (NDIR)*

NDIR technology functions based on infrared (IR) properties and the specific absorption characteristics of different gas molecules. Every gas molecule absorbs IR radiation at a specific wavelength [34].

An NDIR sensor is typically composed of an IR source, a sample chamber or light tube, a wavelength filter, and an IR detector. The light is emitted by the infrared source and travels through the sample chamber containing the gas that has to be

identified. Only the intended wavelengths are allowed to reach the detector thanks to the wavelength filter. After measuring the incoming light's intensity, the detector generates an electrical signal that is processed as the gas concentration [35]. An advantage of NDIR technology is its high selectivity. Because each gas has a unique IR absorption rate, NDIR sensors can precisely detect specific gases in the presence of other gases.

The term "non-dispersive" in NDIR describes the fact that infrared light is not "dispersed" or divided into its many wavelengths prior to detection. Rather, for each type of gas being detected, a certain wavelength of infrared light, referred to as the "active" wavelength, is chosen [36]. This wavelength is chosen based on the specific absorption rate of the gas. The sensor uses a "reference" wavelength, at which the gas does not absorb IR light. The comparison between these two wavelengths enables the sensor to accurately measure the concentration of the gas.

The concentration of gases in the gas streams was monitored with an INFRA.sens® AK5 device from Wi.tec-Sensorik, based on non-dispersive infrared (NDIR) analysis in a dual beam to analyze both CO₂ and CH₄.

2.4. Life Cycle Assessment

The Life Cycle Assessment (LCA) methodology was used to evaluate the environmental impact of the production of activated char and citric acid-modified activated char.

LCA offers a solution to assess processes under a holistic approach. Problem shifting occurs when solutions that improve or solve a targeted problem unintentionally create other problems of an environmental, economic, or social nature somewhere else in the systems of processes. If the totality of these systems is not considered in the analysis, unwanted consequences of our decision will be overseen. The focus of LCA has mainly been on the environmental impacts although both social and economic impacts can be included. LCA has taken an important role in recent years concerning environmental regulations in many parts of the world and it is certified by ISO standardization [37].

The LCA followed the guidelines outlined in the ISO 14040:2006 and ISO 14044:2006 standards (ISO, 2006a; ISO, 2006b), which divide LCA into four key phases, i.e., goal and scope, life-cycle inventory, life-cycle impact assessment, and interpretation. A range of software tools, libraries, and impact assessment methodologies were used for the analysis. Data required for the LCA were collected from the chemical business. For background data, the 'ecoinvent 3 cut-off (S)' library was selected. SimaPro 9.6 software was used to perform the life-cycle impact assessment calculations. The life-cycle impact assessment method used was ReCiPe 2016 Midpoint (H) V1.09 / World (2010) H. Finally, the results were analyzed to

identify the key variables, the most significant impact categories, and the unit processes with the greatest environmental impact.

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Chapter 3. Char Produced from the Rejected Fraction of Post-consumer Plastic Waste

3.1. Liquid effluent treatment

3.1.1. Paper 1: Conversion of char from pyrolysis of plastic wastes into alternative activated carbons for heavy metal removal

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Ledicia Pereira, Ventura Castillo, Mónica Calero, Gabriel Blázquez, Rafael R. Solís, M. Ángeles Martín-Lara

3.1.1.1. Abstract

The valorization of post-consumer mixed plastics in pyrolysis processes represents an abundant reservoir of carbon that can be effectively converted into useful chars. This process not only holds appeal in terms of improving plastic waste concerns but also contributes to the reduction of greenhouse gas emissions, thus aligning with the principles of a circular economy paradigm. In this study, the char produced from the pyrolysis of post-consumer mixed plastic waste has been activated with Na_2CO_3 , KOH, NaOH, and K_2CO_3 to improve the textural, structural, and composition characteristics, leading to improved adsorption capability. These characteristics were studied by N_2 adsorption-desorption isotherms, scanning electron microscopy, elemental and immediate analysis, and X-ray photoelectron spectroscopy. The developed surface area (S_{BET}) was 573, 939, 704 and 592 $\text{m}^2 \text{g}^{-1}$ for Na_2CO_3 , KOH, NaOH and K_2CO_3 activated carbons, respectively. These activated chars (ACs) were tested for the adsorption of heavy metals in both synthetic waters containing Pb, Cd, and Cu and industrial wastewater collected at an agrochemical production plant. Na_2CO_3 -AC was the best performing material. The metal uptake in synthetic waters using a batch set-up was 40, 13 and 12 mg g^{-1} for Pb, Cd and Cu. Experiments in a column set-up using Na_2CO_3 -AC resulted in a saturation time of 290, 16, and 80 min for Pb, Cd, and Cu synthetic waters, respectively, and metal uptakes of 26.8, 4.1, and 7.9 mg g^{-1} , respectively.

The agrochemical effluents, containing mainly Cr, Cu, Mn, and Zn were tested in a plug-flow column. The metal uptake notably decreased compared to synthetic water due to a competition effect for active sites.

Keywords: char; activated carbon; plastic waste; adsorption; heavy metals; agrochemicals

3.1.1.2. Introduction

The increasing prevalence of contaminants within aqueous ecosystems has a far-reaching impact on both human well-being and health. The pollution of aquatic systems has been linked to the emergence of severe illnesses, a factor contributing to an estimated 1-4 million premature deaths worldwide [1]. This concerning trend is exacerbated by the substantial surge in water consumption, which has risen sixfold over the past century, as reported in the 2021 World Water Development Report released by UNESCO [2]. This growth in water demand has placed added stress on water resources, intensifying the challenges associated with ensuring water quality and safety for human consumption [3]. Consequently, understanding and mitigating the adverse consequences of contaminant exposure in aquatic environments have become paramount to safeguarding public health in the face of growing global water demands.

Among the most dangerous components within industrial wastewater, heavy metals stand out as a significant concern owing to their pronounced toxicity and persistent nature in natural environments. This persistence poses substantial health risks to both humans and other forms of life [4,5]. Lead is frequently introduced into the environment, primarily as a result of activities related to metal mining, corrosive lead batteries, paper and glass production, and cleaning processes [6]. In addition to lead, cadmium is another notable contaminant commonly encountered in water sources, stemming from sources such as battery electroplating, photovoltaic cell production, metallurgical operations, and textile manufacturing facilities [7]. Copper, ranked as the third most utilized metal worldwide [8], plays a pivotal role as an algicide in various applications, including ornamental ponds, water supply reservoirs, and a range of industrial processes [9]. The release of copper into aquatic ecosystems through wastewater discharge has led to its widespread presence in water bodies, thereby posing a threat to the quality of drinking water [10,11].

High copper concentrations in drinking water have been linked to a wide spectrum of adverse health effects, including but not limited to abdominal pain, vomiting, diarrhea, nausea, liver and kidney damage, calf cramps, and gastrointestinal irritation [10]. On the other hand, the presence of lead in water sources poses severe health risks, encompassing cardiovascular diseases, heart problems, kidney failure, liver cirrhosis, intestinal disorders, mental retardation, and an increased susceptibility to kidney and liver cancer [12]. On the other hand, cadmium has no significance in the physiological processes occurring in the human body [13]. However, its high toxicity and tendency to accumulate in organisms make cadmium a particularly hazardous contaminant. Exposure to certain concentrations can result in a range of health complications, including hypertension, calcium depletion from bones, bone marrow damage, gastrointestinal disturbances such as

diarrhea, vomiting, and nausea, chest pain, a reduction in red blood cell count, kidney failure, sensory loss, and even central nervous system damage, even at relatively low concentrations [14,15].

To safeguard public health, the World Health Organization (WHO) has established stringent permissible limits for these metals in drinking water, with cadmium, copper, and lead having allowable concentrations of 3, 2000, and 10 $\mu\text{g L}^{-1}$, respectively [16]. These regulatory standards highlight the critical importance of effective water treatment strategies and continuous monitoring to ensure compliance with established safety thresholds.

Diverse methodologies are currently employed for heavy metal and other contaminants removal from water bodies, encompassing techniques such as ion substitution, inverse filtration, precipitate separation, adsorption, coagulation, and extraction [17]. Among these methods, adsorption emerges as the preferred strategy due to its simplicity, high efficiency, and ease of operation, particularly in the removal of metal ions exceeding regulatory limits [18]. Non-carbon nanomaterials have also gained prominence in the realm of water purification and environmental remediation. These materials include iron oxide magnetite nanoparticles, metal oxides (MO), metal-organic frameworks (MOF), ionic liquids (ILs), zeolites, and others [7,19–21]. However, despite their potential, these materials display diverse limitations, which impede their direct applicability in practical scenarios. For instance, MOFs may undergo decomposition when exposed to high humidity levels, limiting their long-term stability and effectiveness [22]. In the case of zeolites, the strong competition for free adsorption sites from water molecules can diminish their overall adsorption capacity, thus reducing their efficiency in removing contaminants [23]. Ionic liquids, while promising, face challenges stemming from their liquid state, which can complicate their handling and application, particularly in water adsorption processes [24]. Carbon materials have gained significant attention as the preferred choice for the remediation of contaminated water owing to their high efficiency, economic viability, and suitability for adsorption processes, as corroborated in previous studies [22,23,25,26].

In particular, post-consumer plastics represent an abundant reservoir of carbon that can be effectively converted into useful materials through pyrolytic techniques [27]. Plastics are essential in modern life, offering outstanding properties for applications in packaging, construction, motoring, electronics or agriculture sectors. Every year, 381 million tons of plastic waste are generated worldwide, which is expected to double by 2034 [28]. It is necessary to develop efficient reduction, reuse and recycling strategies to reduce waste production, which will directly impact carbon dioxide emissions, and tackle climate change and ecological problems [29,30].

Common treatment procedures for post-consumer mixed plastic waste include landfilling, mechanical recycling, and incineration processes. These post-consumer mixed plastic streams are initially subjected to intensive sorting based on plastic type before further reprocessing. The separated plastics are usually mechanically recycled, but the rejection stream of the sorting process, currently ends up in landfilling or incineration. Landfill sites occupy large areas of land, which also come with high taxes and a substantial risk of harmful plastic additives leakage. (e.g. dimethyl phthalate in PVC, bisphenol A in polycarbonates) into soils and groundwater [31]. Energy recovery techniques such as incineration and gasification break down plastics and significantly reduce their volume. The by-products (e.g. heat, gases) can be used as sources of energy. However, incineration is environmentally unfriendly, as it requires high amounts of energy to generate enough heat for breaking down the plastics [32] and produces large quantities of atmospheric carbon dioxide (CO₂) and particulate emissions containing polycyclic aromatic hydrocarbons (PAHs) [33].

Pyrolysis is among the most promising methods for handling post-consumer mixed plastic waste, in addition to the previously described procedures [34]. Pyrolysis has the least environmental impact when compared to gasification, incineration, and landfilling [35]. Specifically, pyrolysis is a thermochemical process that converts waste plastic into valuable products such as gases, organic vapors (liquid oil), and a solid product (char), at moderately high temperatures (> 400 °C) in a deoxygenated environment [28,36,37].

In this study, four different activation agents were considered to convert post-consumer plastic char produced via pyrolysis into adsorbent materials for the removal of Cd, Cu, and Pb from aqueous solutions. To assess their efficacy, the adsorption equilibria with the post-consumer plastic-based materials were tested to define their adsorption isotherms, and dynamic tests in column setup, using synthetic and industrial wastewater samples from a local fertilizer and pesticidal manufacturing facility. This investigation involves a comprehensive evaluation of the material performance concerning the removal of the aforementioned heavy metals. In addition, this work aims to provide a multifaceted approach, highlighting the diverse advantages of carbon-based materials from post-consumer plastics to address both environmental and resource sustainability challenges.

3.1.1.3. Experimental section

Preparation of the activated chars

The native char was produced from the pyrolysis of non-recyclable plastic waste provided by a municipal solid waste (MSW) treatment plant located in Granada (Spain). A characterization of the rejected fraction of mixed plastic waste from the MSW treatment plant was performed; resulting, on average, percentages of 55 % of

polypropylene (PP), 8.6 % of polystyrene (PS), 10.1 % of expanded PS (EPS), and 27.2 % of film [38,39]. To obtain homogeneous and reproducible samples, the mixture was replicated at a laboratory scale.

The pyrolysis was carried out in a fixed horizontal laboratory-scale reactor Nabertherm R 50/250/12 Model furnace at 500 °C for 90 min, with a 10 °C min⁻¹ heating rate under a N₂ atmosphere (800 mL min⁻¹). The conditions have been chosen in accordance with previous work of the authors [27,39,40]. The resulting char was ground, sieved below 500 µm, and named as native char. The native char was stabilized using a 1 M HCl solution in a proportion of 1:20 (wt./v.) to remove ash and leachable components, followed by ultrapure water washing until neutral pH and a drying step at 120 °C for 24 h. This char was named washed char.

The native char was subjected to chemical activation to produce activated chars (ACs) with high textural properties. Four different activating agents were tested: sodium carbonate (Na₂CO₃), potassium hydroxide (KOH), sodium hydroxide (NaOH), and potassium carbonate (K₂CO₃). The char and the activating agent were mixed at a mass ratio of 1:1 accordingly to previous results reported in [41]. According to previous work [41], the thermal treatment consisted of several steps. Firstly, the mixture was heated from room temperature to 300 °C at a rate of 10 °C min⁻¹ and held for 1 h to ensure the melting of the activating agent. Next, the temperature was raised from 300 °C to 800 °C at a rate of 10 °C min⁻¹ and kept for 1 h. All the steps were carried out under inert N₂, with a flow rate of 200 mL min⁻¹. The cooled samples were washed and dried following the previous methodology. The resulting samples were named Na₂CO₃-AC, KOH-AC, NaOH-AC, and K₂CO₃-AC.

Characterization of the chars

The textural properties were assessed by N₂ physisorption at 77 K using a Sync 200 device from 3P Instruments©. The samples were degassed overnight at 150 °C under a vacuum in a J4 prep degasser station of 3P Instruments©. The specific surface area was calculated using the Brunauer-Emmett-Teller method (S_{BET}), and the total specific pore volume (V_T) was calculated from the N₂ uptake at p/p₀~0.99. The t-plot method was used for the estimation of the specific surface of micropores (S_{MP}) and the micropore volume (V_{MP}).

The proximate analysis was conducted to obtain the percentage of moisture, volatiles, fixed carbon, and ash in the samples, through thermogravimetric analysis in a Perking-Elmer STA 6000 thermobalance. The sample was first kept at 30 °C under N₂ (20 mL min⁻¹), then the temperature was raised to 110 °C (heating rate, 40 °C min⁻¹) and maintained for 10 min. Then, the temperature was raised to 875 °C (heating rate, 40 °C min⁻¹) and kept at this temperature for 10 min. Finally, the N₂

was changed into O₂ (20 mL min⁻¹) at 875 °C for another 10 min. The quantification of each of the constituents was carried out by the weight loss in each step and the fixed carbon by the difference.

The content of carbon, hydrogen, nitrogen, and sulfur was determined by elemental analysis in a Thermo Scientific Flash 2000 device. Oxygen was estimated by the difference with the other elements, subtracting the ash content.

The chemical composition of the surface was studied using X-ray Photoelectron Spectroscopy (XPS) in a Kratos AXIS Ultra-DLD device using an X-ray source from Al K α . All the spectra were corrected to the C1_s peak of adventitious carbon to 284.5 eV. The software XPSpeak 4.1® was applied for the processing and deconvolution of the peaks, considering a Shirley background correction.

Scanning Electron Microscopy (SEM) in a FEI Quanta 400 device (30 kV, 3.5 nm resolution) was utilized to observe the morphology of the particles.

Heavy metals adsorption tests in aqueous phase

Batch mode experiments

The solutions of Pb, Cd, and Cu (10–200 mg L⁻¹) were placed in 100 mL Erlenmeyer flasks at room temperature (25 °C) with an adsorbent dose of 2 g L⁻¹. The flasks were agitated in an orbital stirring device at 160 rpm until equilibrium was reached. The samples were filtered with syringe filters (Millipore Millex-GV PVDF, 0.45 μ m), and the concentration of the metal was analyzed by Atomic Absorbance (AA) spectrometry in a PerkinElmer® PinAAcle 500 Flame device. All the experiments were carried out at a free pH, ranging from 4 to 6.

The isotherms were fitted to different models that provides valuable information about activated carbons properties and adsorbate-adsorbent interactions [42]. The Freundlich model [43] assumes that the attraction between the metal ions and the surface of the adsorbent is based on physical forces, such as electrostatic or Van der Waals forces, and describes the equilibrium on heterogeneous surfaces having different affinities for the adsorption sites. Homogeneous surfaces will present $n_F=1$. The expression of the model is as follows:

$$q_e = K_F C_e^{n_F} \quad (3.1)$$

where q_e (mg g⁻¹) is the adsorbed amount in the equilibria; K_F (mg g⁻¹)/(mg L⁻¹) ^{n_F} is the Freundlich's constant; n_F (dimensionless) is the Freundlich's exponent; and C_e (mg L⁻¹) is the equilibrium concentration of the ion in the liquid phase.

The Langmuir model [42] also assumes that the interactions are only physical; however, the following assumptions are considered: i) sorption occurs at specific

sites on the adsorbent surface; ii) each site can hold only one ion (monolayer); iii) the surfaces are homogeneous; iv) all adsorption sites have equal energy and affinity to adsorbates; and v) there are no interactions between adsorbate ions at adjacent sites. The Langmuir isotherm is described by the following expression:

$$q_e = \frac{q_L K_L C_e}{1 + K_L C_e} \quad (3.2)$$

where q_e (mg g^{-1}) and q_s (mg g^{-1}) are the adsorbed amount in the equilibria and the maximum, respectively; K_L ($\text{mg}^{-1} \text{L}$) is the Langmuir's constant; and C_e (mg L^{-1}) is the equilibrium concentration of the ion in the liquid phase.

The Sips three-parameter model [45] combines the Langmuir and Freundlich models and serves to describe heterogeneous surfaces. The model will behave as the Langmuir and Freundlich models at high and low concentrations, respectively. The expression reads as follows:

$$q_e = \frac{q_s (K_s C_e)^{n_s}}{1 + (K_s C_e)^{n_s}} \quad (3.3)$$

where q_e (mg g^{-1}) and q_s (mg g^{-1}) are the adsorbed amount in the equilibria and the maximum, respectively; K_s ($\text{mg}^{-1} \text{L}$) is the Sips's constant; n_s (dimensionless) is the Sips's exponent; and C_e (mg L^{-1}) is the equilibrium concentration of the ion in the liquid phase.

Continuous mode experiments

The best-performing char within the batch experiments, that is $\text{Na}_2\text{CO}_3\text{-AC}$, was selected to perform tests in continuous mode using a plug-flow column. The set-up consisted of a jacketed column of diameter 1.5 cm and height 11 cm, maintained at 25°C , filled with 0.5 g of $\text{Na}_2\text{CO}_3\text{-AC}$ sieved at 355-500 μm and crystal spheres to avoid carryover material. The height of the char material in the column without crystal spheres was 4 cm. The column was fed in up-flow mode with the metal solution (100 mg L^{-1} of Pb, Cd, and Cu) at a rate of 2 mL min^{-1} .

The breakthrough curves were fitted to different models. The Thomas model [46] assumes that the plug flow takes place in the fixed bed, with negligible diffusion restrictions and, second-order reaction kinetics. The equation of Thomas describes the temporal evolution of the normalized concentration as follows:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(K_T C_0 \left(\frac{q_0 m}{v C_0} - t\right)\right)} \quad (3.4)$$

where K_T ($\text{L mg}^{-1} \text{min}^{-1}$) is the Thomas rate constant; q_0 (mg g^{-1}) is the equilibrium adsorption capacity; m (g) is the mass of the adsorbent in the column; v (mL min^{-1})

the inlet flow rate; C_0 (mg L^{-1}) is the initial concentration and, C_t (mg L^{-1}) is the concentration at a given time.

The Yoon–Nelson model [47] assumes that the decrease in the probability of adsorption for each ion is proportional to the probability of adsorption and the probability of breakthrough.

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp(K_{YN}(\tau - t))} \quad (3.5)$$

where K_{YN} (s^{-1}) is the Yoon-Nelson rate constant and τ (min) is the time required to reach 50 % of breakthrough.

The Bohart-Adams model [48] proposes that the adsorption process is not instantaneous and that the rate is proportional to the residual adsorption capacity of the adsorbent and the concentration of the adsorbate.

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(K_{BA}C_0\left(\frac{a_0x}{uC_0}\right) - t\right)} \quad (3.6)$$

where K_{BA} ($\text{L mg}^{-1} \text{min}^{-1}$) is the Bohart-Adams rate constant; a_0 (mg L^{-1}) the initially available adsorption capacity of the adsorbent; x (cm) is the bed height; and u (cm min^{-1}) is the linear flow velocity.

The dose-response model [49] is a simplified model that better fits the breakthrough curves at low and high times as it provides an asymmetric prediction.

$$\frac{C_t}{C_0} = 1 - \frac{1}{1 + (K_{DR}t)^\alpha} \quad (3.7)$$

where α (dimensionless) and K_{DR} (min^{-1}) are the dose-response parameters.

The metal adsorption capacity was extracted from the Thomas model (mg g^{-1}). The saturation time (t_{sat}) is defined as the time at which $C_{\text{tsat}}/C_0 = 0.95$.

The material was also tested using real industrial wastewater (WW) in continuous mode. The WW was collected at an agrochemical production plant (fertilizers, pesticides, and fungicides) located in the province of Granada (Spain). Two different WWs were collected: wastewater from the copper oxychloride (fungicide) production line (WW1) and general wastewater from the production plant (WW2).

The characterization of the WW was done using Hanna test kits for Chemical Oxygen Demand (COD), Nitrates, Phosphates, Sulphates, and Chlorides. Biological Chemical Demand (BOD_5) was measured using Velp Scientifica cap sensors model F102B0133, a Crison MM40 probe was used for Conductivity and Total Dissolved Solids (TDS) and the APHA standard method to determine the Total Suspended Solids (TSS).

The concentration of the different metal elements in the wastewater was done using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) in a PerkinElmer® OPTIMA 8300 device to quantify Al, Ca, Cu, Fe, K, Mn, Na, P, Si, and Zn. Inductively Coupled Plasma coupled to Mass Spectrometry (ICP-MS) was used to quantify Ti, Li, V, Cr, Co, Ni, As, Se, Rb, Sr, Mo, Cd, Hg, Pb, U. The ICP-MS equipment used was a PerkinElmer® NexION 300D using an ion filter plasma torch as the ionization source.

3.1.1.4. Results and discussion

Characterisation of chars

The textural properties, available in **Table 3.1**, show an increase in porosity after activation for all the activation agents tested compared to the native and washed chars. The material with the highest surface area was KOH-AC, which corresponds also to the material with the highest microporosity percentage, being $939 \text{ m}^2 \text{ g}^{-1}$ and 61.4 %, respectively. In contrast, Na_2CO_3 -AC displayed the lowest surface area and microporosity percentage, being $571 \text{ m}^2 \text{ g}^{-1}$ and 41.3 %, respectively. Comparing these results to other chars obtained from plastic precursors in the literature, the reported area for plastic chars activated with KOH varies, ranging from 400 to $3000 \text{ m}^2 \text{ g}^{-1}$; if NaOH is used, the reported values range from 209 to $2000 \text{ m}^2 \text{ g}^{-1}$ [50]. As more specific examples, polyethylene terephthalate (PET) char activated with KOH at an agent/precursor ratio of 1:1 and 700°C for 1 hour (single step with pyrolysis), obtained a surface area of $959 \text{ m}^2 \text{ g}^{-1}$ [51]. Polycarbonate char activated with NaOH at an agent/precursor ratio of 3:1 and 500°C for 1.5 hours (single step with pyrolysis), obtained a surface area of $805 \text{ m}^2 \text{ g}^{-1}$ [52]. Considering other activation agents, municipal plastic char activated with K_2CO_3 at an agent/precursor ratio of 1:1 and 700°C for 1 hour, obtained a surface area of $623 \text{ m}^2 \text{ g}^{-1}$ [53]. Activation of PET chars with CO_2 resulted in surface areas ranging from 1110 to $1830 \text{ m}^2 \text{ g}^{-1}$ [54].

Figure 3.1 depicts the N_2 adsorption-desorption isotherms of the chars after activation. Taking as reference the IUPAC's classification [55], all the ACs describe a Type IV (a) curve, with an initial slope indicating the presence of micropores followed by a H4 hysteresis loop, indicating a moderate presence of mesopores [55]. In the case of KOH-AC, the initial slope is more pronounced, confirming the higher percentage of microporosity obtained.

Table 3.1. Textural properties obtained from N₂ adsorption-desorption isotherms

Sample	S _{BET} (m ² g ⁻¹)	S _{MP} (m ² g ⁻¹)	V _T (cm ³ g ⁻¹)	V _{MP} (cm ³ g ⁻¹)	V _{MP} /V _T (%)
Native Char	2.6	0	0.009	0	0
Washed Char	3.3	0	0.012	0	0
Na ₂ CO ₃ -AC	571.3	425.4	0.535	0.221	41.3
KOH-AC	939.4	821.8	0.653	0.401	61.4
NaOH-AC	704.5	552.5	0.558	0.285	51.1
K ₂ CO ₃ -AC	592.8	457.4	0.519	0.232	44.7

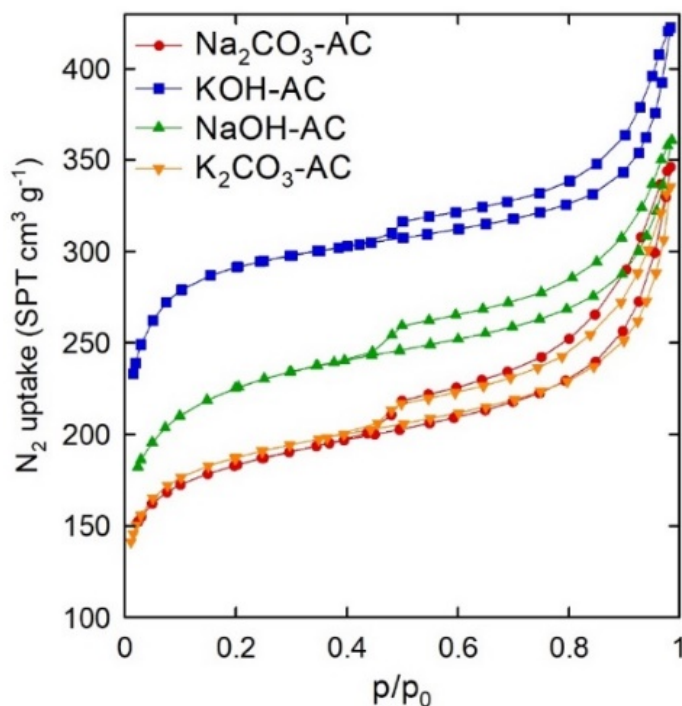


Figure 3.1. N₂ adsorption-desorption isotherms of the activated chars

The proximate and elemental analyses are shown in **Table 3.2**. The carbon content ranges between 47.5 and 55.5 % for the ACs. The carbon content is low compared with biochar from organic origin, e.g., agroforestry. The ACs also show a high ash content due to the high number of impurities and inorganic compounds present in the plastic waste. A study using biochars produced from wheat straw,

softwood, and peach stone reported carbon contents higher than 63.8 % and a maximum ash content of 22.6 % [56]. In contrast, a real mixed plastic sample (35 % polyethylene (PE), 40 % PP, 19 % PS, 5 % PET, and 1 % polyvinylchloride (PVC)) presented a carbon content (29.3 %) lower than the values reported in this study and an ash content (61.4 %) much higher than the values obtained in this study [57].

Table 3.2. Proximate and elemental analysis of the chars before and after activation

Sample	Proximate analysis (%)				Elemental analysis (%)			
	Moisture	Volatile	Fixed carbon	Ash	N	C	H	O*
Native Char	2.9	30.0	28.3	38.8	1.0	37.0	2.4	20.9
Washed Char	1.6	32.0	30.5	36.0	1.5	52.2	5.1	5.3
Na ₂ CO ₃ -AC	2.6	8.8	53.7	35.0	1.0	55.5	0.8	7.7
KOH-AC	7.2	9.3	47.3	36.2	0.6	49.0	0.5	13.7
NaOH-AC	4.8	8.2	55.8	31.2	0.7	55.0	0.7	12.5
K ₂ CO ₃ -AC	1.7	11.0	49.0	38.3	1.0	47.5	1.0	12.7

*Obtained as the difference considering ashes

Figure 3.2 represents the SEM images of the different materials. Native char (**Figure 3.2A**) presents a high heterogeneity, where bulk particles, plain surfaces and plastic fibers can be seen. This heterogeneity is then transferred to the ACs. **Figure 3.2B** shows an augmentation of the native char. A rugous and non-porous surface can be seen. All ACs developed certain porosity after activation. While KOH-AC (**Figure 3.2D**) presents high and well-defined porosity with presence of micropores, Na₂CO₃-AC (**Figure 3.2C**) has a lower quantity of pores which clearly fall into the mesoporous classification. The activating agents KOH and NaOH produced pores which entered deep into the bulk of the material, whereas K₂CO₃ and Na₂CO₃ produced pores which appeared to be shallower.

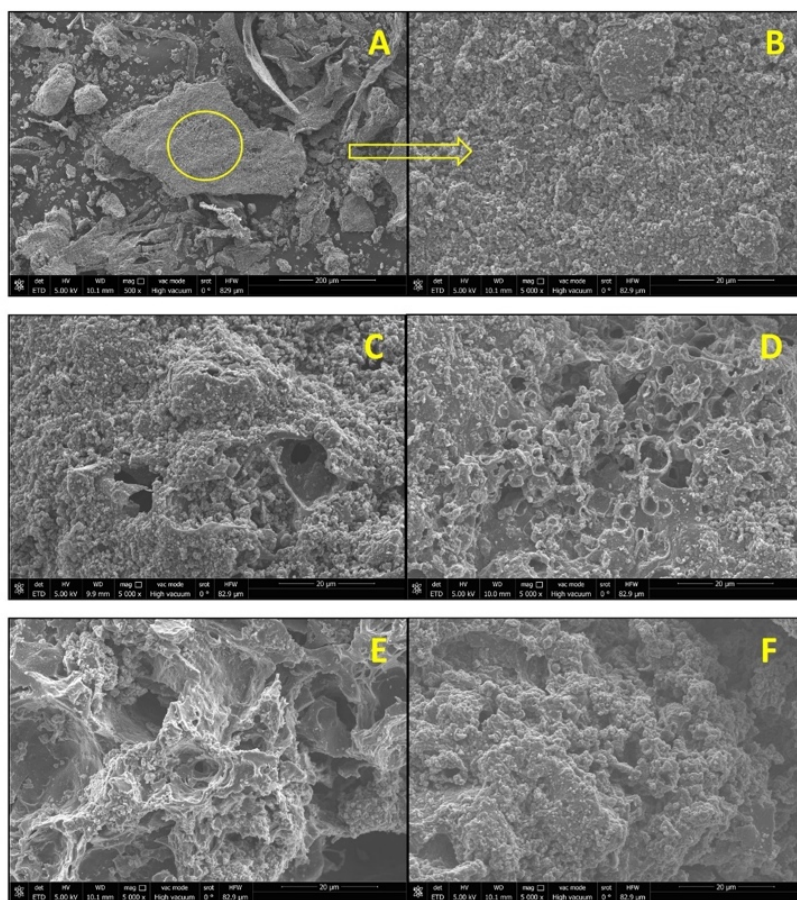


Figure 3.2. SEM images of native char (A and B) and ACs: Na₂CO₃-AC (C), KOH (D), NaOH (E), and K₂CO₃ (F)

The XPS technique was applied to study the surface chemical composition of the different chars. This analysis considers solely the chemical composition of the surface, not the bulk of the particle as in the elemental and proximate analyses. **Table 3.3** displays the results of the elemental composition of the chars' surface and the nature of the functional groups on the surface related to the elements C and O. The following contributions were considered for deconvolution of the C_{1s} spectrum: C=C (284.5 eV), C-C (285.3 eV), C-O (286.6 eV), C=O (288.2-288.7 eV) and O=C-OR (289.9 eV) [59]. For the deconvolution of the O_{1s} spectrum, quinone (530.7 eV), C=O (532.0-532.2 eV), and C-O (533 eV) were considered [57]. The N was not deconvoluted due to the low percentage at which it was detected. As shown in **Table 3.3**, the carbon content decreases after the activation process in favor of oxygen content. However, each sample presents a different carbon content. In addition, the O_{1s} spectrum was deconvoluted considering that oxygen is linked solely to carbon,

while it can also be linked to metals, forming metal oxides. Therefore, to evaluate the percentage of oxygenated carbonaceous groups correctly, the sum of percentages of the peaks area regarding oxygenated groups, i.e. C-O, C=O, and COO⁻, from the C_{1s} region was multiplied by the carbon content (column C_{XPS}-O_X) in **Table 3.3**. Considering this calculation, Na₂CO₃-AC presents the highest C_{XPS}-O_X ratio. Nonetheless, the general tendency is the limited presence of carboxylic groups after activation. Regarding the deconvolution of the C_{1s} spectrum shown in **Figure 3.3**, the most significant difference found is the absence of C=O functional groups and the higher percentage of C-O and COO⁻ groups in Na₂CO₃-AC compared to the other ACs.

Table 3.3. Surface chemical composition of the native, washed and activated chars by XPS

	C _{1s}			O _{1s}			C _{XPS}	O _{XPS}	N _{XPS}	C _{XPS} -O _X
	Type	BE (eV)	% Peak	Type	BE (eV)	% Peak				
Native char	C=C	284.5	56.6	quinone	530.7	27.7	70.5	15.5	0.5	4.2
	C-C	285.3	37.4	C=O	532.0	46.6				
	C-O	286.6	0.0	C-O	533.0	25.7				
	C=O	288.2	3.9							
	COO-	289.9	2.1							
Washed char	C=C	284.5	88.3	quinone	530.7	2.5	83.3	13.9	0.3	9.0
	C-C	285.3	0.9	C=O	532.0	78.3				
	C-O	286.6	2.5	C-O	533.0	19.1				
	C=O	288.5	6.6							
	COO-	289.9	1.7							
Na ₂ CO ₃ -AC	C=C	284.5	47.6	quinone	530.7	4.6	46.1	31.5	1.3	12.6
	C-C	285.3	25.1	C=O	532.0	29.5				
	C-O	286.6	16.6	C-O	533.0	65.9				
	C=O	288.7	0							
	COO-	289.9	10.7							
KOH-AC	C=C	284.5	49.6	quinone	530.7	15.8	51.5	29.7	1.2	11.6
	C-C	285.3	27.9	C=O	532.2	26.5				
	C-O	286.6	7.4	C-O	533.0	57.6				
	C=O	288.7	6.5							
	COO-	289.9	8.6							
NaOH-AC	C=C	284.5	67.6	quinone	530.7	26.8	41.6	32.1	0.3	7.5
	C-C	285.3	14.3	C=O	532.0	56.9				
	C-O	286.6	5.8	C-O	533.0	16.3				
	C=O	288.7	9.6							
	COO-	289.9	2.7							
K ₂ CO ₃ -AC	C=C	284.5	43.1	quinone	530.7	12.1	44.6	34.6	0.9	9.5
	C-C	285.3	35.5	C=O	532.0	27.5				
	C-O	286.6	4.7	C-O	533.0	60.4				
	C=O	288.7	10.7							
	COO-	289.9	6.0							

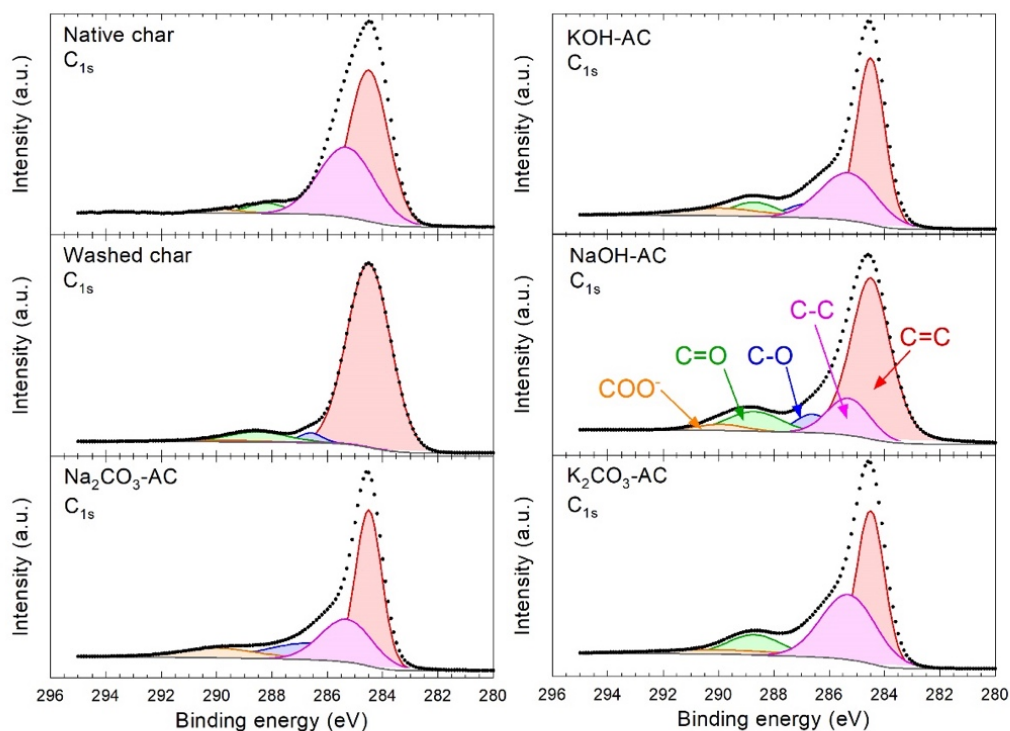


Figure 3.3. XPS deconvolution of the C_{1s} region of the chars before and after activation

Adsorption of heavy metals in water

Isotherms of batch mode experiments

A first approach was done by comparing the adsorption capacity of the char before and after activation to demonstrate the efficacy of the activation process. **Figure 3.4** depicts the results of Pb, Cd, and Cu uptake of washed char compared to the four ACs at an initial metal concentration of 10 mg L^{-1} and char concentration of 2 mg L^{-1} , confirming the improvement of metal uptake after activation. After this first trial, it was decided not to include the washed char in the isotherms study.

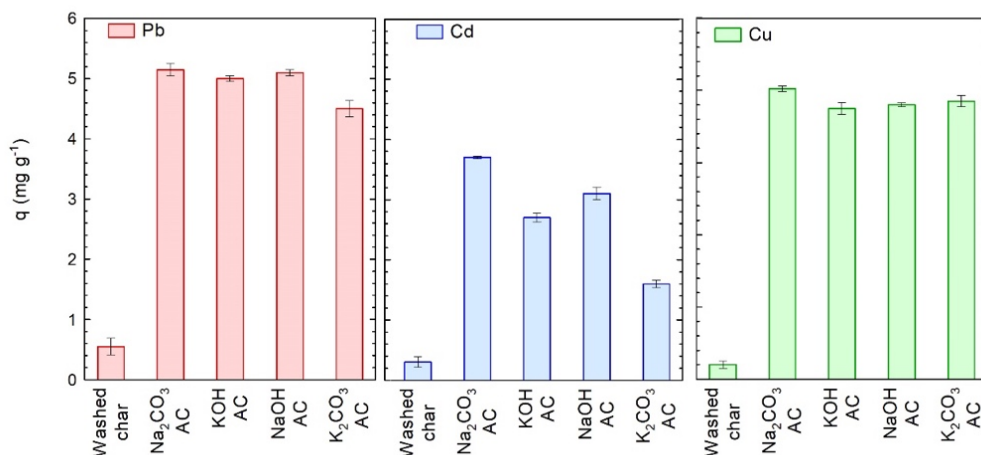


Figure 3.4. Comparison of chars' metal uptake before and after activation. Experimental conditions: $C_0=10 \text{ mg L}^{-1}$; $C_{\text{adsorbent}}=2 \text{ g L}^{-1}$; $T=25 \text{ }^\circ\text{C}$

Figure 3.5 illustrates the adsorption isotherms for the removal of the metals Pb, Cd, and Cu using the four tested materials. The metal Pb is best adsorbed by all materials presenting the highest metal uptake capacity, whereas Cd and Cu present lower metal uptake capacities and are similar between them. The preferential adsorption of Pb^{2+} ions onto the ACs lies in its stronger electronegativity and lower hydrated ionic radius compared to Cd, and Cu ions [60], with the hydrated ionic radius being 4.01, 4.26, and 4.19 Å for Pb, Cd and Cu, respectively [61].

Comparing the activated chars among them, $\text{Na}_2\text{CO}_3\text{-AC}$ slightly outperforms the other ACs, although the differences are minimal. This is an important fact, Na_2CO_3 is an activating agent that better fits with the current environmental goals and is considered a less harmful chemical compared to KOH or NaOH. The model that best fits the isotherms is the Sips model, as shown in **Table 3.4**. The three-parameter Sips model is a combination of the Langmuir and Freundlich isotherms, very suitable for predicting adsorption on heterogeneous surfaces and which reduces some limitations of these models [62].

The XPS analysis shows a limited presence of carboxylic functional groups in the four ACs, suggesting that adsorption may occur through physical means. Metal ions may have a preference for mesoporous materials [63], while the produced chars present a meso-micro porous structure. $\text{Na}_2\text{CO}_3\text{-AC}$ displays the lowest percentage of microporosity (41.6 %) (**Table 3.1**) and a higher ratio of $C_{\text{XPS-OX}}$ (12.6 %) (**Table 3.3**), which might explain the higher metal uptake capacity compared to the other ACs. In contrast, KOH-AC, NaOH-AC, and $\text{K}_2\text{CO}_3\text{-AC}$ present higher microporosity percentages between 44.7 and 61.4 %, and a lower $C_{\text{XPS-OX}}$ ratio between 9.5 and 11.6 % (**Table 3.1** and **Table 3.3**). The reported values for metal uptake in the literature vary in a wide range [63,64]. As a reference, ACs produced

from biomass, e.g., steam-activated coconut for Pb removal has shown a value of 118.1 mg g^{-1} adsorption capacity [65] or date bead carbon activated with ZnCl_2 reached 76.92 mg g^{-1} of Pb uptake [66]. If only chars produced from plastic waste are considered, references found in the literature are limited, and the activated carbons are usually produced from a single type of plastic. A char produced from tire scrap has been reported to present an uptake capacity of 49.79 mg g^{-1} for Pb and 10.40 for Cd mg g^{-1} [67], similar to the values obtained in this study, where the plateaus of the isotherms are reached at 40 and 12 mg g^{-1} for Pb and Cd respectively for $\text{Na}_2\text{CO}_3\text{-AC}$. PET bottle waste resulted in a Fe adsorption capacity of 74 mg g^{-1} [68]. For improved metal adsorption, electrostatic interaction is needed, i.e., ion exchange between metal cations and oxygenated groups existing on the material surface [63]. This may suggest that a post-modification of the AC might be needed to add functional groups and improve metal uptake.

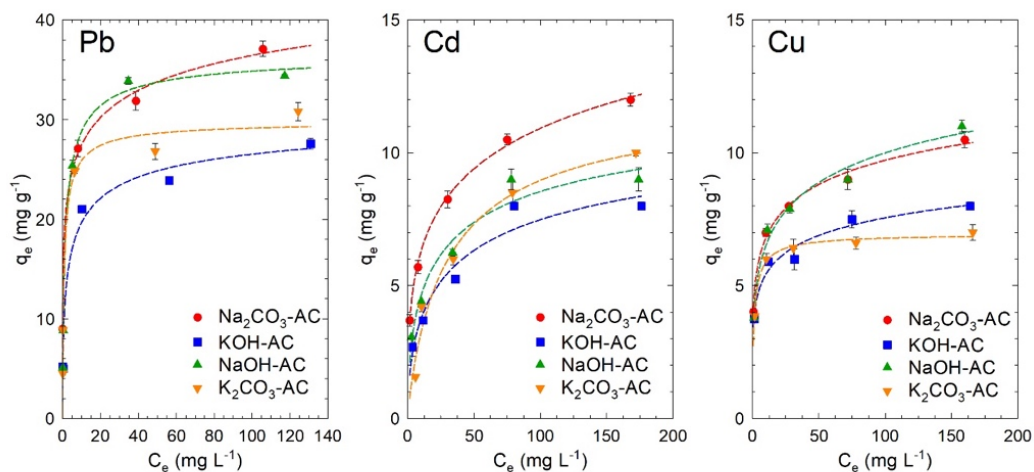


Figure 3.5. Metal adsorption isotherms with the activated chars. The dashed lines represent the fit to the Sips model. Experimental conditions: $C_0=10\text{-}200 \text{ mg L}^{-1}$; $C_{\text{adsorbent}}=2 \text{ g L}^{-1}$; $T=25 \text{ }^\circ\text{C}$

Table 3.4. Fitting parameters of metal isotherms to different models

Metal	Activated char	Freundlich parameters			Langmuir parameters			Sips parameters			
		K_F	n	R^2	q_L	K_L	R^2	q_s	K_s	n	R^2
		$\text{mg}^{1-nF} \text{g}^{-1} \text{L}^{nF}$	-	-	mg g^{-1}	L mg^{-1}	-	mg g^{-1}	L mg^{-1}	-	-
Pb	Na ₂ CO ₃ -AC	17.776	0.173	0.964	33.262	11.792	0.878	58.804	0.061	0.269	0.965
	KOH-AC	10.513	0.207	0.939	25.536	0.762	0.937	31.756	0.264	0.496	0.973
	NaOH-AC	14.643	0.202	0.897	33.764	0.969	0.979	36.854	0.630	0.691	0.998
	K ₂ CO ₃ -AC	13.117	0.188	0.889	28.528	1.671	0.982	29.957	1.147	0.758	0.988
Cd	Na ₂ CO ₃ -AC	3.534	0.244	0.993	11.506	0.148	0.893	25.307	0.005	0.362	0.998
	KOH-AC	1.974	0.285	0.925	8.621	0.071	0.901	12.319	0.022	0.552	0.944
	NaOH-AC	2.526	0.260	0.934	9.436	0.097	0.910	12.974	0.033	0.545	0.958
	K ₂ CO ₃ -AC	1.462	0.383	0.934	11.332	0.039	0.970	12.164	0.032	0.890	0.971
Cu	Na ₂ CO ₃ -AC	4.527	0.166	0.988	9.113	0.814	0.823	19.649	0.009	0.269	0.993
	KOH-AC	3.782	0.150	0.963	7.225	0.701	0.809	15.939	0.006	0.243	0.967
	NaOH-AC	4.064	0.195	0.977	9.656	0.377	0.846	21.348	0.007	0.305	0.982
	K ₂ CO ₃ -AC	4.187	0.108	0.853	6.814	0.747	0.986	6.974	0.768	0.821	0.990

Breakthrough curves of continuous mode experiments

Synthetic effluents

The best-performing char within the batch experiments, that is $\text{Na}_2\text{CO}_3\text{-AC}$, was selected to perform tests in continuous mode using a plug-flow column. The breakthrough curves for Pb, Cd, and Cu obtained in synthetic water using $\text{Na}_2\text{CO}_3\text{-AC}$ are shown in **Figure 3.6**. The rise of the curves starts at 14 min for Pb, and 10 min for Cu, while it immediately starts for Cd. The saturation time was reached at 290, 16, and 80 min for Pb, Cd, and Cu synthetic waters, respectively. **Table 3.5** summarizes the fitting parameters corresponding to the different models used. The Dose-response model is the best fit for the Pb, Cd and Cu synthetic waters. The adsorption capacity predicted by the Thomas model is 26.8, 4.1, and 7.9 mg g^{-1} for Pb, Cd, and Cu, respectively. Comparing these results to the isotherms study, Pb remains as the metal best adsorbed. The metal uptake results of the isotherms study at an initial concentration of 100 mg L^{-1} of metal, using $\text{Na}_2\text{CO}_3\text{-AC}$, are 31.90, 10.50 and 9.00 mg g^{-1} for Pb, Cd, and Cu, respectively, which resemble the breakthrough curves results.

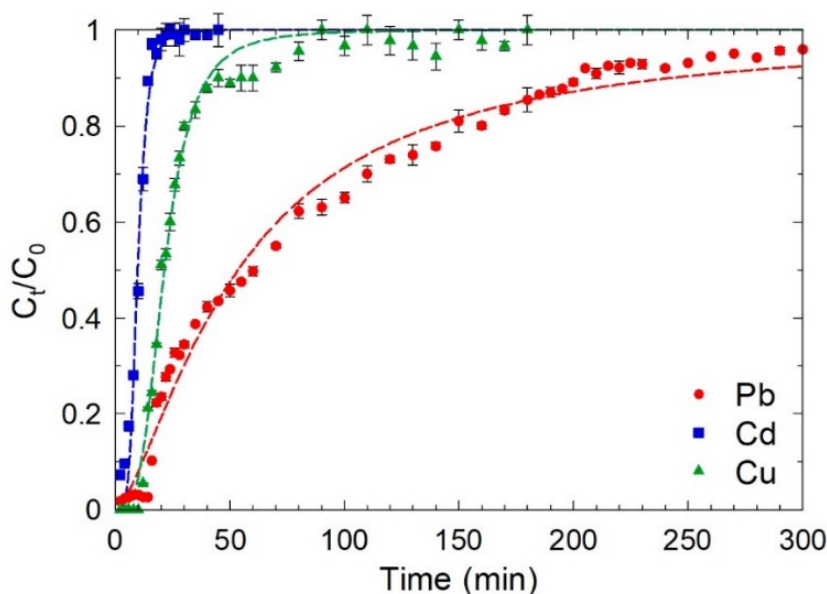


Figure 3.6. Metals adsorption breakthrough curves with $\text{Na}_2\text{CO}_3\text{-AC}$ using synthetic effluents. The dashed lines represent the fitting models corresponding to the Dose-response model. Experimental conditions: $C_0=100 \text{ mg L}^{-1}$; $m_{\text{adsorbent}}=0.5 \text{ g}$; $T=25 \text{ }^\circ\text{C}$, $Q=2 \text{ mL min}^{-1}$

Table 3.5. Fitting parameters of metals breakthrough curves to the models with Na₂CO₃-AC

Model	Parameters		Metal		
			Pb	Cd	Cu
Thomas	K _T	mL mg ⁻¹ min ⁻¹	0.243	4.208	2.065
	q ₀	mg g ⁻¹	26.808	4.136	7.919
	R ²	-	0.939	0.995	0.977
Yoon-Nelson	K _{YN}	min ₋₁	0.022	0.433	0.186
	τ	min	75.135	10.040	21.998
	R ²	-	0.939	0.995	0.977
Bohart-Adams	K _{BA}	mL mg ⁻¹ min ⁻¹	0.243	4.208	2.065
	a ₀	mg L ⁻¹	1479.7	228.3	437.1
	R ²	-	0.939	0.995	0.977
Dose-response	K _{DR}	min ⁻¹	0.019	0.102	0.047
	α	-	1.454	4.681	3.435
	R ²	-	0.985	0.985	0.990

Industrial effluent

The industrial wastewater WW1 and WW2 were characterized, and the results are shown in **Table 3.6** and **Table 3.7**. The WW1 presents a low pH and a high concentration of chlorides. This wastewater was collected at the copper oxychloride production line, used as fungicide. Copper and hydrochloric acid are used as raw materials for the production of this fungicide, explaining the low pH and high chloride presence. On the other hand, WW2 was collected in the general collecting point of the wastewater treatment plant, where water from all the production lines was received. This aspect explains the high amount of nitrates, phosphates, and sulfates coming from the fertilizers and other chemicals added during the production step. The number of elements appearing in WW2 is larger. While in WW1, copper is the heavy metal that appears in a considerably high concentration, i.e., 52.08 mg L⁻¹; WW2 displays a wider variety of elements, including chromium, manganese, and zinc at a range at the same level of concentration as copper.

Table 3.6. Characterization of the industrial wastewater effluents

Parameter		WW1	WW2
pH	-	1.5	8.6
Conductivity	mS cm ⁻¹	65.7	80
TDS	mg L ⁻¹	41.6	51.4
TSS	mg L ⁻¹	224.3	850
COD	mg O ₂ L ⁻¹	7310	10430
BOD ₅	mg O ₂ L ⁻¹	754	168
Nitrates	mg N-NO ₃ ⁻ L ⁻¹	1100	4280
Phosphates	mg P-PO ₄ ³⁻ L ⁻¹	60	820
Sulfates	mg SO ₄ ²⁻ L ⁻¹	115	10000
Chlorides	Mg Cl ⁻ L ⁻¹	>20000	6600

Table 3.7. Elemental characterization of the industrial wastewater effluents

Element	WW1 mg L ⁻¹	WW2 mg L ⁻¹	Element	WW1 mg L ⁻¹	WW2 mg L ⁻¹
Al	0.01	169.90	Cr	0.34	21.23
Ca	19.85	1974	Co	0.06	0.12
Cu	52.08	34.50	Ni	0.16	0.54
Fe	0.41	131.90	As	0.09	0.16
K	246.20	23070	Rb	0.11	2.33
Mn	0.15	26.54	Sr	0.70	5.00
Na	25100	33330	Mo	0.17	9.59
P	-	11740	Cd	0.00	0.19
Si	8.52	13.45	Hg	0.00	0.00
Zn	0.06	32.15	Pb	0.00	0.07
Li	0.09	0.18	U	0.00	1.91
Ti	0.10	5.94			
V	0.08	4.17			

Figure 3.7 depicts the breakthrough curves for Cu adsorption contained in WW1 and WW2 using $\text{Na}_2\text{CO}_3\text{-AC}$. The rise of the curves starts at 5 min for WW1, while it immediately starts for WW2. The saturation time was reached at 45 and 20 min for WW1 and WW2, respectively. The Cu adsorption capacity predicted by the Thomas model is 2.531 and 1.132 mg g^{-1} for WW1 and WW2, respectively (**Table 3.8**). Fitting parameters of copper breakthrough curves to the different models with $\text{Na}_2\text{CO}_3\text{-AC}$ using industrial wastewater are also summarized in **Table 3.8**. As expected, the Cu adsorption capacity decreased in WW1 and WW2 compared to the Cu adsorption capacity in the synthetic water (7.919 mg g^{-1}) due to the presence of other contaminants. However, the Cu adsorption capacity in WW1 could be expected to be higher and closer to the one presented in synthetic water due to the lower presence of other contaminants competing for adsorption sites. This drastic decrease in Cu uptake in WW1 may be due to the low pH presented by WW1. At low pH, the surface of the material may be covered by $\text{H}_3\text{O}^+(\text{aq})$ ions, decreasing the interaction of Cu with binding sites due to repulsion forces [69]. The WWs were used with no modifications to investigate the results.

Regarding WW2, the presence of other contaminants (**Table 3.7**) decreases the Cu adsorption capacity compared to synthetic water. **Figure 3.8** depicts the breakthrough curves of the heavy metals appearing in a relevant concentration in WW2. The adsorption capacity of these elements predicted by the Thomas model are 0.990, 0.989 and 0.820 for Mn, Zn, and Cr, respectively (**Table 3.9**). Taking into account these heavy metals, the order in which they are best adsorbed is as follows: $\text{Cu} > \text{Mn} > \text{Zn} > \text{Cr}$. The order fits with the increasing order of hydrated ionic radius being 4.19, 4.28, 4.30, and 4.61 Å for Cu, Mn, Zn, and Cr, respectively [61].

Although Al, Ca, Fe, K, Na and P also appear in considerable amounts, these elements were not adsorbed.

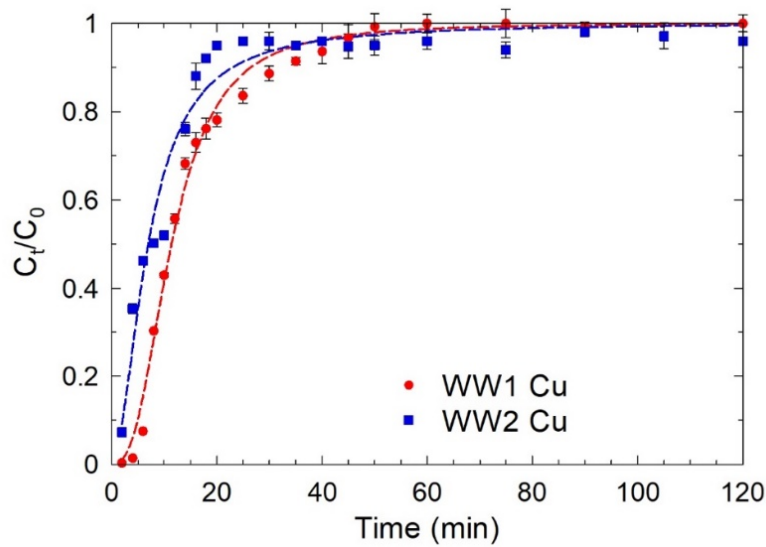


Figure 3.7. Copper adsorption breakthrough curves with $\text{Na}_2\text{CO}_3\text{-AC}$ using industrial effluents. The dashed lines represent the fitting models corresponding to the Dose-response model. Experimental conditions: $m_{\text{adsorbent}}=0.5 \text{ g}$; $T=25 \text{ }^\circ\text{C}$, $Q=2 \text{ mL min}^{-1}$

Table 3.8. Fitting parameters of copper breakthrough curves to the different models with $\text{Na}_2\text{CO}_3\text{-AC}$ using industrial wastewater

Model	Parameters		WW1	WW2
			Cu	Cu
Thomas	K_T	$\text{mL mg}^{-1} \text{ min}^{-1}$	4.704	6.493
	q_0	mg g^{-1}	2.531	1.132
	R^2	-	0.962	0.958
Yoon-Nelson	K_{YN}	min^{-1}	0.245	0.224
	τ	min	12.147	8.206
	R^2	-	0.962	0.958
Bohart-Adams	K_{BA}	$\text{mL mg}^{-1} \text{ min}^{-1}$	4.704	6.493
	a_0	mg L^{-1}	139.672	62.505
	R^2	-	0.962	0.958
Dose-response	K_{DR}	min^{-1}	0.088	0.144
	α	-	2.617	1.838
	R^2	-	0.991	0.959

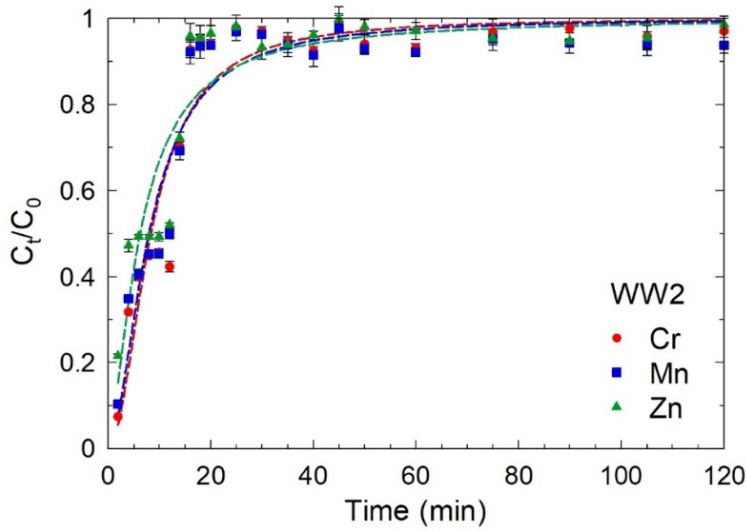


Figure 3.8. Chromium, manganese, and zinc adsorption breakthrough curves with $\text{Na}_2\text{CO}_3\text{-AC}$ using WW2. The dashed lines represent the fitting models corresponding to the Dose-response model. Experimental conditions: $m_{\text{adsorbent}}=0.5$ g; $T=25$ °C, $Q=2$ mL min^{-1}

Table 3.9. Fitting parameters of chromium, manganese and zinc breakthrough curves to the different models with $\text{Na}_2\text{CO}_3\text{-AC}$ using WW2

Model	Parameters		WW2		
			Cr	Mn	Zn
Thomas	K_T	$\text{mL mg}^{-1} \text{min}^{-1}$	10.457	7.930	5.586
	q_0	mg g^{-1}	0.820	0.990	0.989
	R^2	-	0.923	0.928	0.905
Yoon-Nelson	K_{YN}	min^{-1}	0.222	0.210	0.180
	τ	min	9.653	9.322	7.692
	R^2	-	0.923	0.928	0.905
Bohart-Adams	K_{BA}	$\text{mL mg}^{-1} \text{min}^{-1}$	2.489	7.930	5.586
	a_0	mg L^{-1}	190.103	54.624	54.596
	R^2	-	0.923	0.928	0.905
Dose-response	K_{DR}	min^{-1}	0.119	0.125	0.159
	α	-	1.977	1.804	1.496
	R^2	-	0.931	0.939	0.915

The municipal regulation in the province of Granada (Spain) for wastewater discharge into the public sewer system regarding heavy metals, states the following limits for the metals appearing in WW2: 3 mg L⁻¹ of Cu, 2 mg L⁻¹ Mn, 10 mg L⁻¹ Zn and 3 mg L⁻¹ of Cr. Considering these limits and using the Thomas model for predicting the operation time in which the effluent of the column would remain within discharge limits, WW2 could be discharged in the public sewer system until an operation time of 2 mins. Experimental conditions should be recalculated to comply with discharge limits for a longer time and allow the developed activated carbon to present a more realistic application at industrial scale. Hence, according to predictions using the Thomas model, the mass of Na₂CO₃-AC needed for maintaining the discharge within limits for 15 minutes has been calculated with same flow rate (2 mL min⁻¹). The resulting mass was 0.935 g of Na₂CO₃-AC for complying with the 4 metal limits for 15 minutes, compared to the 0.5 g used in the experiment set-up. Zn represents the most restrictive element, fixing the mass of activated carbon needed.

3.1.1.5. Conclusions

Activated carbons produced from post-consumer mixed plastic have interesting properties for heavy metal adsorption. The Na₂CO₃-AC presented the best performance in batch mode experiments compared to KOH, K₂CO₃ and NaOH ACs, presenting a surface area of 571 m² g⁻¹, the lowest percentage of microporosity (41.3 %) and the highest percentage of oxygenated groups linked to surface carbon (12.6 %). Metal ions may have a preference for mesoporous materials according to the lowest percentage of microporosity obtained. Although Na₂CO₃-AC presented the highest percentage of oxygenated groups linked to surface carbon, the XPS analysis showed a limited amount of oxygenated functional groups, suggesting that the adsorption is physical, and a post-modification of the activated char might be needed to add functional groups and improve the metal uptake. On the other hand, the activation agent Na₂CO₃ is an excellent eco-friendly alternative to other harmful chemicals, such as KOH.

Pb is the metal best adsorbed with a metal uptake of 40 mg g⁻¹ using Na₂CO₃-AC and synthetic water, followed by Cd and Cu, with a metal uptake value of 13 and 12 mg g⁻¹ respectively (experimental plateau).

Experiments in a column set-up using Na₂CO₃-AC resulted in a saturation time of 290, 16, and 80 min for Pb, Cd, and Cu synthetic waters, respectively, and metal uptakes of 26.8, 4.1, and 7.9 mg g⁻¹, respectively.

Regarding agrochemical industrial wastewater, the adsorption is heavily affected by the specific characteristics of the effluents. Cu uptake was recorded as 2.531 and 1.132 mg g⁻¹ for WW1 and WW2 respectively. Concretely, WW1 presents a low pH

and WW2 has a varied content of metals competing for binding sites, mainly Cr, Cu, Mn, and Zn. To achieve an effluent (WW2) compliant with local legislation in terms of discharge to the sewer system in a continuous operation time of 15 min, the adsorbent dose should be increased from 0.5 g to 0.935 g, keeping constant the other experimental conditions.

Much effort is put into investigating novel adsorption materials. However, techno-economical and Life Cycle Assessments will be the focus of future investigations to determine the viability of industrial applications.

Acknowledgments

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3.1.1.6. References

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3.1.2. Paper 2: Plastic waste to carbon adsorbent: activation with sodium carbonate and functionalization with citric acid

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Ledicia Pereira, María Ángeles Martín-Lara, Guillermo García-García, Concepción Calvo, Tatiana Robledo, Rafael R. Solís, Mónica Calero.

3.1.2.1. *Abstract*

Plastic waste management is currently a challenge of great importance. The valorization of non-recyclable fractions into carbonaceous adsorbents is an interesting strategy that promotes the circular economy. In this work, a waste-to-adsorbent strategy was pursued with the char from plastic pyrolysis. The char (non-porous, surface area $\sim 3 \text{ m}^2 \text{ g}^{-1}$) was activated with chemical activation, with sodium carbonate boosting the textural properties (surface area $\sim 418 \text{ m}^2 \text{ g}^{-1}$, pore volume $0.436 \text{ cm}^3 \text{ g}^{-1}$), triggering the formation of activated carbon with a large mesoporosity (71 %). X-ray photoelectron spectroscopy and thermal programmed desorption characterization confirmed the enrichment of the surface with carboxylic groups by treatment with citric acid, with a slight loss of textural properties. The activated carbon showed an enhanced adsorption uptake of lead in water ($\sim 52 \text{ mg g}^{-1}$ functionalized vs. $\sim 37 \text{ mg g}^{-1}$ non-functionalized) and limited influence on the adsorption of acetaminophen. The preparation costs and the consumption cost per unit of removed pollutants confirm the benefits of the activation and functionalization of the original carbonaceous precursor. However, the plausible metal lixiviation from plastic additives and the environmental impact according to a life cycle assessment still make this kind of valorization strategy controversial.

Keywords: plastic waste char; activated carbon; sodium carbonate activation; citric acid modification; water contaminant removal; characterization; economic and environmental assessment

3.1.2.2. *Introduction*

Effective waste management is essential for preserving environmental sustainability and safeguarding public health [1]. Poor waste disposal practices, especially concerning plastics, significantly contribute to land and water pollution, disrupt ecosystems, and pose severe risks to wildlife [2]. Plastic pollution has become a global crisis, with millions of tons of plastic waste entering oceans and landfills annually, where it can persist for centuries [3]. This pollution not only endangers marine life but also breaks down into microplastics, infiltrating food chains and adversely affecting human health [4]. As populations and consumption levels

continue to rise, it is increasingly urgent to address plastic waste through improved waste management systems to mitigate long-term ecological damage and reduce greenhouse gas emissions [5].

One promising strategy for mitigating plastic pollution is its conversion into activated carbon, a highly porous material with excellent adsorptive properties that can be used to remove contaminants from water [6–12]. Activated carbon is typically produced by carbonizing organic material and subsequently activating it using either physical or chemical methods [11–13]. Physical activation involves exposing the carbonized material to gases, such as steam or carbon dioxide, at high temperatures (800–1100 °C), which enhances pore formation [14]. In contrast, chemical activation entails impregnating the carbon precursor with activating agents, often resulting in activated carbon with a higher surface area and larger pore volume compared to physical activation [15,16]. The preparation of activated carbon from diverse plastic waste has been largely investigated. Commonly, specific items or simple polymeric formulas are addressed [7,11,17]. For instance, caps, bottles, or bags have been successfully transformed into activated carbon with competitive textural and chemical properties for adsorption applications [9,11]. The use of complex plastic mixtures, such as those reported in the rejection fraction of plastic waste management plants, has been less explored due to the challenges that must be tackled [10].

Among various chemical agents, KOH is widely used for producing activated carbon with an enhanced porosity and surface area [18]. In addition to KOH, other chemical agents such as H_3PO_4 , ZnCl_2 , NaOH, and K_2CO_3 , among others, are also commonly used in the production of activated carbon [19]. Among these activating agents, Na_2CO_3 has emerged as an environmentally friendly alternative, offering a balance between efficiency and ecological impact. This relatively mild agent is effective for developing mesoporosity, which is ideal for the retention of larger molecules.

The activation of materials using Na_2CO_3 has been the focus of various studies in recent years, primarily targeting the production of activated carbon [20,21] for a variety of applications, including the removal of heavy metals [22,23] and organic pollutants [24], and in the development of alkali-activated electrodes [25,26], binders in geopolymers [27], and construction materials [28]. The use of Na_2CO_3 in the alkali activation of high-carbon biomass fly ash demonstrates that increasing the $\text{Na}_2\text{CO}_3/\text{Na}_2\text{SiO}_3$ ratio improved the compressive strength and density of the resulting materials [21]. The adsorption capacity of activated carbon produced from biological materials, such as rice husk [23,29] and oil palm fronds [20,30], has also been investigated. These studies demonstrate that chemical activation with Na_2CO_3 enhances the porosity and specific surface area of activated carbon [26,29], resulting in greater adsorption efficiency for pollutants such as heavy metals, such as Ni [31]

or Pb [32], and organic dyes [24,33,34]. Optimizing parameters like activation temperature and the ratio of sodium carbonate to raw materials is essential to maximize adsorption capacity. Several articles compare different activation methods, emphasizing that chemical activation with Na_2CO_3 offers advantages over other activators due to the lower corrosion if compared to alkalis and to safer management in real applications [20,35]. For example, using Na_2CO_3 to produce activated carbon from wastepaper resulted in materials with superior properties for adsorbing dyes like methylene blue [33]. The use of Na_2CO_3 is not limited to biomass-derived materials. The activation of chars obtained from post-consumer mixed plastic waste proved that Na_2CO_3 -activated carbon (Na_2CO_3 -AC) exhibits superior performance in the adsorption of heavy metals such as Pb (40 mg g^{-1}), Cd (13 mg g^{-1}), and Cu (12 mg g^{-1}) [22]

The optimization of activation processes and the exploration of new feedstock sources remain areas of ongoing interest, promising a bright future for the use of sustainable materials in various industrial applications. Furthermore, integrating chemical activation methods can significantly mitigate environmental issues, making Na_2CO_3 activation a valuable option in the circular economy and developing cleaner technologies. In addition to Na_2CO_3 activation, modifying activated carbon with citric acid (CA) has gained attention for further improving its adsorption capabilities. Citric acid is a biodegradable, non-toxic organic compound that introduces carboxyl groups to the carbon surface, making citric acid-modified materials suitable for a wide range of applications, particularly for water treatment strategies [36–43]. For instance, citric acid-based residues were employed to produce activated carbon formulas with a superior adsorption uptake of volatile organic compounds such as ethyl acetate [38]. Citric acid can be used to add carboxyl groups onto the surface of the adsorbent, which improves the binding potential of organic adsorbates such as metolachlor, raising the uptake of the non-treated adsorbent from $\sim 51 \text{ mg L}^{-1}$ to $\sim 74 \text{ mg L}^{-1}$ following citric acid treatment [40]. Citric acid can be used as a green cross-linker with potential applications in bio-adsorbents, which highlights them for biomedical applications such as tissue engineering and drug delivery [36].

Based on the aforementioned context, the primary objectives of this research are to (1) prepare activated carbon from plastic waste char through sodium carbonate activation and citric acid modification; (2) comprehensively characterize the resulting activated carbon in terms of surface area, porosity, elemental composition, proximate analysis, and others; (3) evaluate its effectiveness in removing specific contaminants from wastewater; and (4) evaluate the economic viability and environmental sustainability of the process.

3.1.2.3. Experimental section

Preparation of Activated Carbon from Plastic Waste

The plastic waste used for this study came from the rejected fraction of a municipal solid waste facility. The composition of the plastics was determined as follows (wt. %): 55.0 % polypropylene, 8.6 % high-impact polystyrene, 10.1 % expanded polystyrene, and 27.7 % polyethylene film [44]. The material was crushed to a size smaller than 1 mm and subjected to pyrolysis in a horizontal tubular furnace (Nabertherm) under an N₂ flow of 50 L h⁻¹. The temperature increased at 10 °C/min from room temperature to a final pyrolysis temperature of 500 °C, with a holding time of 90 min. The resulting material was denoted as “char”.

The pyrolyzed char was chemically activated using Na₂CO₃ (PanReac AppliChem, Barcelona, Spain). The char was ground and mixed with the activating agent at a 1:1 mass ratio. The mixture was heated in a tubular furnace under N₂ flow (12 L h⁻¹) under the following program: heating from room temperature to 300 °C at 10 °C/min, held at 300 °C for 60 min, and then heated to 800 °C (10 °C/min) and held for 60 min. The amount of Na₂CO₃ and the activation temperature were based on previous studies [10,45]. After activation, the activated char was washed with 1 M HCl (PanReac AppliChem, Barcelona, Spain) solution (20 mL per 1 g of char), filtered, and rinsed with water until a neutral pH was achieved. The final activated material was dried at 120 °C overnight and labeled “AC”. For comparison purposes, the non-activated “char” was also washed following the same procedure.

For the citric acid (PanReac AppliChem, Barcelona, Spain) functionalization, the prepared “AC” was immersed in a citric acid solution ranging from 0.5 to 1.5 M, with a liquid-to-solid ratio of 25:4 (mL of solution per gram of activated carbon). The mixture was stirred continuously at room temperature for 30 min to ensure uniform contact between the citric acid and the activated carbon’s surface. After impregnation, the mixture was filtered and washed several times with distilled water to remove the residual citric acid. Finally, the washed activated carbon was dehydrated at 50 °C for 24 h and re-dried at 100 °C to remove moisture before storage. The resulting materials were labeled “AC-CA-X”, where X refers to the citric acid concentration during the impregnation step (0.5–1.5 M). For comparison purposes, the non-activated char was also modified with citric acid, leading to the material denoted as “char-CA-X”. **Figure 3.9** schematizes the activation of the char to prepare AC and the functionalization with citric acid, AC-CA-X

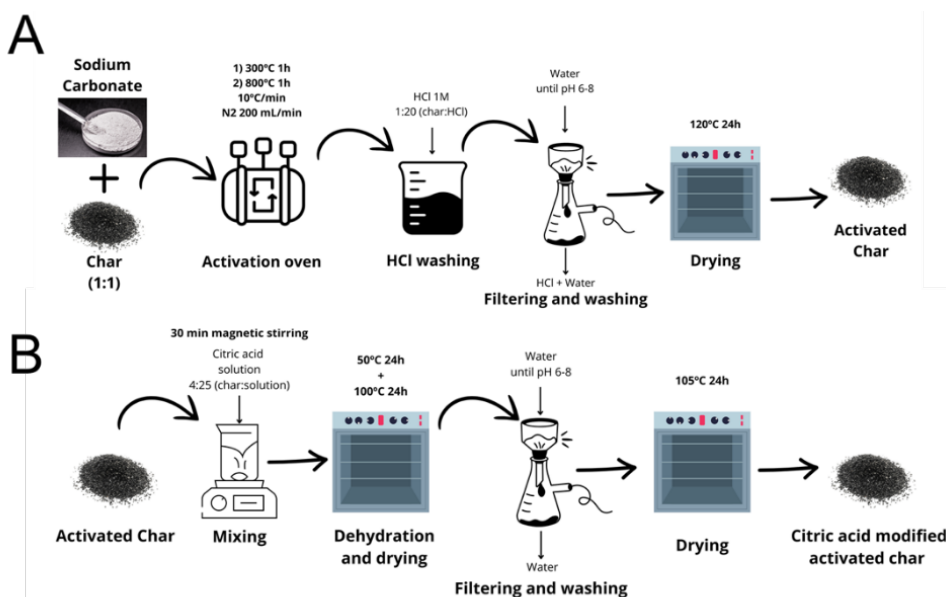


Figure 3.9. Activation of the char with Na_2CO_3 (A) and post-thermal citric acid treatment (B)

Characterization of Activated Carbon

The textural properties were evaluated through static gas adsorption in a Sync 200 instrument (3P Instruments[®], Odelzhausen, Germany). Samples were degassed at 150 °C under vacuum for 12 h using a Prep J4 unit (3P Instruments[®], Odelzhausen, Germany). The N_2 adsorption–desorption isotherms were obtained at 77 K, leading to the total surface area (S_{BET}) ascertained using the BET method. The micropore surface area (S_{MP}) and micropore volume (V_{MP}) were determined using the t-plot method. The pore size distribution was derived from CO_2 adsorption at 273 K, applying the Horvath–Kawazoe (HK) model [46,47].

The bulk chemical composition was determined by proximate and elemental analysis. Proximate analysis was performed using a Perkin Elmer[®] STA 6000 thermobalance (Waltham, Massachusetts, USA). Samples were heated under N_2 (20 mL min^{-1}) with the following temperature profile: held at 30 °C for 20 min, then heated to 110 °C (20 °C min^{-1}), and held for 20 min to measure moisture content. The volatile matter was determined by heating to 850 °C (20 °C min^{-1}) and holding for 20 min. Ash content was measured by switching the gas from N_2 to O_2 (20 mL min^{-1}) and maintaining it at 850 °C for 20 min. Elemental analysis (CHNS) was carried out using a Thermo Scientific[™] Flash 2000 analyzer (Waltham, Massachusetts, USA). Samples were combusted at approximately 1400 °C, producing CO_2 , H_2O , NO_x , and SO_2 , which were separated chromatographically and

detected with a thermal conductivity detector. The oxygen content was tentatively estimated by subtracting the CHNS values and ash content.

The surface chemical composition was analyzed using X-ray photoelectron spectroscopy (XPS) on a Kratos AXIS Ultra-DLD device from Jenck S.A. (Buenos Aires, Argentina), with Al K α radiation as the X-ray source. Spectra were calibrated to the C_{1s} peak (284.6 eV) of adventitious sp³ carbon, and peak deconvolution was performed using XPSpeak software (version 4.1) under a Shirley background correction. The chemical surface was further analyzed by thermal programmed desorption (TPD) with NH₃ on an AMI-300Lite chemisorption station from Altamira Instruments® (Pittsburgh, Pennsylvania, USA) equipped with a Thermal Conductivity Detector (TCD). Briefly, 100 mg of sample was loaded and submitted to adsorption with NH₃ (10 % NH₃ in He) under 100 °C, and a temperature program from 100 °C to 1000 °C was applied.

Adsorption Experiments

Batch adsorption experiments for lead and acetaminophen were conducted at 25 °C in 100 mL Erlenmeyer flasks. Solutions containing Pb at concentrations ranging from 10 to 300 mg L⁻¹ and acetaminophen at concentrations ranging from 10 to 1000 mg L⁻¹ were prepared, using an adsorbent dose of 2.0 g L⁻¹, and stirred at 160 rpm, maintaining the temperature at 25 °C until equilibrium was reached. The samples were filtered through Millipore Millex-GV PVDF 0.45 µm syringe filters, and the concentration was measured by atomic absorption spectroscopy (PerkinElmer® PinAAcle 500, Waltham, Massachusetts, USA) for Pb; high-pressure liquid chromatography (HPLC) using a Waters™ Alliance e2695 HPLC (Milford, Massachusetts, USA) with a 2998 photodiode array detector was used for the quantification of acetaminophen. A Zorbax Bonus-RP column (4.6 mm × 150 mm, 5 µm) was used as the stationary phase.

The adsorption uptake reached at equilibrium (q_e) was fitted to the two-parameter models of Langmuir (Equation (3.8)) and Freundlich (Equation (3.10)), and the three-parameter model of Sips (Equation (3.9)):

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (3.8)$$

$$q_e = K_F C_e^{1/n_F} \quad (3.9)$$

$$q_e = \frac{q_{\max} K_S C_e^{1/n_S}}{1 + K_S C_e^{1/n_S}} \quad (3.10)$$

where q_e is the amount of adsorbate per unit mass of adsorbent at equilibrium (mg g^{-1}); C_e is the equilibrium concentration of adsorbate in the liquid phase (mg L^{-1}); q_{max} is the theoretical maximum adsorption capacity (mg g^{-1}); K_L is the Langmuir constant related to the affinity of the binding sites ($\text{mg}^{-1} \text{L}$); K_F is the Freundlich constant related to the adsorption capacity ($\text{mg} \cdot \text{g}^{-1} / (\text{mg} \cdot \text{L}^{-1})^{1/n_F}$); n_F and n_S are the heterogeneity factors, indicating the intensity of adsorption (dimensionless) of the Freundlich and Sips models, respectively; and K_S is the Sips constant related to the affinity of the binding sites ($\text{mg}^{-1} \text{L}$)^{1/ n_S} .

Finally, the prepared char-based material adsorbents were also subjected to leaching tests under unmodified pH conditions to ensure the sustainability of the treatment process. The experiment involved preparing a mixture of 10 g of char with 100 mL of water, maintaining a ratio of 1:10. This mixture was agitated at a speed of 10 rpm for 24 h. Following the agitation period, the leachate was filtered using a 0.45 μm filter (PVDF Millex-HV, Merck KGaA, Darmstadt, Germany), and the released metals were quantified by Induced Coupled Plasma-Mass Spectrometry (ICP-MS) in a Perkin Elmer Nexion 300D device (Waltham, Massachusetts, USA).

Environmental Assessment

For the environmental assessment, the life cycle analysis (LCA) methodology was applied. The standards that define the LCA methodology are the Standard “UNE-EN ISO 14040:2006. Environmental management. Life cycle analysis. Principles and reference framework” [48] and “Standard UNE-EN ISO 14044:2006/A1:2018. Environmental management. Life cycle assessment. Requirements and guidelines” [49]. In this study, the SimaPro 9.4.0.1 PhD software (PRé Sustainability B.V.) and the ReCiPe 2016 method were employed for the process modeling and assessing environmental impacts.

3.1.2.4. Results and discussion

Characterization of the Char-Based Materials

Table 3.10 summarizes the effect of Na_2CO_3 activation and citric acid modification at different dosages on the key properties of the char materials, including surface area, microporosity, and CO_2 adsorption capacity at 100 kPa. The untreated char displays a low specific surface, no microporosity, and null CO_2 adsorption, while the char submitted to activation with Na_2CO_3 , without citric acid modification, shows the highest specific surface area ($S_{\text{BET}} = 417.6 \text{ m}^2 \text{ g}^{-1}$) and a significant micropore contribution ($S_{\text{MP}} = 247.2 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{MP}}/V_{\text{T}} = 28.9 \%$). This material also led to the highest CO_2 adsorption capacity ($q_{\text{CO}_2} = 73.7 \text{ mg g}^{-1}$), suggesting that Na_2CO_3 activation alone significantly enhances the char’s adsorption capacity. As reported in the activation of other plastics such as polyacrylonitrile, the thermal decomposition of Na_2CO_3 can develop porosity in the structure [50].

However, as observed in the N_2 isotherms illustrated in **Figure 3.10A**, a type IV isotherm was observed according to the IUPAC guidelines [51], with an important rise at low pressures, which suggests that the material comprises a mixed contribution of mesopores and micropores.

Table 3.10. Textural properties after Na_2CO_3 activation and citric acid modification by N_2 adsorption isotherms at 77 K and CO_2 adsorption at 273 K

Sample	S_{BET} ($m^2 g^{-1}$)	S_{MP} ($m^2 g^{-1}$)	V_T ($cm^3 g^{-1}$)	V_{MP} ($cm^3 g^{-1}$)	V_{MP}/V_T (%)	q_{CO_2} at 100 kPa ($mg g^{-1}$)
char	2.6	0.0	0.009	0.000	0.0	16.8
char-CA-1.0	19.4	0.0	0.074	0.000	0.0	22.1
AC	417.6	247.2	0.436	0.126	28.9	73.8
AC-CA-0.5	324.9	175.5	0.371	0.093	25.1	57.5
AC-CA-1.0	341.0	141.6	0.424	0.072	16.9	55.0
AC-CA-1.5	356.4	186.0	0.392	0.098	25.0	59.3

S_{BET} : total specific surface area by BET method; S_{MP} : micropore surface area by t-plot method; V_T : total pore volume from N_2 uptake at $p/p_0 \sim 0.99$; V_{MP} : micropore volume by t-plot method; q_{CO_2} : CO_2 uptake at 100 kPa and 273 K

The char modified with CA 1 M led to a minimal rise in the textural properties, $S_{BET} = 19.4 m^2 g^{-1}$, and $V_T = 0.074 cm^3 g^{-1}$, probably due to the reaction of labile carbon during the acid treatment. However, microporosity was completely absent both in the char before and after CA modification. The CA treatment of the activated char with Na_2CO_3 produced a decrease in the total surface area and pore volume in all cases. The surface interactions of CA with the original AC display the occlusion of micropores and partial reaction with the most reactive surface groups, indicating lower micropore contribution with lower V_{MP}/V_T ratios. Similar findings have been reported during the CA modification of commercial activated carbon formulas, in which 34 % of the surface area was registered [52]. From all the CA-modified samples, the AC-CA-1.0 outlines the highest mesoporosity reached after CA treatment, and consequently the lowest CO_2 uptake due to the preferred microporosity contribution required by the adsorption of this molecule. Regarding the micropore size distribution, due to the use of Na_2CO_3 as an activating agent, the micropore size contribution registered in **Figure 3.10B** is addressed at 0.6–0.7 nm due to the CO_2 released during the thermal decomposition of Na_2CO_3 [53].

The proximate analysis was used as a tool to predict the carbon content in all the samples, leading to the results presented in **Table 3.11**. The non-activated and untreated char exhibits relatively low moisture (2.9 %) and high ash content (38.8

%), highlighting a significant inorganic presence; the fixed carbon content remains as low as 28.3 %, suggesting limited carbon retention, to the detriment of volatile matter (30.0 %). After activation with Na_2CO_3 , the volatile matter content decreased and the ash content increased, an effect ascribed to the concentration of inorganic matter. The CA modification of the char increased the fixed carbon percentage, demonstrating the anchorage of CA molecules onto the surface. Following the CA functionalization of the activated char, a certain balance emerges. For instance, with 0.5 M citric acid, the fixed carbon remains high at 33.6 %, while the ash content is somewhat controlled at 46.3 %. At a higher CA concentration, i.e., 1.5 M citric acid, the fixed carbon declines slightly to 31.3 %, and the ash content increases to 48.5 %. This phenomenon suggests that the combination of Na_2CO_3 activation and CA post-treatment enhances the contribution of carbon, and the citric acid concentration must be carefully optimized to balance carbon fixation and ash minimization.

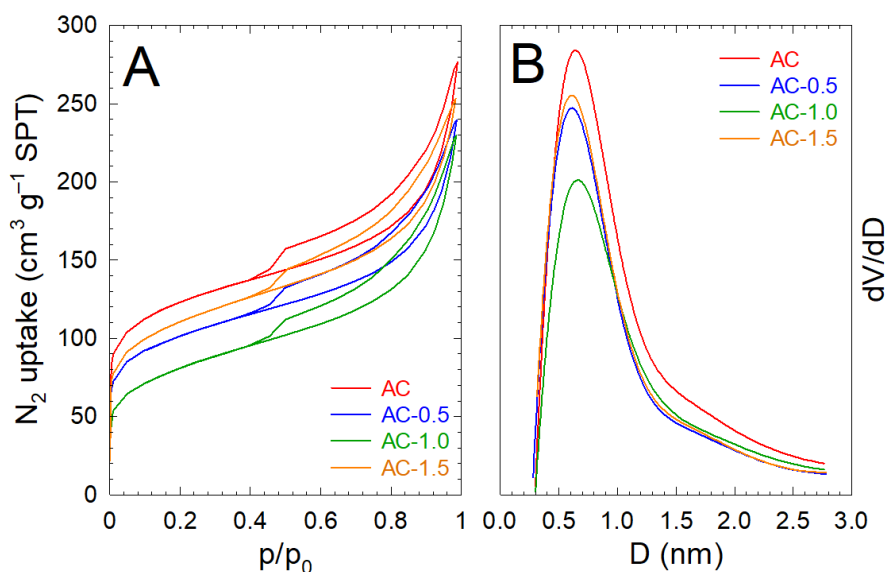


Figure 3.10. N_2 adsorption–desorption isotherms at 77 K (A) and micropore size distribution (B) by the HK method obtained from the CO_2 adsorption isotherm at 273 K of the activated carbon after citric acid modification

Table 3.11. Proximate and elemental analysis (wt. %) after Na_2CO_3 activation and citric acid modification.

Sample	Proximate Analysis				Elemental Analysis *			
	Moisture	Volatile	Fixed Carbon	Ash	C	H	N	O
Char	2.9	30.0	28.3	38.8	37.0	2.4	1.0	20.8
char-CA-1.0	3.2	16.1	36.8	43.9	44.3	2.0	1.8	8.0
AC	8.6	9.4	20.9	61.1	32.8	1.3	0.7	4.4
AC-CA-0.5	8.8	11.3	33.6	46.3	39.1	1.3	0.9	12.4
AC-CA-1.0	7.9	12.4	32.4	47.3	39.4	1.3	0.8	11.2
AC-CA-1.5	7.4	12.8	31.3	48.5	39.7	1.1	0.9	9.8

* No S was detected in any sample. The O is estimated as the difference after ashes subtraction.

The carbon content in the bulk of the samples was estimated by elemental analysis, as shown in **Table 3.11**. All the samples exhibited moderate carbon content. The char exhibited 37.0 %, whereas the activation with Na_2CO_3 decreased the value to 32.8 %, which is commonly observed during chemical activation with a wide range of different reagents [54]. The combination of a strong oxidizing medium and dehydrating effects justifies this increase in the C content [55]. The citric acid modification increased the carbon content either in the non-activated char or in that activated with Na_2CO_3 . Concretely, the CA modification of the non-activated char led to the highest carbon content, e.g., 44.3 %, whereas the CA-modified activated carbon displayed ~39 % C. The CA functionalization of activated carbon has been reported to increase the C content [56] due to the anchorage of CA leaving the formation of C=O species [57]. The H content remained relatively stable among all the samples but tended to slightly increase after CA treatment. The N content slightly decreased after Na_2CO_3 activation, possibly due to chemical reactions that eliminate nitrogen-containing compounds during the activation step [58]. The O contribution was estimated by the difference after ash removal. The activation with Na_2CO_3 leads to a paramount decrease in O, i.e., from 20.8 % (char) to 4.4 % (AC), due to the reaction of Na_2CO_3 with the oxygenated groups on the surface of the char and the associated dehydration reactions. The CA post-treatment in the CA post-treated AC samples raised the O content, probably due to the cross-linking effect of CA.

The surface composition was analyzed by the XPS technique. The quantification results are shown in **Table 3.12**. Different trends regarding the surface carbon

content (C_{XPS}) were observed compared to the bulk percentages reported by elemental analysis. However, C_{XPS} also decreased after activation with Na_2CO_3 , and the samples functionalized with CA also displayed a growth in C_{XPS} content. The O_{XPS} content should be taken under caution since the presence of oxygenated metals hinders the calculation of the specific O content linked to the carbonaceous matrix. Furthermore, the presence of some metals was registered, specifically Si and Ti, which are commonly dosed in plastic polymers as additives. Silica, silicon dioxide, and $CaCO_3$ are commonly added as reinforcing fillers while Ti is dosed as TiO_2 due to its whiteness and brightness to modify the color of the final polymeric product [59]. The surface contents of these inorganic components increase from the char to the char-CA and the AC-CA-X samples as they are concentrated in the solid. In addition, the nature of the chemical bonding of C and O was assessed by the deconvolution of C_{1s} and O_{1s} spectra. The high-resolution C_{1s} spectrum was interpreted by the deconvolution of the following contributions: sp^2 C=C (284.6 eV), sp^3 C-C (285.3 eV), C-O (286.6 eV), C=O (288.0 eV), and O=C-O-R (289.9 eV) [60,61]. As an example, **Figure 3.11** illustrates the deconvolution for the samples char, AC, and AC-CA-1.0. The contributions of each of the samples are available in **Table 3.12** and depicted in **Figure 3.11**. The process of activation increases the percentage of sp^2 carbon to the detriment of sp^3 , probably due to the thermal dehydration reactions during the Na_2CO_3 activation. The CA modification of the AC led to a decrease in the sp^2 C=C bonds and positively impacted the formation of oxygenated groups, especially C=O and C-O. Concretely, if the percentage of oxygenated carbon is accounted for (Sum C_{ox}), the performance of the materials is described in the following order: char (4.5 %) < char-CA-1.0 (17.2 %) < AC (15.6 %) < AC-CA-0.5 (18.0 %) < AC-CA-1.0 (30.1 %) < AC-CA-1.5 (24.0 %). Hence, a positive effect from the activation with Na_2CO_3 is deduced, especially with CA functionalization to enhance the presence of oxygenated carbonaceous groups. The activated and modified AC-CA-1.0 displays the highest value, i.e., double the value of the unmodified AC sample. In this sample, although all the oxygenated contributions were raised, the C-O outweighed the rest. The high-resolution O_{1s} region was adjusted into three plausible contributions, i.e., quinone (530.7 eV), C=O (531.5–532.0 eV), and C-O (~533 eV) [62]. From the evolution of their relative contributions, we ascertained a rise in C=O to the detriment of the quinone groups as the samples were treated with CA, with the AC-CA-1.0 being the sample in which this effect is most noticeable.

Table 3.12. XPS surface chemical composition and C_{1s} contribution after Na₂CO₃ activation and citric acid modification

Sample	Surface Composition (wt. %)				C _{1s}		O _{1s}	
	C _{XPS}	O _{XPS}	N _{XPS}	O _{thers}	Type	Peak (%)	Type	Peak (%)
char	86.4	10.8	0.7	1.3 (Si) 0.8 (Ti)	C=C	44.7	Quinone C=O C-O	37.6 34.2 28.3
					C-C	42.7		
					C-O	4.5		
					C=O	-		
					COO-	-		
					Sum COx	4.5		
char-CA-1.0	71.1	18.7	1.9	3.5 (Si) 3.5 (Ti)	C=C	65.6	Quinone C=O C-O	32.6 43.4 24.0
					C-C	17.2		
					C-O	2.9		
					C=O	8.1		
					COO-	6.2		
					Sum COx	17.2		
AC	32.2	38.6	1.0	10.8 (Si) 11.0 (Ti) 2.1 (P) 2.1 (Ca) 1.9 (Fe)	C=C	68.2	Quinone C=O C-O	35.5 40.3 24.2
					C-C	16.2		
					C-O	-		
					C=O	10.5		
					COO-	5.1		
					Sum COx	15.6		
AC-CA-0.5	49.3	32.3	1.0	9.9 (Si) 5.1 (Ti) 1.1 (P)	C=C	59.9	Quinone C=O C-O	28.4 42.3 29.2
					C-C	22.1		
					C-O	2.4		
					C=O	10.5		
					COO-	5.1		
					Sum COx	18.0		
AC-CA-1.0	47.7	33.0	1.3	11.0 (Si) 4.2 (Ti) 1.3 (P)	C=C	44.6	Quinone C=O C-O	28.0 49.5 22.5
					C-C	25.3		
					C-O	17.2		
					C=O	8.3		
					COO-	4.6		
					Sum COx	30.1		
AC-CA-1.5	49.9	30.8	1.3	10.8 (Si) 4.6 (Ti) 1.2 (P)	C=C	60.5	Quinone C=O C-O	24.4 45.9 29.7
					C-C	15.4		
					C-O	9.7		
					C=O	5.9		
					COO-	8.4		
					Sum COx	24.0		

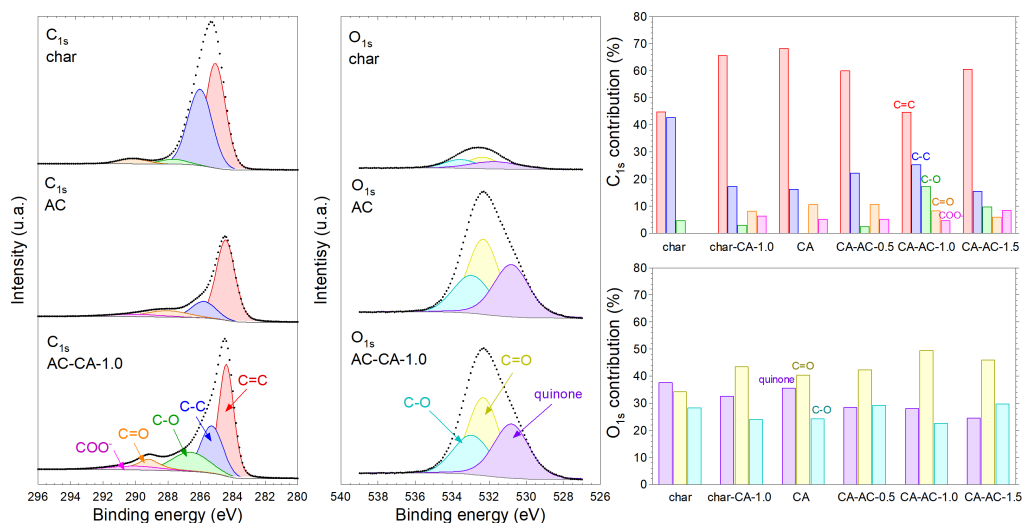


Figure 3.11. High-resolution XPS spectra of C_{1s} (left) and O_{1s} (middle) regions for char, AC, and AC-CA-1.0, and the deconvoluted contribution for all the samples (right)

The nature of the oxygenated groups was further qualitatively evaluated by TPD. The TPD profiles are depicted in **Figure 3.12**. A tentative deconvolution was conducted based on the temperature at which the oxygenated functional groups decompose. According to the literature [63], carboxylic acids decompose below 400 °C, carboxylic anhydrides decompose between 350 and 600 °C, and lactones reveal a peak above 600 °C. Phenol groups are registered in a middle-temperature range of 500–750 °C, while carbonyl/quinone groups release CO above 700 °C. Finally, pyrone-like groups, if present, are released at 950 °C. On this basis, the TPD profiles were deconvoluted. The char showed the lowest release of TCD signal, attributable to low oxygenated species on the surface. After CA treatment of the char, the TCD signal rose, as a consequence of the oxygenated groups increasing. The activation of the char with Na_2CO_3 led to a material with the presence of carboxyl groups, phenol, and carbonyl groups resistant to thermal treatment, close to pyrone behavior. The CA post-thermal modification enriched the variety of carbonyl and quinone groups, with contributions at lower temperatures compared to the non-modified AC. Interestingly, the TPD profiles confirm that the modification with CA destroyed the presence of carboxyl groups as the concentration of CA increased. From the profiles attained, it can be concluded that the modification with CA enriched the variety of contributions ascribed to the range of release of carbonyl and quinone, mainly.

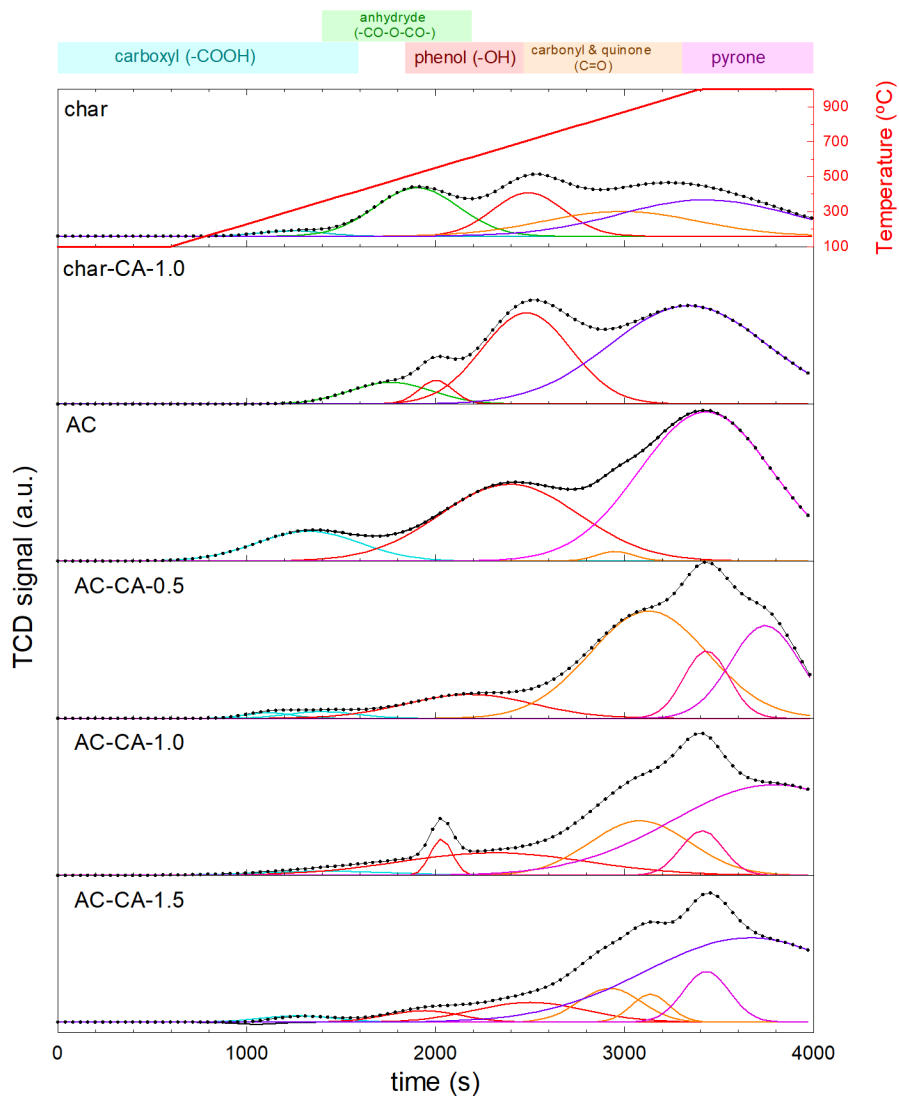


Figure 3.12. TPD profiles of the char and the activated carbon after citric acid modification

Adsorption of Lead and Acetaminophen

The modification of the activated carbon with CA was first studied on the adsorption of lead in water, a metal whose occurrence remains a problem in drinking water at the ppb level [64]. The performance of each sample is illustrated with the isotherms in **Figure 3.13**. From the isotherm, it is possible to define the maximum adsorption capacity ($q_{\max}$) for each material, as shown in **Table 3.13**. The isotherms were fitted to common models such as Langmuir, Freundlich, and Sips. The Langmuir isotherm is an empirical model that assumes monolayer formation, with homogeneous sites on the surface, and all the adsorbent sites display equal affinity towards the adsorbate, with no adsorbate transmigration in the surface plane [65]. In contrast, the Freundlich model considers the plausible formation of a multilayer and the heterogeneity of the adsorbent surface [66]. The Sips model emerges as a combination of the former two, considering the heterogeneity of the adsorption systems as well as circumventing the limitations associated with the high concentration registered by the adsorbate under the Freundlich model [67]. The three-parameter Sips model was selected as the best due to a better definition of the initial increase and the plateau at high concentration. The better fitting provides insights into the plausible mechanism in which a low concentration may promote the formation of multilayers due to considerable heterogeneity, and when the activated sites are saturated, no extra adsorption takes place, reaching the characteristic plateau of the Langmuir model. The results show notable variations in the $q_{\max}$ values based on the treatment conditions, underscoring their significant influence on the char's adsorption potential. The untreated char exhibits a low value, i.e., $q_{\max} = 3.1 \text{ mg g}^{-1}$, indicating minimal adsorption capacity. However, after activation with Na_2CO_3 , the CA solid displayed a higher uptake, $q_{\max} = 37.2 \text{ mg g}^{-1}$. This significant enhancement can be attributed to the improved surface area and a higher presence of surface oxygenated groups linked to the carbon matrix, facilitating better adsorption thanks to their interactions with lead-hydrated ions.

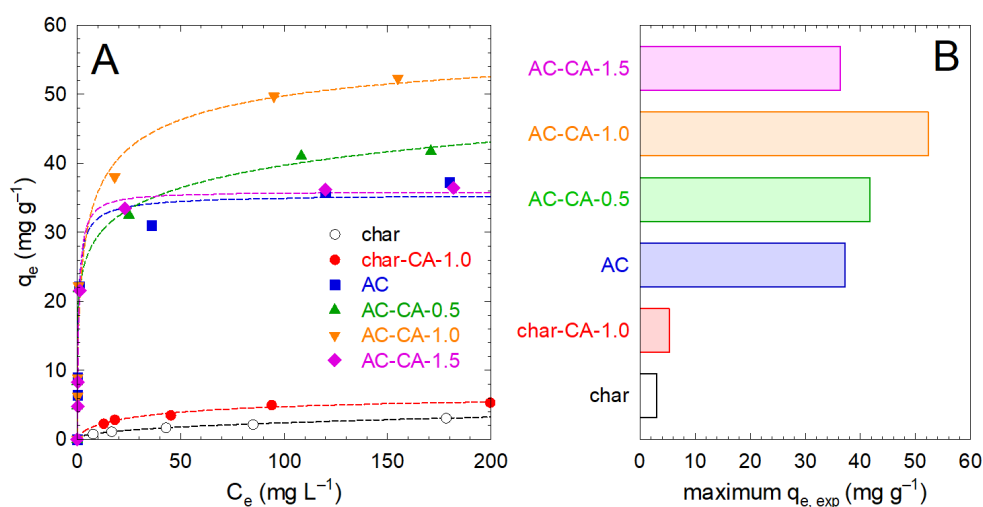


Figure 3.13. (A) Adsorption isotherms of lead with char and the activated carbon after citric acid modification. The dashed lines correspond to the Sips modeling. (B) Maximum experimental uptake of lead registered

Table 3.13. Model fitting parameters of lead isotherm onto the char and the activated carbon after citric acid modification

Model	Parameter	Char	char-CA-1.0	AC	AC-CA-0.5	AC-CA-1.0	AC-CA-1.5
Langmuir	$q_{\max}$	3.59	5.86	34.67	38.74	48.04	35.93
	K_L	0.02	0.05	2.36	2.36	1.08	1.32
	R^2	0.959	0.952	0.979	0.953	0.948	0.995
Freundlich	K_F	0.34	1.22	16.34	20.44	17.94	15.71
	n_F	2.35	3.48	6.05	6.94	4.52	5.64
	R^2	0.999	0.944	0.907	0.947	0.932	0.874
Sips	$q_{\max}$	5.00	7.22	35.66	50.0	60.81	35.93
	K_S	0.04	0.09	1.60	0.85	0.46	1.32
	n_S	1.46	1.49	1.35	3.17	2.01	1.00
	R^2	0.985	0.964	0.981	0.945	0.955	0.995

$q_{\max}$, theoretical maximum adsorption capacity (mg/L); K_L , Langmuir constant (L/mg); K_F , Freundlich constant; n_S is the heterogeneity factor of Sips model (dimensionless); and K_S , is the Sips constant

In the case of the char modified with CA, the $q_{\max}$ rises slightly to 5.3 mg g⁻¹, revealing the limited effectiveness of the functionalization on the non-activated char. In contrast, the CA functionalization of the activated samples boosts the metal adsorption uptake. Specifically, the values obtained were 41.7 mg g⁻¹ (AC-CA-0.5), 52.3 mg g⁻¹ (AC-CA-1.0), and 36.4 mg g⁻¹ (AC-CA-1.5). This performance matches

the contribution of oxygenated carbon as deduced with XPS, with the sample AC-CA-1.0 being the most enriched. Thus, there exists an optimal range for citric acid concentration, which leads to an enhanced contribution of oxygenated groups in the carbon matrix that triggers the maximum lead adsorption efficiency. Therefore, an optimum functionalization of the carbon material maximizes the capacity to retain metal, which is crucial for applications in environmental remediation. Comparative studies have reported similar results for Na_2CO_3 -activated carbon derived from other feedstocks. For example, the activation of rapeseed oil cake with Na_2CO_3 improves the adsorption capacity for lead ions if compared to the non-activated material, achieving a maximum lead uptake of $q_{\text{max}} = 130 \text{ mg g}^{-1}$, indicating the effectiveness of this activating agent [68]. Additionally, the maximum adsorption capacity for lead ions using Na_2CO_3 -activated carbon prepared from *Cedrus deodara* bark was reported to be 236.4 mg g^{-1} [32]. In a study focused on activated carbon prepared from rice husk and treated with 5 % Na_2CO_3 , the lead adsorption capacity was approximately 0.6 mg g^{-1} [23]. Furthermore, the modification of citric acid enhances the adsorption uptake of lead to $q_{\text{max}} = 41.7 \text{ mg g}^{-1}$ [69].

Citric acid functionalization was also assessed for the adsorption of a representative contaminant of emerging concern, such as acetaminophen [70, 71]. **Figure 3.14** portrays the acetaminophen isotherms, and **Table 3.14** summarizes the results achieved for fitting with the most common adsorption models, with the Sips model generally providing the best fit for the experimental data. The untreated char exhibits a relatively low acetaminophen uptake, experimentally around 10 mg g^{-1} , indicating a poor adsorption performance. In contrast, the activated carbon boosts the maximum q_{max} to ca. 80 mg g^{-1} , showcasing the effectiveness of this activation method in creating a more porous structure with a higher surface area, which facilitates better acetaminophen adsorption. The citric acid modification did not substantially alter the acetaminophen efficiency, with a very similar maximum experimental adsorption capacity observed. This suggests that citric acid alone does not enhance, and may even hinder, the char's ability to absorb acetaminophen. Nevertheless, when combined with Na_2CO_3 activation, the adsorption uptake is enhanced to a value of roughly 80 mg g^{-1} . The modification of the activated material with citric acid did not improve the adsorption uptake compared to the non-modified sample. This evidence suggests that the mechanism of acetaminophen adsorption does not require the presence of carboxylic acid, which, according to the XPS characterization, is the prime oxygenated group after citric acid functionalization. The literature reports very different adsorption uptakes, strongly affected by the chemical activating agent used and the nature of the carbonaceous precursor material. For example, the activation of Brazil nutshell with ZnCl_2 can create an adsorbent with an uptake as high as 285 mg g^{-1} [72]. The activation of spent tea leaves with H_3PO_4 only retains about 59 mg L^{-1} [73]. Or, in the case of the activation of rice with NaOH only, the acetaminophen removal rate is 50 mg g^{-1}

[74]. Regarding the role played by citric acid in similar carbonaceous materials, the activation of materials from citrus waste with FeCl_3 only reached an acetaminophen yield of 45 mg g^{-1} [75].

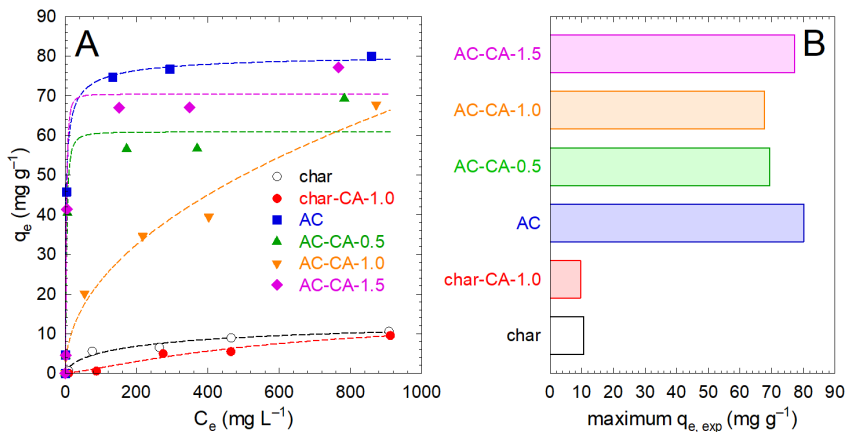


Figure 3.14. (A) Adsorption isotherms of acetaminophen with char and the activated carbon after citric acid modification. The dashed lines correspond to the Sips modeling. (B) Maximum experimental uptake of acetaminophen registered

Table 3.14. Model fitting parameters of acetaminophen isotherm onto the char and the activated carbon after citric acid modification

Model	Parameter	Char	char-CA-1.0	AC	AC-CA-0.5	AC-CA-1.0	AC-CA-1.5
Langmuir	$q_{\max}$	11.07	23.26	77.77	62.00	90.77	71.66
	K_L	0.01	0.00	0.53	0.27	0.00	0.29
	R^2	0.943	0.970	0.997	0.951	0.947	0.968
Freundlich	K_F	0.91	0.05	33.09	20.16	2.67	22.91
	n_F	2.73	1.31	6.93	5.36	2.12	5.27
	R^2	0.941	0.964	0.917	0.844	0.979	0.858
Sips	$q_{\max}$	14.87	7.28	81.27	60.97	100.00	70.46
	K_S	0.02	0.01	0.71	0.15	0.01	0.15
	n_S	1.50	1.76	1.71	0.67	1.31	0.57
	R^2	0.957	0.942	1.000	0.958	0.949	0.980

Stability of the Material: Leachates Analysis

The stability of the prepared carbonaceous adsorbent was examined and aimed at the analysis of the plausible metals released in an aqueous solution. **Table 3.15** summarizes the concentrations of the major and minor metallic elements of a selection of the materials prepared, i.e., char, char-CA-1.0, AC, and AC-CA-1.0. The leachate analysis revealed that the activation with Na_2CO_3 , and the further modification with citric acid, significantly alters the concentration of the released

species in the solution. Na_2CO_3 generally increases the levels of major elements like Ca and P, detected on the surface by the XPS technique. The citric acid treatment influences minor elements such as Cd, Co, and Sb. The sequential activation with Na_2CO_3 and citric acid functionalization tends to maximize the concentration of several components, especially Ti and Sb. The findings suggest that using plastic residues as precursors for the preparation of activated carbon requires a detailed investigation of the leaching of metallic impurities incorporated in the polymeric structure of this residue as an additive [59]. The components that are lixiviated to a larger extent, such as Ca, P, Si, and Ti, do not display any problems for environmental applications in water due to the lack of toxicity. In contrast, the metals that might compromise the toxicity of the released effluent were detected at low concentrations, bearing in mind that the presented data in **Table 3.15** correspond to a solid–water (m/v) ratio of 1:10, an abnormally high dosage.

Table 3.15. Leached metals into aqueous solution by selected samples. Solid-to-water ratio (m/v) 1:10

Elements	char	char-CA-1.0	AC	AC-CA-1.0
Major elements (mg L^{-1})	Al	0.95	0.60	0.03
	Ca	44.2	3.04	83.88
	Fe	0.03	0.54	<0.01
	K	0.18	0.97	0.59
	Mg	12.19	1.05	19.46
	Na	0.08	5.46	<0.01
	P	11.49	0.41	122.50
	S	1.50	1.91	5.60
	Si	11.18	1.28	53.16
	Zn	1.18	1.97	>0.01
Minor elements ($\mu\text{g L}^{-1}$)	As	2.6	6.6	0.6
	Ba	739.5	401.9	2.4
	Cd	1.8	65.0	0.9
	Co	10.2	134.3	19.9
	Cr	12.0	64.7	3.6
	Cu	116.5	37.6	91.8
	Ga	18.9	20.4	0.1
	Li	28.1	43.6	25.5
	Mn	91.6	115.1	10.7
	Mo	0.1	82.3	0.2
	Ni	116.5	156.3	91.8
	Pb	140.1	4.1	12.4
	Rb	13.4	16.0	8.0
	Sb	0.4	470.4	0.0
	Se	3.3	4.1	5.4
	Sr	311.9	255.5	22.5
	Ti	2.5	194.0	45.0
	V	2.5	4.1	21.7

Economic and Environmental Assessment

An economical pre-evaluation was tentatively conducted to evaluate the role of the activation process and citric acid modification on the adsorption efficiency. **Table 3.16** summarizes the costs associated with the adsorption of lead and acetaminophen using char materials, expressed as EUR per kilogram of the contaminants retained, and the preparation cost of each analyzed material. The yield during the synthesis, as shown in **Table 3.16**, was accounted for in the cost estimation. Briefly, the activation with Na_2CO_3 led to a 31.7 % yield and the post-treatment with citric acid did not substantially alter this value. The untreated char shows moderate adsorption costs for both lead (2214.0 EUR/kg) and acetaminophen (1046.3 EUR/kg). In contrast, the application of Na_2CO_3 activation reduced these costs, with lead adsorption costs dropping to 1169.7 EUR/kg and acetaminophen to 582.4 EUR/kg. This cost reduction is the consequence of the enhanced adsorption capacity achieved after activation, making the process more economically viable for both contaminants. The citric acid modification of the non-activated char increased the costs of lead (5008.9 EUR/kg) and acetaminophen (5029.0 EUR/kg) removal. This suggests that citric acid alone may hinder the adsorption efficiency, leading to higher costs per unit of contaminant retained. Conversely, with the citric acid functionalization of the activated char at low CA dosage (0.5 M), the costs decrease to 1506.8 EUR/kg for lead and 906.9 EUR/kg for acetaminophen, demonstrating that a strategic combination of treatments can enhance the adsorption efficiency while maintaining low costs. At high citric acid concentration (1.5 M), the costs rise, especially for lead adsorption (2493.9 EUR/kg), indicating that excessive citric acid modification diminishes economic feasibility for certain applications. In addition, the preparation costs of each material vary between 4.7 and 25.1 EUR/kg. Although the results found are a preliminary estimation based on laboratory-scale consumption and do not include some aspects to be considered at a large scale, they are like those found by other researchers. The cost of chemical activation strongly depends on the carbonaceous precursor and the activation agent, ranging within values between 8.60 USD/kg (≈ 7.9 EUR/kg) and 2.33 USD/kg (≈ 2.1 EUR/kg) [76]. In conclusion, while Na_2CO_3 activation significantly enhances performance and reduces costs, careful consideration of citric acid concentrations is necessary to maintain economic viability. These findings indicate that the development of optimized adsorbent materials can lead to effective and affordable solutions for environmental remediation, making them attractive options for treating hazardous contaminants like heavy metals and organic anthropogenic pollutants of emerging concern.

Table 3.16. Effects of activation and citric acid modification on preparation and treatment costs.

Sample	Yield (%)	Preparation Costs (EUR/kg Material) ¹	Lead Removal Costs (EUR/kg) ²	Acetaminophen Removal Costs (EUR/kg) ²
Char	-	4.7	2214.0	1046.3
char-CA-1.0	67.7	14.9	5008.9	5029.0
AC	31.7	13.8	1169.7	582.4
AC-CA-0.5	31.1	17.5	1506.8	906.9
AC-CA-1.0	31.4	21.3	1714.5	1258.1
AC-CA-1.5	30.9	25.1	2493.9	1172.5

¹ Preparation costs per kg of material prepared; ² material costs associated with the treatment per kg of contaminant removed.

The environmental impact of the four char preparation methods was estimated, considering not only the adsorption efficiency but also the environmental performance under different scenarios. The environmental impact assessment was undertaken following a streamlined life cycle assessment (LCA) methodology. LCA is widely used to determine the environmental impact of processes, considering upstream and downstream emissions and the resources consumed. Four plausible scenarios were modeled based on the treatment of 1 g of char, i.e., the functional unit defined for this study. The inputs and outputs employed to build the data inventory include the reagents consumed, heating, and emissions to water, as shown in **Table 3.17**. The upstream and downstream emissions and use of resources were collated from the commercial database Ecoinvent 3.10 using the allocation, cut-off by the classification system model. The software SimaPro 9.6.0.1 was applied to manage the data and perform life cycle calculations. The comparative results are presented in **Figure 3.15**.

The results depicted in **Figure 3.15** demonstrate that the scenarios involving citric acid utilization have an environmental impact that is markedly higher than that observed in scenarios that do not employ citric acid. This conclusion applies to all environmental impact categories. Overall, the environmental impact of washing and modifying the char with citric acid is 12 times higher than that of washing alone. Additionally, the environmental impact of washing, activating, and modifying the char with citric acid is 1.4 times higher than just the activated char. For all environmental impact categories, the scenario exhibiting the highest impact is one including washing, activation, and functionalization with citric acid. Furthermore, the process of activation makes a considerable contribution to the overall environmental impact. In all scenarios, the most significant contributor to the overall environmental impact is human carcinogenic toxicity, followed by freshwater and marine ecotoxicity. This is largely attributable to the high energy requirements of the drying processes. In conclusion, although modifying the char with citric acid

may enhance the adsorption performance, it also considerably increases the environmental impact. Therefore, citric acid usage leads to enhanced adsorption uptake and minimizes the preparation and removal costs; however, its use results in detrimental consequences from an environmental point of view [77–79].

Table 3.17. Inputs and outputs of LCA inventory. Data referred to 1 g of treated char

	Parameters	Unit	char	Char-CA-1.0	AC	AC-CA-1.0
Inputs	Water for washing	mL	0.617	0.617	1000	1000
	Water for 2 nd washing	L	0	2.5	0	2
	HCl 37 % w/w	mL	1.11	1.11	2.25	2.25
	Citric acid 1 M	g	0	6.25	0	6.25
	Calcium carbonate	g	0	0	1	1
	Electric energy for the oven	kJ	0	0	364.8	364.8
	Electric energy for drying	kJ	0	6.48	6.48	6.48
	Electric energy for 2 nd drying	kJ	0	3.24	0	9.72
	Electric energy for 3 rd drying	kJ	0	6.48	0	6.48
Outputs	HCl 37 % w/w	mL	1.11	1.11	2.25	2.25
	Wastewater from washing	mL	0.617	0.617	1000	1000
	Wastewater from 2 nd washing	L	0	2.5	0	1
	Wastewater from citric acid solution	mL	0	5.05	0	5.05

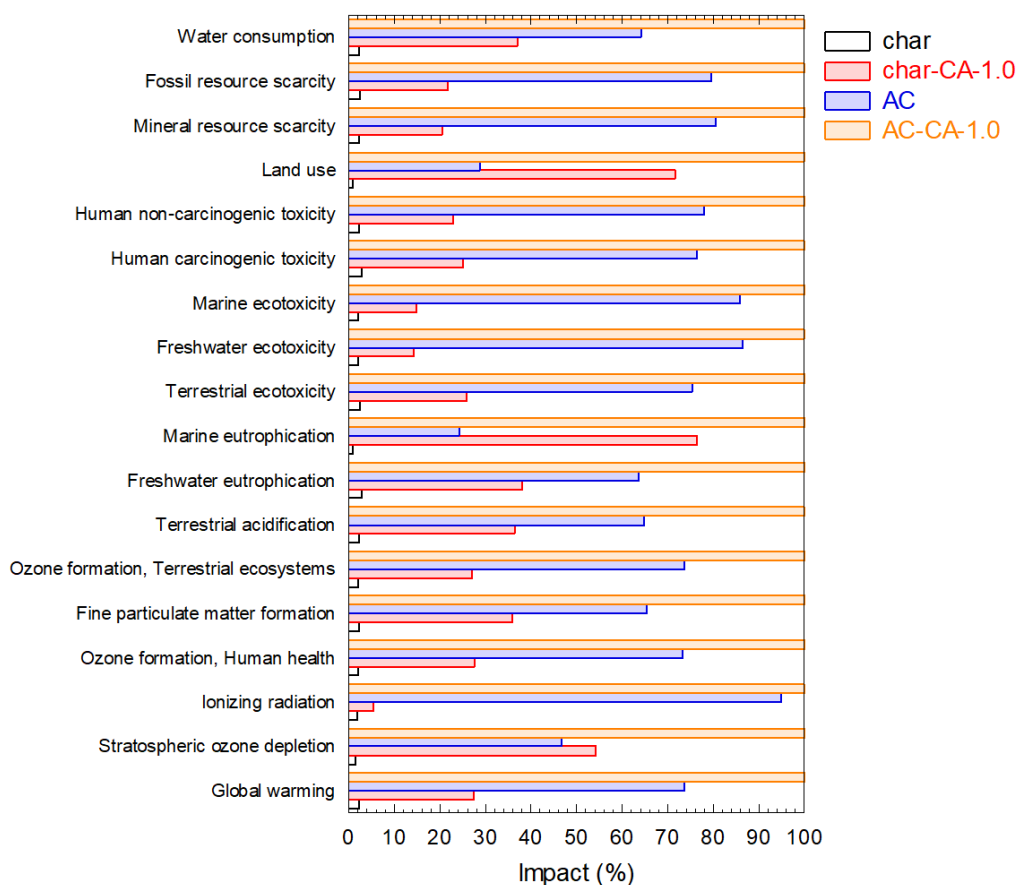


Figure 3.15. Environmental impact comparison of the four scenarios

3.1.2.5. Conclusions

Plastic waste that is no longer suitable for mechanical recycling due to a lack of quality or to the complexity of a mixed composition can be successfully transformed via pyrolysis and chemical activation into activated carbon, with potential environmental applications as an adsorbent. Activation with sodium carbonate triggers the formation of mesoporous activated carbon, i.e., non-porous char $\sim 3 \text{ m}^2 \text{ g}^{-1}$ vs. the activated char $\sim 418 \text{ m}^2 \text{ g}^{-1}$ and pore volume $0.436 \text{ cm}^3 \text{ g}^{-1}$ with 71 % mesopores contribution. The surface oxygenated groups can be enriched with a post-treatment process involving citric acid impregnation. Although a partial surface loss is observed due to a partial blockage of the cross-linked citric acid, the presence of carbonyl and carboxyl groups is considerably boosted. The oxygen-enriched terminal carbonaceous groups were relevant in the adsorption uptake of lead in water, raising the maximum lead uptake from water $\sim 37 \text{ mg g}^{-1}$ (activated carbon)

to $\sim 52 \text{ mg g}^{-1}$ (activated material after citric acid functionalization). In the case of acetaminophen adsorption, the citric acid did not show any substantial improvement concerning the activated material (80 mg g^{-1} acetaminophen uptake). The higher efficiency of the activated and citric acid-treated adsorbents minimizes the material required, but these materials are employed at a higher cost. Nevertheless, the environmental impact associated with activation steps, citric acid modification, and washing of the material negatively impacts the released emissions. According to a life cycle assessment, sodium carbonate activation strongly increases the impacts compared to the additional environmental costs of citric acid functionalization.

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Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors upon request.

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3.1.2.6. References

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3.2. Gas effluent treatment

3.2.1. Paper 3: Transforming a mixture of real post-consumer plastic waste into activated carbon for biogas upgrading

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Rafael R. Solís, Mónica Calero, Leticia Pereira, Sandra Ramírez, Gabriel Blázquez, María Ángeles Martín-Lara

3.2.1.1. *Abstract*

Plastic waste management is a current environmental issue that demands potential solutions since complete mechanical recycling is limited to the complexity and feasibility regarding the quality and purity of plastic waste. Pyrolysis has emerged as a reasonable solution for the recycling of those fractions that are not further suitable for recycling. Although the implementation of this technology is mature, the generated solid fraction or char has not been completely inserted in the closed loop of plastic recycling. This work explores the possibility of using the carbonaceous char as a precursor for the preparation of porous activated carbons for environmental application as CO₂ adsorbent and biogas upgrading. The effect of the pyrolysis temperature (450 or 500 °C) on the obtained chars has been assessed for the benefits in the second stage of chemical activation, exploring the possibility of the use of diverse chemical agents. The composition, textural, and surface properties of the porous materials were characterized. N₂ isotherms showed that the char prepared at 500 °C provided the best textural properties with a performance of K₂CO₃ ~ KOH > Na₂CO₃ > NaOH > ZnCl₂ > FeCl₃. Isotherms of CO₂ adsorption showed that the activation with K₂CO₃ displayed the best uptake (130.2 mg g⁻¹ at 273 K), closely followed by KOH (125.0 mg g⁻¹ at 273 K), also confirmed by dynamic tests in a fixed bed column configuration. The uptake was well correlated with the ultramicropore volume and the oxygenated functional groups. The CO₂ and CH₄ adsorption were studied either in static or dynamic assays. The behavior of the sample activated with K₂CO₃ was studied in detail in column tests, suggesting that the activated material exhibits promising behavior for biogas upgrading.

Keywords: plastic waste; char pyrolysis; chemical activation; CO₂ adsorption; biogas upgrading

3.2.1.2. *Introduction*

In recent years, the identification and evaluation of carbon-based materials have received great attention [1]. Of particular interest are adsorbents derived from low-cost precursors or waste materials, such as those found in large quantities in nature

or obtained as a by-product from another industry [2]. Researchers have proposed a great number of low-cost materials, including date stones [3,4], neem biowaste [5] rice husk [6], pineapple plant leaves [7], sludge [8], sugarcane bagasse [9], walnut shell [10], pistachio shell [11], between others, to remove a wide spectrum of organic and inorganic contaminants from aqueous solutions and gaseous effluents.

Even though plastics are extremely important materials for modern society, despite corporate promises, and international, national, or local governmental responses, plastics production and waste generation continue to rise with deteriorating environmental implications. To reduce environmental impacts throughout the value chain, there is an urgent need to make the lifecycle of plastics more circular.

Pyrolysis is an emerging recycling technology that allows the breaking down of waste plastics into valuable secondary raw materials, including oil, char, and gas [12,13]. Oil can be used as a starting point to produce new chemicals or polymers, and gas is usually used as a versatile energy source that can supply the energetic cost of the process itself. However, during the past decades, little attention has been paid to char products [14]. Pyrolysis addresses environmental issues such as waste management and reducing greenhouse gas emissions. Scaling up pyrolysis treatment can create new revenue streams from the sale of char and oil while reducing reliance on fossil fuels. Economic benefits include job creation, cost savings, generation of renewable energy sources, and potential cost savings through waste management and resource recovery. Environmental benefits include reducing greenhouse gas emissions through char production, converting waste materials into valuable resources, and promoting circular economy principles [15,16].

Plastic-based activated carbons are carbonaceous materials prepared from plastic waste that have been subjected to an activation process to improve their surface area and porosity to raise the capacity to adsorb different types of compounds [17]. These materials are highly versatile and can be designed to specifically target and remove pollutants, mainly from air and water-polluted effluents [18]. Plastic-based activated carbons offer a cost-effective and efficient solution for plastic pollution, especially for plastic waste that cannot be mechanically recycled, closing up the plastic loop [14].

Diverse activated carbons have already been successfully prepared from plastic-based wastes and implemented to remove diverse contaminants, such as heavy metals [19,20], contaminants of emerging concern [21], or polynuclear aromatic hydrocarbons [22], thus reducing the risk of water contamination and preventing from detrimental effects on ecosystems. Additionally, the use of plastic-based activated carbons in the adsorption of CO₂ from gas effluents has shown promising results, either for the CO₂ capture from combustion effluents [23], hence reducing

the CO₂ emissions, or offering a potential solution to upgrade biogas into biomethane. A complete review of the use of plastic precursors for the preparation of activated carbons and their evaluation in CO₂ capture has been recently published [17]. One of the most studied plastic wastes to produce plastic-based activated carbons and its evaluation for CO₂ adsorption is polyethylene terephthalate (PET) [24–29], due to its abundant availability and high carbon content [30]. The PET-derived activated carbons have been demonstrated to perform excellent CO₂ adsorption capacity. For instance, the activation of PET from plastic bottles with KOH at 700 °C has reported a CO₂ uptake of 4.42 mol kg⁻¹ [27], obtained from the isotherms under static analysis. In a similar study, the CO₂ uptake of PET activated with KOH at 700 °C was 2.31 mol kg⁻¹, obtained in thermobalance analysis [25]. However, PET has not been the only plastic waste used in the development of plastic-based activated carbons for CO₂ capture. Polystyrene (PS) spheres have also been activated, with a previous hydrothermal step, with ZnCl₂ leading to a material able to adsorb 3.62 mol CO₂ kg⁻¹ [31]. Polyurethane was also studied using KOH as a chemical activation agent, obtaining an adsorption capacity of 4.33 mol CO₂ kg⁻¹ at 25 °C [32]. Polyacrylonitrile was also used as a precursor for the preparation of activated carbons that have shown to be good CO₂ adsorbents, reporting adsorption values of 2.5 mol CO₂ kg⁻¹, in the sample activated with KOH at 800 °C for 2 h [33]. Also, recently, the rejected post-consumer plastic fraction of recycling plants, composed of a mixture of plastics representative of their occurrence in real wastes, have been used as the precursor of the char that was further activated, leading to moderate results of CO₂ adsorption, i.e. 1.11 mol kg⁻¹ under KOH activation at 780 °C [34]. However, research using a real mixture of post-consumer plastic polymers in the preparation of activated carbons and their application remains quite limited. In addition, to our knowledge, no studies have investigated the effect of carbonization temperature on the properties and adsorption capacity of plastic-based activated carbons obtained from mixtures of post-consumer plastics.

In this context, with the purpose to help to advance the state of knowledge, this work aims at the development of novel plastic-based activated carbons from a real mixture of post-consumer plastics, collected from the rejected fraction of a municipal solid waste treatment plant. Diverse chemical activating agents have been applied to activate the char collected after the pyrolysis or carbonization of the plastic mixed precursor. Either the temperature of pyrolysis or the nature of the activating agent have been studied on the development of textural properties, and the CO₂ and CH₄ uptake were obtained under static analysis. The activating method with the best performance was selected for a detailed study of the adsorption of CO₂, CH₄, their mixtures, and a simulated biogas formula in dynamic assays in a fixed-bed column setup.

The biogas upgrading integration with pyrolysis creates a holistic approach to waste management that benefits both the environment and the economy. The process promotes circular economy principles and waste materials conversion into valuable resources.

3.2.1.3. Experimental section

Chemicals

All the chemicals used were purchased at Merck® as reagent grade (>99 %) and used without further purification. Ultrapure water (18.2 MΩ cm) was obtained from a Direct-Q®-UV device (Millipore®). The commercial formula of zeolite 13X pellets with spherical shape on average 2 mm diameter was used for comparison purposes with the prepared material.

Preparation of the novel plastic-based activated carbons

The mixture of post-consumer plastics was collected from the rejection fraction of a municipal solid waste treatment plant. The mixture analysis led to the following composition (wt. %): polypropylene, 55.0 %; high-impact polystyrene, 8.6 %; expanded polystyrene, 10.1 %; and polyethylene film, 27.7 %. The characteristics of the plastic waste feedstock were reported in a previous study [35]. The mixture, after being crushed to a size inferior to 1 mm, was submitted to a pyrolysis treatment in a horizontal tubular furnace of Nabertherm, under N₂ supply, flowrate of 50 L h⁻¹. The temperature program set stated with a heating rate of 10 °C min⁻¹ from room temperature to the target pyrolysis temperature, i.e. 450 or 500 °C, and then hold to this value for 90 min.

The resulting char from the pyrolysis was activated under the action of diverse chemical agents, concretely KOH, NaOH, K₂CO₃, Na₂CO₃, FeCl₃, and ZnCl₂. The chars were crushed and mixed with the chemical activating agent at a mass ratio of 1:1. The mixture was then placed in the tubular furnace and submitted to the following heating program under N₂ feeding (flowrate, 200 mL min⁻¹): heating from room temperature to 300 °C (heating rate, 10 °C min⁻¹), next the temperature was kept at this value for 60 min, further raise to 800 °C (heating rate, 10 °C min⁻¹), and holding at this value for 60 min. Both activator amount and activation temperature were chosen in accordance with our previous works [14,36]. Then, the resulting solid after the activation stage was washed with HCl solution 1 M, at a proportion of 20 mL per 1 g of char. Following that, the char was filtered and washed with water until obtaining a neutral pH in the filtrate. Finally, the washed activated material was dried overnight at 120 °C.

Characterization of the plastic-based activated carbons

The proximate analysis was conducted using a thermobalance from Perkin Elmer®, model STA 6000. A certain amount of sample was placed in a crucible and subjected to the following temperature program under an N₂ atmosphere (flow rate, 20 mL min⁻¹). Firstly, the sample was kept at 30 °C for 20 min and then raised to 110 °C (heating rate, 20 °C min⁻¹) to be held at 110 °C for 20 min, obtaining the moisture from the weight loss at this stage. Afterward, the volatiles were obtained by raising the temperature to 850 °C (heating rate, 20 °C min⁻¹) and kept at this value for 20 min. For the determination of the ash content, the feeding gas was changed from N₂ to O₂ (20 mL min⁻¹), holding the temperature at 850 °C for 20 min.

The elemental analysis was quantified in a Thermo Scientific™ CHNS/O analyzer, model Flash 2000. The combustion of the sample at roughly 1400 °C led to the release of CO₂, H₂O, NO_x, and SO₂ gases that were separated in a chromatographic column and detected on a thermal conductive detector. The oxygen content was estimated from the difference between the CHNS content and the ashes. The surface chemical composition was analyzed by X-ray Photoelectron Spectroscopy (XPS) in a Kratos AXIS Ultra-DLD device equipped with an X-ray source from Al K α . All the spectra were corrected to the C_{1s} peak of adventitious sp³ carbon to 284.6 eV. The deconvolution of the peaks was processed with the aid of the software XPSpeak 4.1®, under a Shirley background correction.

The textural properties were obtained by static physisorption in a Sync 200 device from 3P Instruments©. The samples were previously degassed at 150 °C under vacuum for 12 h on a Prep J4 unit of 3 P Instruments©. The N₂ adsorption-desorption isotherms were obtained at 77 K, leading to the obtention the total surface area by the BET method (S_{BET} , m² g⁻¹), the micropore surface area (S_{MP} , m² g⁻¹) by t-plot method, the total pore volume (V_{T} , cm³ g⁻¹) from the N₂ uptake at $p/p_0 \sim 0.99$, and the micropore volume (V_{MP} , cm³ g⁻¹) from the t-plot method. The distribution of micropore size was obtained by carrying out CO₂ adsorption isotherms at 273 K, applying the Horvath–Kawazoe (HK) method [37,38].

The morphology of the activated samples was analyzed by Scanning Electron Microscopy (SEM) in a FEI Quanta 400 device (30 kV, 3.5 nm resolution). The morphology and chemical composition were further analyzed by Transmission Electron Microscopy (TEM) in a TALOS F200C G2 device (200 kV, 0.3 nm resolution) coupled to an EDX detector Bruker X-flash 6T-30.

The disorder degree of carbon and the presence of crystalline impurities was analyzed by X-ray Diffraction (XRD) in a Bruker D8 Discover device equipped with a detector Pilatus3R 100 K-A, working with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The diffractograms were registered between the 2θ ranges of 10–85°.

Adsorption assays of CO₂ and CH₄ on the plastic-based activated carbon

Static adsorption tests

The adsorption of CO₂ and CH₄ was carried out under static mode in a physisorption device (Sync 200 device from 3P Instruments©), obtaining the isotherms at 273 and 298 K up to 100 kPa. The gas, either CO₂ or CH₄, uptake (q , mg g⁻¹) was adjusted to the Freundlich model [39]:

$$q = K_F p^{1/n_F} \quad (3.11)$$

where p is the equilibrium pressure of the gaseous adsorbate, and the K_F (mg g⁻¹ kPa^{-n_F}) and n_F stand for, respectively, the Freundlich constant and exponent.

The CO₂/N₂ and CO₂/CH₄ selectivity at 298 K was obtained as a function of the total pressure employing the ideal adsorbed solution theory (IAST), considering the typical composition of a post-combustion effluent as 15:85 (v/v) CO₂:N₂ [40] or a biogas fuel as 40:60 (v/v) CO₂:CH₄ [40]. Hence, the selectivity CO₂/N₂ or CO₂/CH₄ was calculated as follows [42,43]:

$$S_{CO_2/N_2} = \left(\frac{V_{CO_2}}{V_{N_2}} \right) \left(\frac{p_{N_2}}{p_{CO_2}} \right) \text{ or } S_{CO_2/CH_4} = \left(\frac{V_{CO_2}}{V_{CH_4}} \right) \left(\frac{p_{CH_4}}{p_{CO_2}} \right) \quad (3.12)$$

where V_i stands for the gas uptake (STP cm³ g⁻¹) and p_i is the partial pressure of the i component in the mixture ($p_{N_2}/p_{CO_2}=0.85/0.15$, and $p_{CH_4}/p_{CO_2}=0.60/0.40$).

The isosteric heat of adsorption (ΔH_{ads}) of CO₂ and CH₄ were calculated as a function of the gas uptake with the Clausius–Clapeyron equation [44,45]:

$$\Delta H_{ads} = -R \ln \left(\frac{p_2}{p_1} \right) \frac{T_1 T_2}{(T_2 - T_1)} \quad (3.13)$$

For the application of the equation, two isotherms for each gas were carried out and the fitting parameters of the Freundlich model were applied to predict the pressures (p_1 and p_2) at different coverages uptakes (q) at $T_1=273$ K and $T_2=298$ K, leading to the isosteric adsorption calculation.

Dynamic adsorption tests in fixed-bed column

Dynamic adsorption tests of CO₂, CH₄, and their mixtures using N₂ as a gas carrier were conducted in a fixed-bed column, leading to the obtention of the breakthrough curves. The plastic-based activated carbon (1 g) was placed in a thermostatic column, 10 cm height and 1 cm internal diameter equipped with a porous ceramic porous at the base, operating at 30 °C and atmospheric pressure. Glass balls were inserted in the top of the column to prevent possible dragging of the solid. Different adsorption assays feeding 100 mL min⁻¹ of gas stream composed

of CO₂/N₂ or CH₄/N₂ mixtures from 20/80 to 80/20 (v/v) were conducted to define the breakthrough curves. The adsorption of CO₂/CH₄ mixtures was also assessed ranging from 50/50 to 80/20 (v/v). Furthermore, the adsorption behavior with simulated landfill biogas composed of 55 % (v/v) CH₄, 39 % CO₂, 6 % N₂, and trace amounts of O₂ and H₂S was also determined. The concentration of gases in the gas streams was monitored with an INFRA.sens® AK5 device from Wi.tec-Sensorik, based on non-dispersive infrared (NDIR) analysis in a dual beam to analyze both CO₂ and CH₄. The evolution over time of the concentration of gases at the outlet was used to depict the breakthrough curves. The gas adsorption uptake, either for CO₂ or CH₄, was quantified as the area below the adsorbed gas, which means the $1 - C_t/C_{inlet}$ curve, being C_t and C_{inlet} the concentration of the gas at a certain time and the inlet value respectively. The area was computed from the initial time until the saturation time (t_{sat}), defined as the time in which $C_{tsat}/C_{inlet}=0.95$ [46]:

$$q = \frac{\vartheta C_0 \int_0^{t_{sat}} \left(1 - \frac{C_t}{C_0}\right) dt}{m_{AD}} \quad (3.14)$$

where ϑ means the volumetric flow rate (100 L min⁻¹), C_0 (mol L⁻¹) is the inlet CO₂ or CH₄ concentration, and m_{AD} (g) means the mass of adsorbent loaded in the column.

The removal capacity (R) was calculated as the amount of CO₂ retained in the column concerning the total fed CO₂:

$$R = \frac{q_{CO_2} m_{AC}}{\vartheta C_0 t_{sat}} = \frac{\int_0^{t_{sat}} \left(1 - \frac{C_t}{C_0}\right) dt}{t_{sat}} \quad (3.15)$$

To assess the performance of the CH₄ upgrading, key parameters were estimated: productivity, CH₄ purity, and CH₄ recovery. The molar yield of CH₄ (Y_{CH_4} , mol g⁻¹ s⁻¹) with a selected purity level (90 %) was determined from the integration of the molar flowrate profile of CH₄ leaving the gas outlet between the time interval of t_1 to t_2 , defined as the time where CH₄ reaches the purity selected as 90 % [47,48]:

$$Y_{CH_4} = \frac{1}{m_{AD} t_{cycle}} \int_{t_1}^{t_2} F_{CH_4}(t) dt \quad (3.16)$$

where $F_{CH_4}(t)$ is the molar flow of CH₄ in the outlet stream, and t_{cycle} means the necessary time to reach the inlet conditions. Besides, the CH₄ purity was calculated as the percentage of the CH₄ in the outlet gas as follows:

$$CH_4 \text{ purity} = \frac{\int_{t_1}^{t_2} F_{CH_4}(t) dt}{\int_{t_1}^{t_2} F_{CH_4}(t) dt + \int_{t_1}^{t_2} F_{CO_2}(t) dt} \quad (3.17)$$

The CH₄ recovery was estimated as the CH₄ extracted in the raffinate during the interval t_1 - t_2 concerning the amount fed during the cycle:

$$\text{CH}_4 \text{ recovery} = \frac{\int_{t_1}^{t_2} F_{\text{CH}_4}(t) dt}{\int_0^{t_{\text{cycle}}} F_{\text{CH}_4}(t) dt} \quad (3.18)$$

The adsorption-desorption cycles of reusing with a CO₂-CH₄ mixture were carried out by swapping the inlet with pure N₂ at the same flow rate, i.e. 100 mL min⁻¹. The desorption cycle was finalized when the monitored CO₂ and CH₄ concentrations were negligible.

3.2.1.4. Results and discussion

The evaluation of the solid yield during the production of the plastic-based activated carbons is a relevant aspect to consider since low values increase production costs. **Table 3.18** shows the solid yield defined as the ratio between the mass of plastic-based activated carbon and the mass of plastic precursor used, both on a dry basis, as a function of carbonization or pyrolysis temperature, and the chemical activating agent used. The solid yield was especially affected by the chemical activating agent. However, low changes were observed with the carbonization temperature. Only a low decrease in solid yield was observed as the temperature was increased. The activation with hydroxides (NaOH and KOH) produced the greatest loss of mass, achieving a yield close to 40 % with KOH and 30 % with NaOH. The use of carbonates instead of hydroxides usually reports a higher activated material yield due to the promoted reactions of hydrolysis, depolymerization, and polymerization with the carbon precursor, triggered in contrast to the oxidation reaction of hydroxides [49]. KOH exhibits more ability to remove more volatile matter during activation if compared to K₂CO₃ [50]. Similarly, the activation process with chlorides, i.e. FeCl₃ and ZnCl₂, harvested high production yields, providing solid yield values slightly above 50 %. The higher yield achieved during the activation with chloride salts can be explained based on the much more violent reaction triggered by KOH [51]. Additionally, in the case of ZnCl₂, it has been claimed that displays an inhibition effect on the volatile matter loss, stabilizing it and eventually increasing the yield in comparison with KOH [52].

Characterization of the plastic-based activated carbon

The proximate analysis is shown in **Table 3.18** as a function of carbonization temperature and the chemical activating agent used. In general, high ash and low fixed carbon contents were observed in the samples. Also, after cleaning the char with HCl, the ash content decreased, raising the fixed carbon. The chemical activation led to an increase of the fixed carbon, especially in those chars prepared at the higher carbonization temperature, i.e. 500 °C. The highest content of fixed carbon was achieved under activation with sodium-based salts, i.e. NaOH and Na₂CO₃, reaching values of 55.8 % and 53.7 %, respectively.

Table 3.18. Elemental and proximate analyses of the plastic-based activated carbon from chars obtained at 450 and 500 °C

Material	T* (°C)	Yield (%)	Elemental analysis (wt., %)					Proximate analysis (wt., %)			
			C	H	N	S	O	Moisture	Volatile	Fixed carbon	Ash
Char	450	-	35.4	2.6	1.0	-	21.8	0.9	36.0	23.9	39.2
Char-washed		-	49.3	4.1	1.5	-	14.4	0.7	36.4	32.1	30.8
Char-NaOH		30.0	35.2	0.8	-	-	16.2	5.4	15.4	31.4	47.8
Char-Na ₂ CO ₃		45.2	48.7	0.8	0.9	0.6	17.0	7.7	28.7	31.5	32.1
Char-KOH		40.5	24.8	0.9	0.3	-	16.9	6.5	17.6	18.7	57.2
Char-K ₂ CO ₃		38.5	43.9	0.6	0.8	0.8	11.1	5.4	10.2	41.6	42.9
Char-FeCl ₃		51.0	45.4	0.6	0.8	0.7	13.2	2.8	8.1	49.8	39.4
Char-ZnCl ₂		44.5	42.0	0.5	0.9	0.8	11.3	5.9	7.0	42.7	44.5
Char	500	-	37.0	2.4	1.0	-	19.9	2.9	30.0	28.3	38.8
Char-washed		-	52.2	5.1	1.5	-	5.3	1.6	32.0	30.5	35.9
Char-NaOH		29.4	55.0	0.7	0.7	-	12.5	4.8	8.2	55.8	31.2
Char-Na ₂ CO ₃		41.1	55.5	0.8	1.0	-	7.7	2.6	8.8	53.7	35.0
Char-KOH		34.7	49.0	0.5	0.6	-	13.7	7.2	9.3	47.3	36.2
Char-K ₂ CO ₃		40.6	47.6	1.0	0.5	-	12.7	1.7	11.0	49.0	38.3
Char-FeCl ₃		53.0	49.1	0.5	0.8	0.7	5.2	2.3	7.1	46.9	43.7
Char-ZnCl ₂		55.0	48.0	0.4	-	0.7	7.4	1.6	5.6	49.3	43.5

*Temperature for the carbonization or pyrolysis of the plastic mixture.

Some researchers reported similar results regarding the elemental and proximate analysis of char obtained from plastic waste. For example, the pyrolysis of high-density polyethylene (HDPE) waste at temperatures of 400 °C and 450 °C found that the char contained 42.6 % of C and 3.1 % of H [53]. Also, the pyrolysis of a real mixture of plastic waste from municipal waste has reported an ash content of the char of 61.4 % and a carbon content of 29.3 %, values in the order of magnitude of those found in the char of the current work [54]. In addition, the char from the pyrolysis of polyethylene in other studies has been characterized by a volatile matter content of 55.46 %, a fixed carbon content of 15.2 %, and an ash content of 23.6 % [55]. Therefore, certain variations that highly depend on the characteristics of the plastic raw material used as a precursor to produce the char can be envisaged.

The textural properties were evaluated by N₂ adsorption-desorption isotherms, leading to the results depicted in **Figure 3.16** and the data summarized in **Table 3.19**. The plastic-based activated carbons showed isotherms of type IV according to the IUPAC classification. On the one hand, the isotherms developed a hysteresis between the adsorption and desorption branches because of capillary condensation, which indicates the existence of mesopores. On the other hand, the marked slope at low relative pressures proves the existence of micropores. The char obtained by pyrolysis at temperatures either 450 °C or 500 °C exhibited very low S_{BET} (below 4 m² g⁻¹). After treatment with HCl, a slight increase is observed, probably due to the cleaning effect during the acid treatment, which reduces the ash content and contributes to cleaning some micro, and overall mesopores [56]. However, an outstanding increase in porosity was accounted for after chemical activation, an essential factor for CO₂ adsorption, in which micropore volume has been claimed as the key parameter to enlarge the CO₂ uptake at mild conditions [57]. Little differences in the textural properties were observed after activation of the chars carbonized at 450 °C and 500 °C by each chemical agent. As revealed in **Table 3.19**, the porosity order was K₂CO₃ > Na₂CO₃ > KOH > NaOH > ZnCl₂ > FeCl₃ for those chars pyrolyzed at 450 °C. For the chars pyrolyzed at 500 °C, the effect of KOH overpassed the Na₂CO₃, probably due to the higher reactivity of KOH if compared to Na₂CO₃. Interestingly, the chars carbonized at 500 °C led to the highest microporosity, being the uppermost $V_{\text{MP}}/V_{\text{T}}$ ratios registered after activation with K₂CO₃ (58,9 %, $V_{\text{MP}}=0.307$ cm³ g⁻¹) and KOH (50.0 %, $V_{\text{MP}}= 0.212$ cm³ g⁻¹). The micropore size distribution, depicted in **Figure 3.16** C-D demonstrates a centered distribution of micropores around 0.7 nm, with a better definition in the chars carbonized at 500 °C and activated with K₂CO₃ and KOH.

Our findings show that the carbonization temperature exerts a positive effect on the activation process, with better results obtained at 500 °C compared to 450 °C. The reactions in the carbonization process included volatilization, functional group breakage, and aromatic ring polycondensation [58]. However, the plastic waste

cannot be carbonized completely at low temperatures. If the temperature is too high, some pores are sintered, decreasing the specific surface area and pore volume. For example, it has been reported that the carbonization temperature significantly influenced the specific surface area and pore volume of activated coal char, firstly increasing with the carbonization temperature and then dropping as the carbonization temperature rose [59]. The activated carbon with the best pore structure was the one that was carbonized at 600 °C. The textural properties of activated coal char were positively correlated with the CO₂ adsorption capacity, with the microporous volume being the primary factor.

If surface areas of developed plastic-based activated carbons in this study are compared with commercial activated carbons, the obtained values are quite low compared to those obtained from biomass. In this case, the composition of plastic plays an important effect. The complex and heterogenous composition of the mixture of plastics used in this work resulted in an activated carbon product with a lower surface area, i.e. 804 m²/g, than other commercial activated carbons prepared mainly from homogeneous biomass precursors as summarized in **Table 3.20**.

Table 3.19. Textural properties and CO₂ uptake of the plastic-based activated carbons

Material	T* (°C)	N ₂ isotherm at 77 K						CO ₂ uptake at 100 kPa	
		S _{BET}	S _{MP}	V _T	V _{MP}	V _{MP} /V _T	D _{MP}	q _{CO2} at 273 K	q _{CO2} at 298 K
		(m ² g ⁻¹)	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(%)	(nm)	(mg g ⁻¹)	(mg g ⁻¹)
Char	450	3.3	-	0.015	-	-	-	16.8	10.4
Char-washed		7.4	-	0.035	-	-	-	16.8	11.0
Char-NaOH		265.0	178.9	0.268	0.091	34.0	0.70	42.8	29.2
Char-Na ₂ CO ₃		608.9	387.8	0.551	0.200	36.3	0.75	93.5	64.1
Char-KOH		483.1	311.1	0.421	0.163	38.7	0.74	58.6	41.3
Char-K ₂ CO ₃		750.3	545.8	0.583	0.262	44.9	0.75	107.0	67.6
Char-FeCl ₃		93.3	26.6	0.207	0.013	6.3	0.67	58.4	33.7
Char-ZnCl ₂		350.2	242.8	0.343	0.123	35.8	0.73	55.0	34.6
Char	500	2.1	-	0.009	-	-	-	20.3	13.6
Char-washed		2.7	-	0.012	-	-	-	17.0	11.2
Char-NaOH		290.8	147.6	0.298	0.074	24.8	0.74	45.3	29.1
Char-Na ₂ CO ₃		529.7	352.1	0.470	0.171	36.4	0.74	84.1	58.3
Char-KOH		80.4	406.3	0.424	0.212	50.0	0.75	125.0	84.8
Char-K ₂ CO ₃		803.7	577.2	0.521	0.307	58.9	0.74	130.2	82.1
Char-FeCl ₃		83.1	16.8	0.195	0.009	4.6	0.67	47.1	43.5
Char-ZnCl ₂		288.4	180.0	0.304	0.097	31.9	0.75	38.6	29.8

*Temperature for the carbonization or pyrolysis of the plastic mixture.

Table 3.20. Comparison of surface area of commercial activated carbons

Commercial activated carbon	Surface area ($\text{m}^2 \text{g}^{-1}$)	Reference
Norit® SX2 POCH-Poland	659	[60]
YP-50F, Kuraray Chemical Corporation, Japan	1690	[61]
Precursor coconut shell, Kuraray Co.,Ltd	1700	[62]
Precursor coconut shell, Kuraray Co.,Ltd	2426	
Precursor coconut shell, Fuzhou Yihuan Carbon Co. Ltd.	2429	
Precursor coconut shell, Beike 2D materials Co. Ltd.	1327	
Precursor petroleum coke, XFNANO Co, Ltd	2125	
Precursor petroleum coke, Fuzhou Yihuan Carbon Co. Ltd.	2074	
Precursor petroleum coke, Fuzhou Yihuan Carbon Co. Ltd.	2145	[63]
Precursor not specified	1370	
Precursor coconut shell	1343	

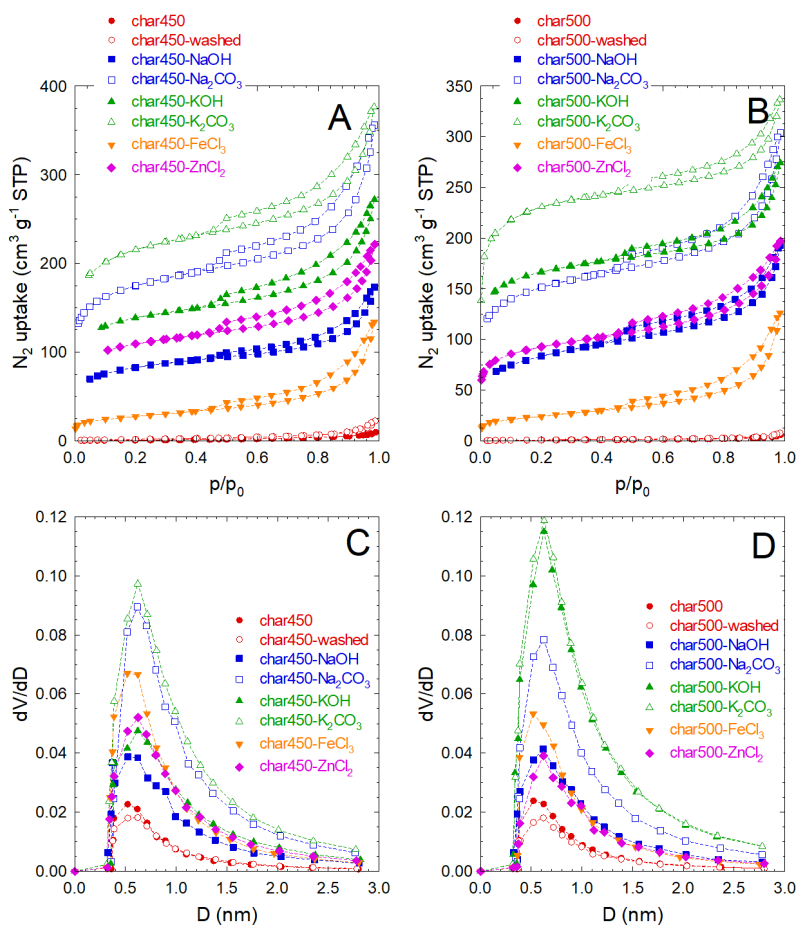
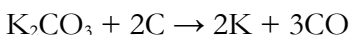


Figure 3.16. N₂ adsorption-desorption isotherms of plastic-based activated carbons prepared from carbonized chars at 450 °C (A) and 500 °C (B) and their respective pore-size distribution (C and D)

Generally, KOH is the most popular chemical activating agent due to its strong basic character to destroy diverse carbon walls, leaving the formation of micropores, even in plastic-based precursors such as PET bottles [21,26,27], PVC [65], polystyrene foams [66], and tires [67,68]. However, the porosity generated, strongly depends on the composition of the precursor, among other variables. The development of pores during KOH activation is intrinsically associated with a gasification reaction, which occurs according to the overall reaction provided below.



When KOH is added to the carbonized plastic, the formation of K₂CO₃ is expected at around 400°C, leading to a complete transformation of KOH into K₂CO₃ at around 600°C. Later, K₂CO₃ oxidizes the carbonaceous matter to CO yielding porosity in the carbon residue with a maximum release of CO up to 800°C [69,70] according to the following chemical reaction.



The difference between the potassium hydroxide and carbonate relies on the oxidation of the carbon matter, which starts at over 600-700 °C for K₂CO₃ [71], whereas the redox reaction of KOH with the carbon precursor is triggered at lower temperatures (~ 400 °C) [72]. This may explain the controlled reaction of K₂CO₃ versus the most aggressive KOH, leading to better conservation of the micropore morphology by the carbonate [49]. Probably the greater aggressivity of KOH explains the lower microporosity for the plastic-based char if compared to K₂CO₃. In fact, the comparison performance of K₂CO₃ and KOH has been reported a better control the micropore size distribution by K₂CO₃, enhancing the CO₂ capture when used as adsorbent [73]. Regarding the effect of NaOH or Na₂CO₃, much less researched as an activating agent inf compared to their K salts [17], it should be noticed that NaOH is less corrosive than KOH, Na₂CO₃ offers a lower catalytic activity of Na₂CO₃ for carbon gasification and the higher temperature of decomposition into CO₂, e.g. 1000 °C [74]. Concerning the use of chlorides (neutral activating agents), the main mechanisms for pore formation are oxidation, template, and gasification. ZnCl₂ performed better ability to develop micropores whereas the surface created by FeCl₃, much lower, was mainly of a mesopore nature. ZnCl₂ plays a key role in the removal of hydroxyl groups during activation, enabling the removal of oxygenated groups from the structure, and accelerating the dehydration reaction which releases more porous structures if compared to FeCl₃ [75].

To investigate the influence of the activating agent on the presence of oxygenated surface groups, XPS was conducted, selecting the char activated at 500 °C due to

the better performance observed of the textural properties. The composition of the surface is summarized in **Table 3.21**. The results demonstrate the presence of carbon and oxygen at the surface as major components. The minor detected elements were Si and Ti, among others such as Ca or Fe. The existence of these elements is due to the addition of popular chemical additives to the formulation of the plastic, for instance, colorants (TiO_2) lubricants (siloxane), flame-retardants (SiO_2), and fillers (CaCO_3 and silicate) [76]. These minor elements suffered a concentration effect after activation during their accumulation. The activating agent reacts with the carbon content to develop the porosity, leaving them more concentrated in the final material. The activation process positively impacted the release of oxygenated groups, especially with KOH (27.5 %) and K_2CO_3 (29.1 %), followed by their sodium counterparts. However, FeCl_3 and ZnCl_2 did not exert this effect as the oxygen at the surface was barely 12 %. The lower oxygen content for the carbons activated with ZnCl_2 if compared to KOH has been attributed to the catalytic dehydration effect caused by ZnCl_2 [52]. The activation of ZnCl_2 leads to higher the removal of the hydrogen and oxygen atoms from the activated carbon structure [77]. It has been stated that hydroxides and carbonates display a great ability to create highly oxygenated basic groups if compared to acidic metals which tend to develop neutral and faintly acidic groups [49,78]

Table 3.21. Chemical surface composition by XPS of the activated chars at 500 °C

Material	Composition (% wt.)				
	C	O	Si	Ti	Others
Char	79.6	13.1	0.6	-	Ca (4.3)
Char-washed	87.2	10.4	1.6	0.9	-
Char-NaOH	51.6	25.2	8.0	4.1	Ca (2.3) Fe (1.8) Na (1.0)
Char- Na_2CO_3	55.1	23.2	5.1	6.7	Ca (1.4) Fe (2.0) Na (1.8)
Char-KOH	50.7	27.5	5.7	6.0	Ca (1.4) Fe (3.7) K (1.0)
Char- K_2CO_3	65.0	29.1	6.3	4.0	Ca (1.2) K (1.7)
Char- FeCl_3	80.3	12.3	2.0	1.4	Ca (1.5) Fe (2.1)
Char- ZnCl_2	77.4	12.9	4.3	1.5	Zn (3.2)

A qualitative analysis of the oxygenated groups was further assessed in the samples prepared from the chars activated at 500 °C. As an example, the high-resolution spectra for C_{1s} and O_{1s} of the samples char500-KOH and char500- K_2CO_3 , are depicted in **Figure 3.17**. The distribution of the different considered

groups is shown in **Table 3.22** for all the samples. Regarding the C_{1s} spectrum, the following contributions were considered for the deconvolution: C=C (284.6 eV), C-C (285.3 eV), C-O (286.6 eV), C=O (288.0 eV), and O=C-OR (289.9 eV) [79]. In terms of oxygen bonded to surface carbon, it is appreciated that the washing led to an important abatement of the contribution of oxygenated carbon as shown in the result of **Table 3.21** for char before and after washing with HCl. The activation with NaOH and Na_2CO_3 led to the development of C-O groups. The C-O groups are more abundant in char500-KOH while C=O is the more abundant contribution in char500- K_2CO_3 . The activation with $FeCl_3$ is enriched with C-O groups while $ZnCl_2$ conducts the formation of C=O. The O_{1s} region was fitted to quinone (530.7 eV), C=O (531.5-532.0 eV), and C-O (~533 eV) [80]. From the analysis of the O_{1s} region, it is appreciated an outstanding contribution of C=O, attributable to ketones, lactones, acids, esters, and quinonic groups in the char500- K_2CO_3 and char500- $ZnCl_2$. The sample activated with KOH displayed an equilibrated contribution in which a major contribution of C-O (ethers and alcohols) was observed. Finally, regarding the metals at the highest concentration, i.e. Si and Ti, their high-resolution spectra suggested their presence at their highest oxidation estate, which means Si^{4+} and Ti^{4+} . The Si_{2p} spectra in **Figure 3.17** depict a maximum peak centered at roughly 103.5 eV, a value close to the reported for SiO_2 [81]. In the case of Ti_{2p} , a peak at 459.1 eV for $Ti_{2p3/2}$ and another at 465.0 eV for $Ti_{2p1/2}$ were recorded. These values suggest the presence of Ti^{4+} as reported in the literature [82].

Table 3.22. Surface oxygenated composition by XPS of the chars prepared at 500°C

Sample	C_{1s}			O_{1s}		
	Type	BE (eV)	% Peak	Type	BE (eV)	% Peak
Char500	C=C	284.4	43.4	quinone	531.3	39.7
	C-C	285.3	27.0	C=O	532.5	33.2
	C-O	286.0	26.3	C-O	533.7	27.1
	C=O	288.5	2.6			
	COO ⁻	290.0	0.7			
Char500-washed	C=C	284.4	51.2	quinone	531.6	38.2
	C-C	285.3	42.6	C=O	532.4	34.0
	C-O	286.7	3.0	C-O	533.6	27.8
	C=O	288.9	3.3			
	COO ⁻	290.0	0.0			
Char500-NaOH	C=C	284.5	45.4	quinone	531.3	24.8
	C-C	285.3	27.1	C=O	533.0	51.0
	C-O	286.5	15.0	C-O	534.3	24.2
	C=O	288.9	1.5			
	COO ⁻	289.4	11.0			
Char500- Na_2CO_3	C=C	284.5	47.4	quinone	531.9	32.7
	C-C	285.3	35.0	C=O	532.5	41.1
	C-O	286.5	13.0	C-O	533.6	26.1
	C=O	289.0	3.5			

Char500-KOH	COO ⁻	290.0	1.1			
	C=C	284.5	52.7	quinone	530.8	30.5
	C-C	285.3	22.4	C=O	531.8	25.3
	C-O	286.6	18.3	C-O	532.8	44.2
	C=O	288.7	0.2			
Char500-K ₂ CO ₃	COO ⁻	289.9	3.8			
	C=C	284.5	48.4	quinone	531.0	44.7
	C-C	285.3	42.1	C=O	532.0	33.0
	C-O	286.6	0.6	C-O	533.2	22.3
	C=O	288.6	7.1			
Char500-FeCl ₃	COO ⁻	289.9	0			
	C=C	284.5	49.9	quinone	530.6	17.2
	C-C	285.3	37.2	C=O	532.4	50.3
	C-O	286.5	0.0	C-O	533.8	32.5
	C=O	288.5	12.9			
Char500-ZnCl ₂	COO ⁻	290.0	0.0			
	C=C	284.5	50.8	quinone	531.2	16.7
	C-C	285.3	23.3	C=O	532.5	32.5
	C-O	286.5	17.2	C-O	533.6	50.8
	C=O	289.2	2.1			
Char500-KOH	COO ⁻	290.2	6.6			
	C=C	284.5	50.8	quinone	531.2	16.7
	C-C	285.3	23.3	C=O	532.5	32.5
	C-O	286.5	17.2	C-O	533.6	50.8
	C=O	289.2	2.1			

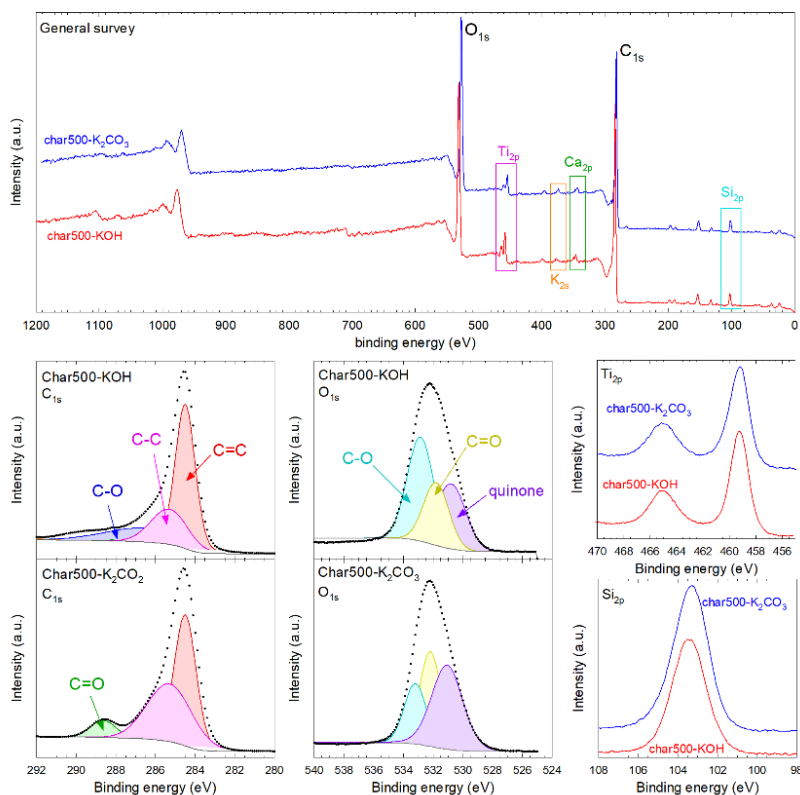


Figure 3.17. XPS general survey (top) and high-resolution spectra of the C_{1s} (bottom left), O_{1s} (bottom middle), Si_{2p} , and Ti_{2p} (bottom right) regions of samples char500-KOH and char500- K_2CO_3

The analysis of the disorder degree of carbon and the presence of crystalline impurities was analyzed by XRD. **Figure 3.18** portrays the diffractograms of the two samples with the best-developed textural properties, i.e. char500-KOH, and char500- K_2CO_3 . The disorder degree has been reported in activated carbon with the presence of broadband centered at roughly 24 and 43°, attributed to the (002) and (100) diffraction planes [83], being the response of the small number of stacked layers with uniform interlayer distance associated to the presence of ordered graphite or graphene structures [84]. However, this was not the case for the prepared activated carbon from plastic residue. A considerable important contribution of crystalline phases is depicted, linked to the presence of impurities. The identification of the crystalline pattern concluded the presence of the orthorhombic phase of the perovskite $CaTiO_3$ (COD-9013383). According to XPS analysis, considerable amounts of Ca and Ti were detected on the surface which is consistent with the conclusion reached by XRD.

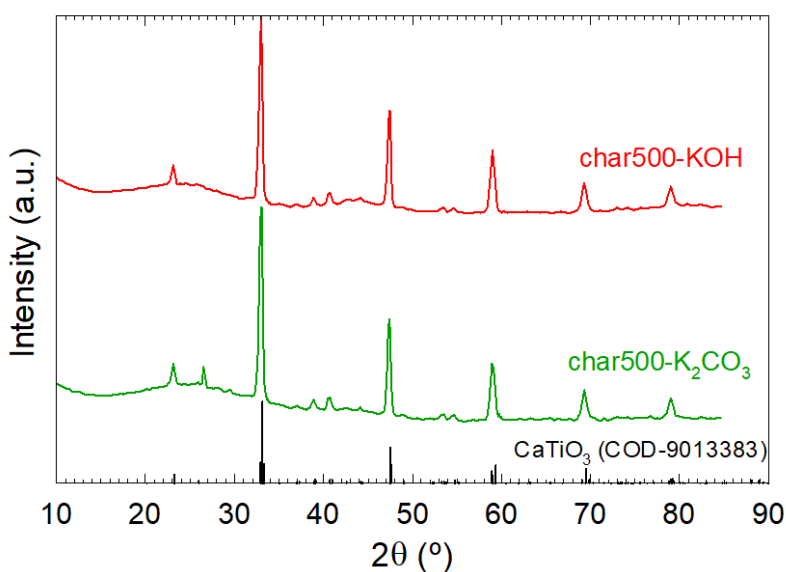


Figure 3.18. XRD patterns of the char500 activated with KOH and K_2CO_3

The morphology of the most porous samples, i.e. char500-KOH and char500- K_2CO_3 was analyzed by SEM microscopy. The SEM micrographs illustrated in **Figure 3.19** suggest the development of a porous surface after activation using both activation agents. No significant morphological differences were appreciated since the mechanism of both relies on the reaction and decomposition of the chemical agent with the organic content to release CO and CO_2 . However, as claimed in the

literature [49], the activation with K_2CO_3 triggers a less aggressive reaction leading to a material that resembles the structure pattern of the carbon precursor. In contrast, KOH has ability of destroying at higher extend the carbon material.

Finally, it is important to specify that the high boiling point of KOH (1327 °C) suggests that some of it remains after the activation process after the acid washing. This leftover KOH may be extremely dangerous to the environment if not disposed of properly. These consequences tend to outweigh the advantages of producing porous carbons using KOH-based chemical activation, and they highlight the need to look for more effective yet environmentally acceptable chemical activation reagents [85]. In addition, KOH has some limitations concerning its corrosiveness, equipment deterioration, and environmental toxicity [78].

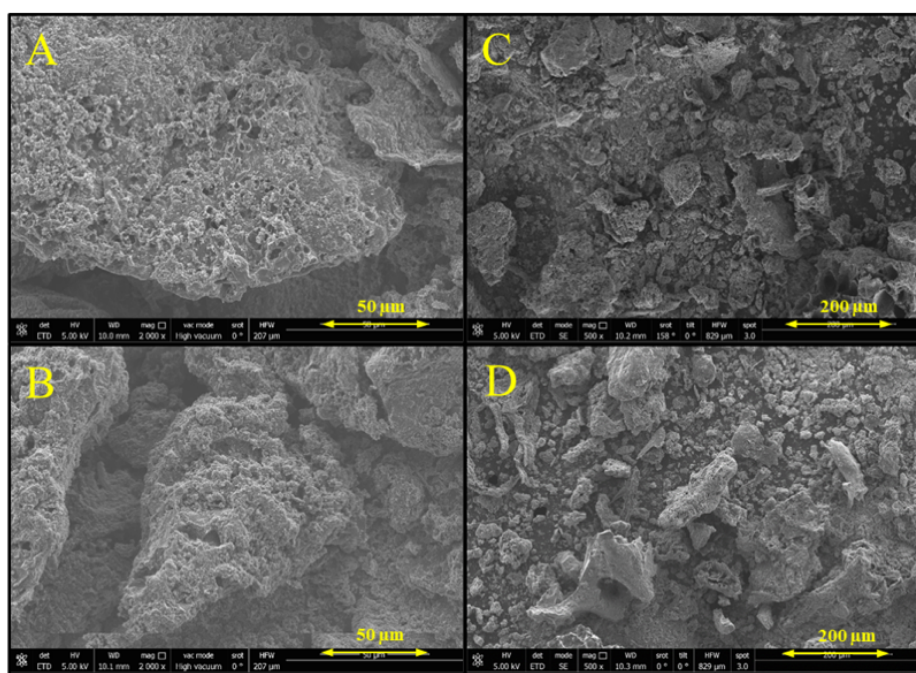


Figure 3.19. SEM pictures of the samples char500 (A), char500-washed (B), char500-KOH (C), and char500- K_2CO_3 (D)

Transmission electron microscopy (TEM) images, see **Figure 3.20**, of the activated carbon samples, also offered valuable insights into the structural and morphological characteristics. TEM images of char500 and char500-washed show that the particles are predominantly irregular sheets, typical of carbon materials after thermal activation processes. However, after activation certain destruction of the carbon particles can be envisaged. The presence of wrinkled sheets, pores, and cavities is predominant, reflecting a consistent activation process. Moreover, some TEM images show occasional impurities and inclusions, possibly remnants of

additives of plastic precursor materials. The EDS analysis of the sample displayed some regions with crystalline opaque particles of Ca and Ti (**Figure 3.20 D1**), compatible with the CaTiO_3 detected by the XRD technique.

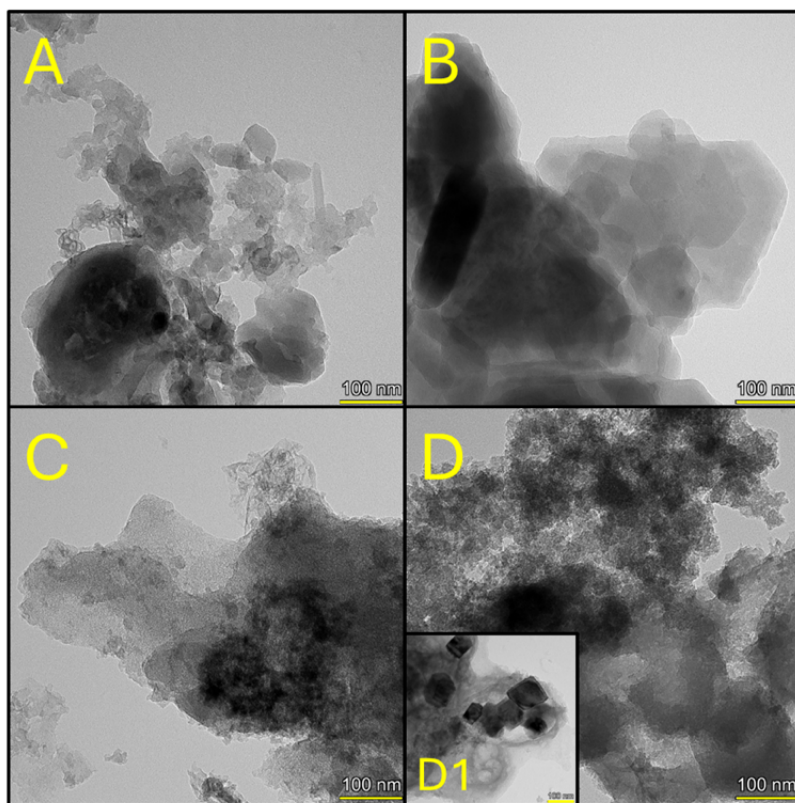


Figure 3.20. TEM pictures of the samples char500 (A), char500-washed (B), char500-KOH (C), and char500- K_2CO_3 (D and D1)

Adsorption capacities of CO_2 and CH_4

Table 3.19 also summarizes preliminary adsorption uptakes of CO_2 at 100 kPa. It is observed that the native and cleaned char had a low adsorption capacity, slightly increased when the temperature was elevated from 450 to 500 °C. The activated samples, whose CO_2 adsorption capacity is much higher in some activating agents, corroborated that the char prepared at 500 °C displayed better affinity towards CO_2 adsorption, due to better reactivity toward the activating agent and therefore raised the development of micropores. Based on that, the adsorption behavior of CO_2 and CH_4 was detailly assessed in static assays in a physisorption device up to 100 kPa, for those chars carbonized at 500 °C due to the boosted micropore volume in these activated chars.

The CO₂ uptake reported for other plastic-based activated carbon is very variable depending on the origin of the material devoted for the preparation of the char and the method followed for the activation. For example, the activation with KOH and NaOH of PET bottles has reported a CO₂ uptake of, respectively, 195 and 170 mg g⁻¹ [27]. These values are in the same order as reported in another study, also revalorizing PET bottles, and applying diverse activating agents such as KOH, H₃PO₄, ZnCl₂, and H₂SO₄ [86]. The KOH-activated char led to the best performance, establishing a retention of 110 mg CO₂ g⁻¹, and a CO₂ uptake sequence by activating agents of KOH > H₃PO₄ > ZnCl₂ > H₂SO₄. Polyurethane has reported the highest CO₂ capacity, 293 mg g⁻¹ (273 K), after activation with KOH, highly linked to the extremely microporous developed porosity [32]. In this work, the maximum CO₂ uptake (130.2 mg g⁻¹) was defined by the activation with K₂CO₃, lower than the values reported in the literature for residue composed of one polymer type. It should be considered that the waste used in this work was a complex mixture of plastic waste with no further practical separation since it comes from the rejected fraction of municipal solid waste.

The thermodynamic behavior was assessed by monitoring the isotherms for either CO₂ or CH₄ at 273 and 298 K, allowing the obtention of the isosteric adsorption heat. **Figure 3.21** depicts the CO₂ isotherms at both temperatures, which defined a growing increase explainable by the Freundlich model ($R^2 > 0.99$) with the lack of a well-defined plateau. The empirical Freundlich model describes non-ideal and reversible adsorption onto a monolayer or multilayer packing on a heterogeneous surface [39]. The expected exothermicity of the process was corroborated by a decreasing CO₂ uptake with the increase in the operating temperature. The adsorption behavior pertaining to the chemical activating agent described the order of micropore volume: K₂CO₃ > KOH > Na₂CO₃ > NaOH > ZnCl₂ > FeCl₃; being the uptake of the non-activated char negligible. **Table 3.19** summarizes the CO₂ uptake at near ambient pressure of the chars carbonized at 450 and 500 °C, further confirming the benefits of the higher carbonization temperature on the CO₂ uptake. The IAST selectivity of simulated exhausted fuel fumes with a 15/85 ratio of CO₂/N₂. The non-activated char displayed, although adsorbed very low CO₂, showed the highest selectivity, probably due to the negligible N₂ uptake at 298 K. depicted in **Figure 3.21** C, decreased as the strong active sites of the surface are covered as pressure raises, a consequence of the heterogeneity of the sample. The Freundlich model assumes a logarithmic decrease of the adsorption energy with the number of available adsorption sites. All the obtained values were below 40 kJ mol⁻¹, typically described as physisorption interaction [87]. Interestingly, the adsorption heat of CO₂, all exothermic except for the activation with FeCl₃, followed the same order registered for CO₂ performance: K₂CO₃ > KOH > Na₂CO₃ > NaOH > ZnCl₂ > FeCl₃; supported from a thermodynamic perspective the behavior among the samples. The activated sample depicted selectivity values (**Figure 3.21**

D) in the same order of magnitude, being those activated with chlorides the most selective in this sense ($S_{\text{CO}_2/\text{N}_2}$ values at 100 kPa): ZnCl_2 (64) $\sim$ FeCl_3 (63) $>$ NaOH (53) $>$ Na_2CO_3 (48) $>$ K_2CO_3 (46) $>$ KOH (38).

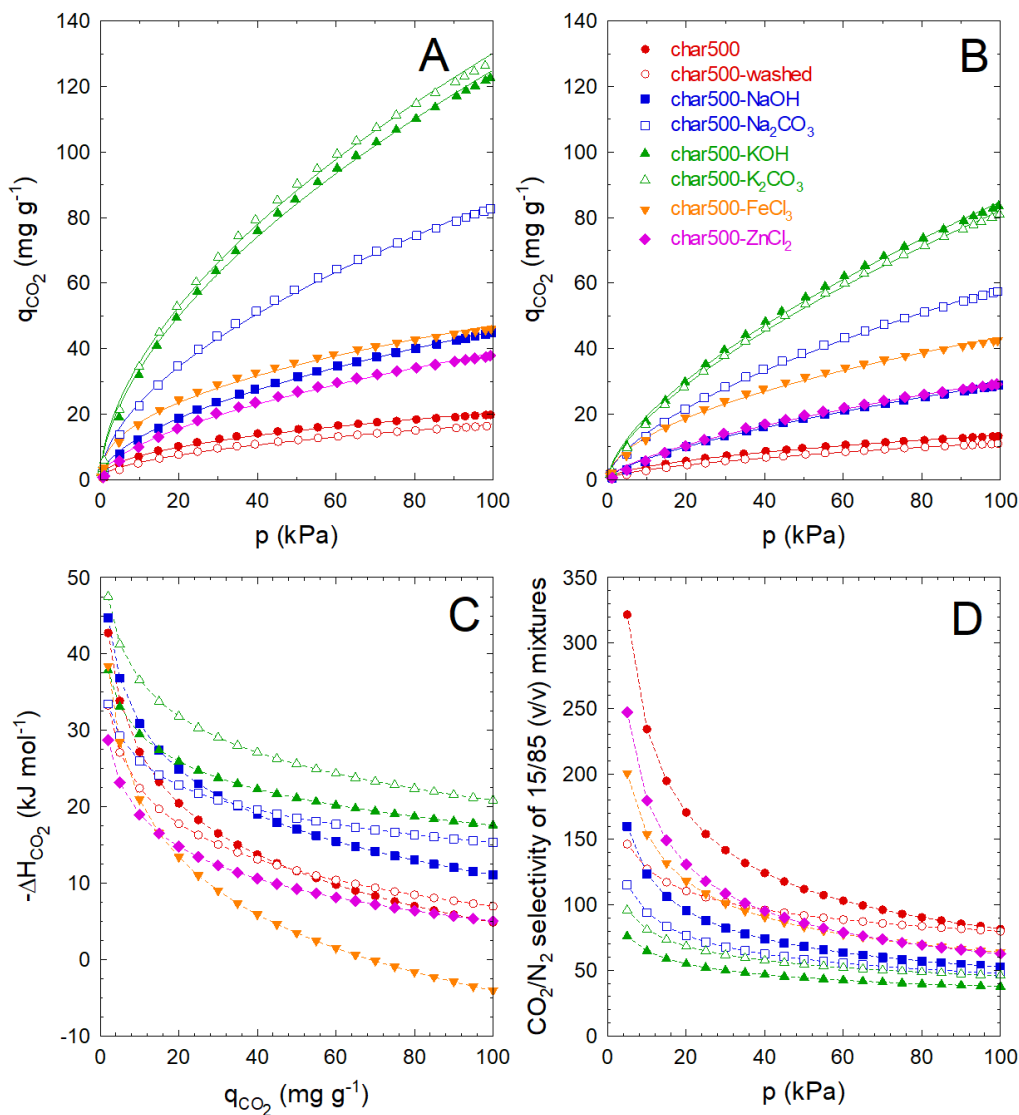


Figure 3.21. Influence of the activating agent on the CO₂ uptake of chars carbonized at 500 °C at 0 °C (A) and 25 °C (B). Isosteric heat of CO₂ adsorption as a function of the pressure (C) and IAST CO₂/N₂ selectivity at 25 °C of 15/85 (v/v) mixtures (D) and. The lines of subfigures A and B depict the fitting to the Freundlich model

Similarly, the CH₄ uptake behavior was also assessed on the chars carbonized at 500 °C after different activating agents, see **Figure 3.22**. Interestingly, some changes are depicted among the most active samples, i.e. the order for CH₄ adsorption followed was KOH > K₂CO₃ > Na₂CO₃ > FeCl₃ > NaOH > ZnCl₂, which implies a better selectivity of the sample activated with K₂CO₃ versus KOH in CO₂/CH₄ mixtures. The selectivity of simulated biogas with 40/60 (v/v) of CO₂/CH₄ was higher for the activation with K₂CO₃ and KOH as illustrated in **Figure 3.22 D**, displaying the highest value with ZnCl₂. The thermodynamics also supported this tendency, the KOH displayed a slightly higher adsorption heat of CH₄ than the K₂CO₃ and the ZnCl₂ the lowest value, explaining a poorer interaction of CH₄ with the surface and the highest selectivity of CO₂.

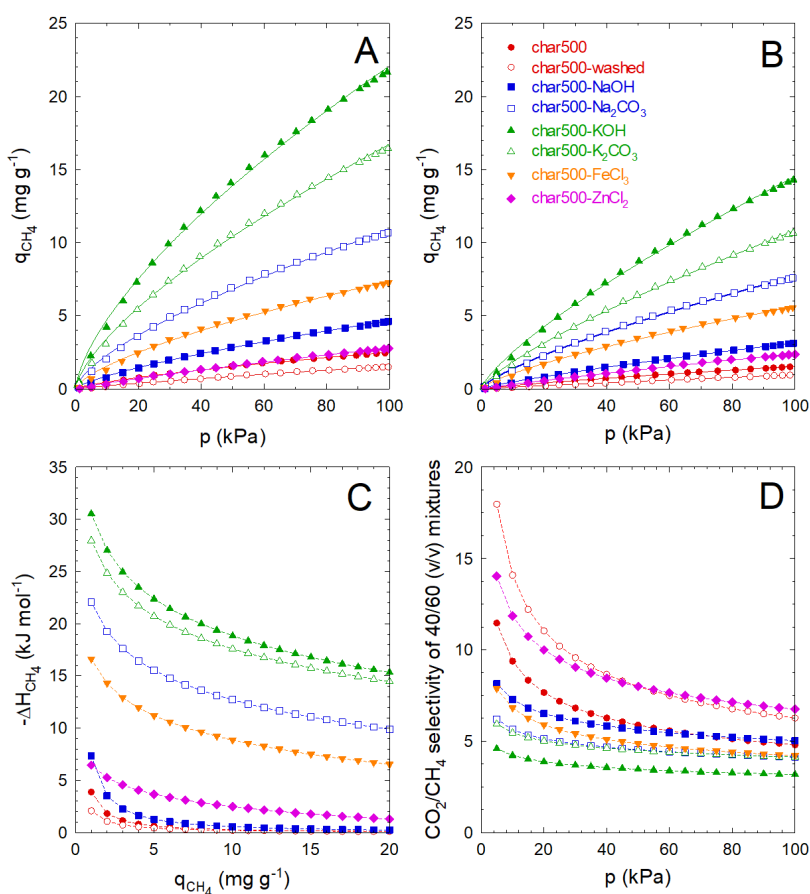


Figure 3.22. Influence of the activating agent on the CH₄ uptake of chars carbonized at 500 °C at 0 °C (A) and 25 °C (B). Isosteric heat of CH₄ adsorption as a function of the pressure (C) and IAST CO₂/CH₄ selectivity at 25 °C of 40/60 (v/v) mixtures (D). *The lines of subfigures A and B depict the fitting to the Freundlich model*

The CO₂ adsorption mechanism onto porous carbonaceous materials has been described through van der Waals forces, whereas the presence of surface functional groups promotes the adsorption via electrostatic forces [57]. Thus, van der Waals interactions outline in narrow pores as the molecule can increase the potential interaction with multiple points from the adjacent walls of the pore [88]. It has been described in the literature that CO₂ adsorption on activated carbons takes place typically in volume-filling rather than surface coverage, as happens with mesoporous materials. Consequently, the micropore size is quite important, being the optimum value described as twice the size of the adsorbate, i.e., as CO₂ size is around 0.33 nm the optimum micropore size should be roughly 0.7–0.8 nm [57]. **Figure 3.23** delineates the effect of CO₂ uptake (273 K and 100 kPa) versus the ultra-micropore volume, i.e. inferior to 1 nm, or the percentage of the oxygenated surface area of micropores estimating the surface oxygenated contribution by XPS analysis for all the plastic-chars activated at 500 °C. Regarding the relationship of q_{CO_2} and $V_{\text{MP}} (<1 \text{ nm})$, it is observed a good linear correlation between the two variables, as reported in other precursors such as biomass in the literature [57], except for the non-activated chars or the char-activated with FeCl₃, whose CO₂ uptake goes far from the predicted tendency. This abnormally high CO₂ uptake of these poorly micropore samples may be caused by other different reasons than the existence of micropores. As a matter of fact, it has been claimed that FeCl₃ displays a high ability to develop oxygenated surface groups. The Fe₂O₃ produced during the activation process reacts with carbon, leading to the formation of oxygenated groups and Fe₃O₄ [83]. Accordingly, the CO₂ uptake results are better explained based on the oxygenated surface of micropores. Therefore, the integrated interaction of van de Waals forces in micropores below 1 nm and the presence of oxygenated groups that contribute via electrostatic interaction better explains the results achieved with the different activating chemicals.

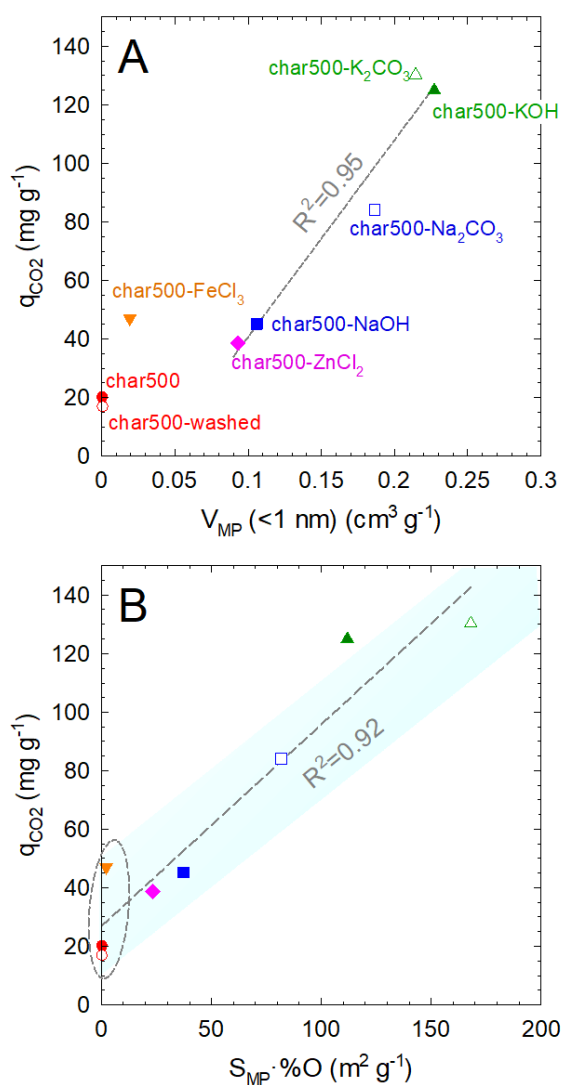


Figure 3.23. Correlation of the CO₂ adsorption uptake (273 K and 100 kPa) vs ultra-micropore volume HK method (A), and correlation of the CO₂ adsorption uptake (273 K and 100 kPa) and the percentage of oxygenated micropores (B) for the plastic-based activated carbon prepared from the pyrolyzed char at 500 °C

Dynamic adsorption tests of CO₂ and CH₄ and their mixtures

As a first screening test, the behavior of the different chemical activating agents on the dynamic tests was carried out in a fixed-bed column with the chars carbonized at 500 °C, due to the better performance as previously stated. **Figure 3.24** depicts the breakthrough curves obtained feeding an inlet gas stream composed

of a mixture of 40/60 (v/v) of CO_2/N_2 . From the results attained in this figure, a similar behavior concerning the assays conducted under static mode is obtained, being the two most effective samples those activated with K_2CO_3 and KOH , in which K_2CO_3 performs the best CO_2 retention.

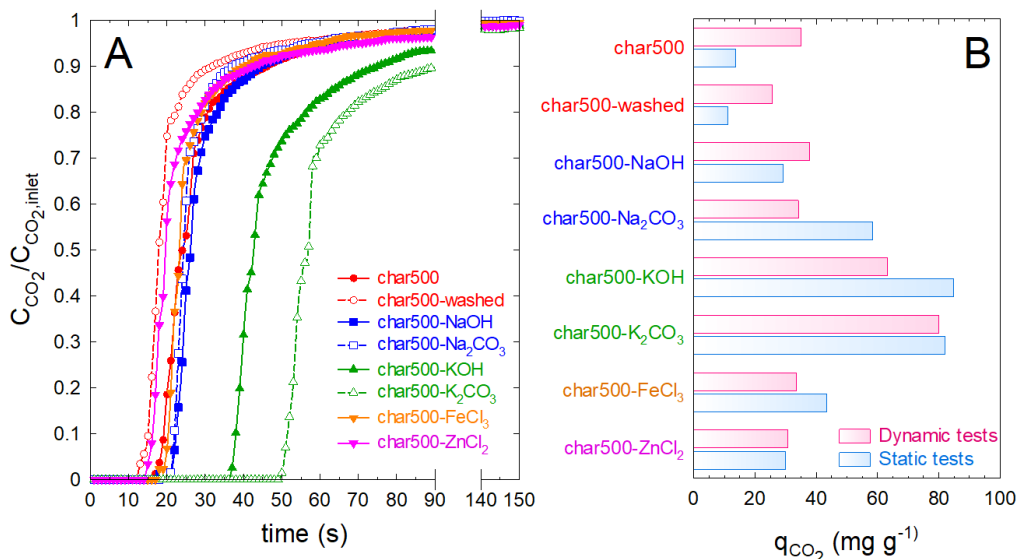


Figure 3.24. Breakthrough curves of the plastic-based activated carbons prepared from the chars carbonized at 500 °C under 40/60 (v/v) CO_2/N_2 mixtures at 298 K (A) and the comparison of the CO_2 uptake from dynamic and static tests (B) at atmospheric pressure

Regarding the results achieved, excellent performance was observed with the char activated with K_2CO_3 very convenient as this activating agent is considered a harmless and greener chemical. Compared to KOH , K_2CO_3 is a milder alkali compound, less toxic, and more corrosive [49]. Also, to our knowledge, there is scarce information in the literature about the preparation of activated carbons based on plastic waste by chemical impregnation using K_2CO_3 as an activating agent, neither their application for CO_2 nor CH_4 adsorption. Accordingly, the plastic-based activated carbon prepared with K_2CO_3 was selected for a further and detailed study on dynamic adsorption tests, aimed at analyzing the influence of CO_2 or CH_4 composition in their corresponding CO_2/N_2 or CH_4/N_2 mixtures. Hence, the CO_2/N_2 or CH_4/N_2 ratios varied from 20/80 to 80/20 (v/v), leading to the breakthrough curves illustrated in **Figure 3.25** and the main characteristic parameters in **Table 3.23**.

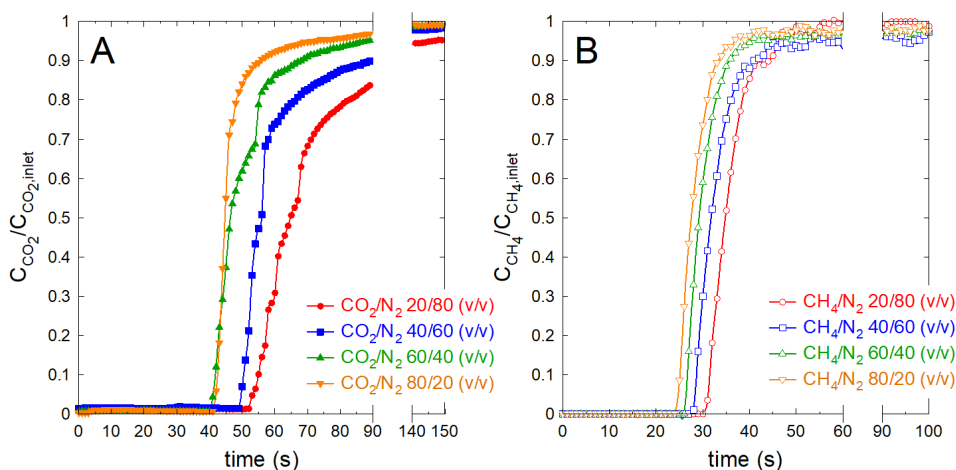


Figure 3.25. Breakthrough curves of CO₂ and CH₄ with char500-K₂CO₃ under CO₂/N₂ (A) and CH₄/N₂ mixtures (B)

Table 3.23. Adsorption parameters evaluated from breakthrough curves of CO₂ and CH₄ with char500-K₂CO₃ under CO₂/N₂ and CH₄/N₂ mixtures

Mixture	Composition (v/v)	t _{break} (s)	t _{sat} (s)	Removal (%)	q (mg g ⁻¹)
CO ₂ /N ₂	20/80	55	207	40.8	55.3
	40/60	51	122	49.8	79.5
	60/40	42	80	61.3	96.3
	80/20	41	77	57.0	125.3
CH ₄ /N ₂	20/80	32	60	66.8	8.6
	40/60	29	53	63.5	16.0
	60/40	27	41	74.3	21.7
	80/20	25	40	71.4	27.2

As expected, the breakthrough times shown in **Table 3.23** were higher in the case of CO₂ than CH₄ due to the higher selectivity, which was translated into higher adsorption capacity. As the adsorbate concentration, either CO₂ or CH₄, increased, the breakthrough time gradually decreased. For instance, in the case of CO₂, the breakthrough time decreased from 55 to 41 s, whereas for CH₄ was from 32 to 25 s. This indicates that by increasing the initial concentration of the adsorbate, the column saturates faster and the volume of treated gas, delimited by the breakpoint, is lower. Besides, the adsorption capacity was enlarged with increasing adsorbate concentration in the inlet effluent. For example, in the case of CO₂, the values moved from 55.3 mg g⁻¹ (20/80 of CO₂/N₂) to 125.3 mg g⁻¹ (80/20 of CO₂/N₂). Similarly, although with lower values, in the case of CH₄, the adsorption capacity also rose from 8.6 mg g⁻¹ (20/80 of CH₄/N₂) to 26.2 mg g⁻¹ (80/20 of CH₄/N₂). This positive effect is commonly observed in dynamic tests on a fixed-bed column

[89]. The benefits exerted by inlet adsorbate concentration on the adsorbate uptake can be justified based on a greater probability of several adsorbate molecules interacting with the active points of the adsorbent [90,91]. Subsequently, the higher the adsorbate concentration gradient, the lower the resistance to the mass transfer, launching the driving force for the adsorption process. Additionally, if the gas uptake obtained in the dynamic tests is compared to the static assays, some slight differences are observed, in the case of CO_2 the values were 82.1 mg g^{-1} (static) versus 125.3 mg g^{-1} (dynamic), and CH_4 displayed 10.7 mg g^{-1} (static) versus 27.2 mg g^{-1} (dynamic). The usually overestimated values depicted by dynamic tests if compared to static assays may be attributed to the different operating fluid dynamics in each case [92,93]. Where the sample was static and inside the cell in the static assays, in the fixed-bed setup the contact is more favorable since the gas is forced to cross the adsorbent, increasing the possibility of gas retention.

To assess the behavior of the optimum material, i.e. char500- K_2CO_3 , some assays were conducted in CH_4/CO_2 mixtures to simulate the biogas composition for real practical application. Since the content of CH_4 in biogas usually exceeds 50 % [41,94–96], 50/50, 60/40, 70/30, and 80/20 (v/v) CH_4/CO_2 mixtures were carried out. The breakthrough curves of CO_2 and CH_4 are depicted in **Figure 3.26** whereas the main characteristic parameter extracted from the curves are available in **Table 3.24**.

As expected by the higher CO_2 selectivity, the curves depicted in **Figure 3.26** define first the appearance of CH_4 , followed by CO_2 after saturation. The quality of separation is provided by the difference period defined by the breaking times of both components, in which the material is already saturated in CH_4 , but still absorbing CO_2 , leading to a gas outlet enriched in CH_4 . From a practical point of view, the time of a continuously operating process cycle is determined by the difference between the breaking times (t_{break}) of both components. Moreover, it is observed that there is a sharp increase in the output of CH_4 , reaching values higher than the input concentration of CH_4 which can reach values above up to 100 % in some cases to further decrease until reaching the saturation conditions (t_{sat}). As CO_2 is adsorbed, the outlet gas is enriched in CH_4 , reaching theoretical values of 100 % CH_4 if all the CO_2 is retained.

The selective adsorption of solid porous adsorbents helps the separation of CH_4 - CO_2 mixtures and mostly results from one or more of the following mechanisms: thermodynamic equilibrium effect, steric effect, and kinetic effect. Strongly adsorbed molecules are separated from weakly adsorbed molecules during adsorption according to the equilibrium effect, which might happen due to the different adsorbate molecules' attraction to the adsorbent surface. An adsorption-based separation can also be based on the size and the shape of the guest molecules, in which small molecules are adsorbed with a kinetic diameter smaller than the pores,

leaving larger particles unadsorbed due to steric impediment. Finally, while the affinity is decisive in equilibrium separation, kinetic separation is highly dependent on the rate at which the adsorbed molecules, with different sizes and shapes, can diffuse in the solid structure [97]. However, the precise mechanism should be studied in detail, and only then more specific predictions can be made for industry-scale process design [98]. Some specific chemical groups of the plastic-based activated carbons, e.g. mainly oxygen functional groups, prefer to adsorb CO_2 over the CH_4 molecules, which increases the selectivity for CO_2 molecules. Also, the separation performance in activated carbons was greatly affected by the nature of the pores of the materials. The increasing microporous surface and binding sites let greater adsorption of CO_2 than CH_4 due to the stronger quadrupole moment and polarizability of CO_2 , leaving a much more disadvantageous environment for CH_4 adsorption [99].

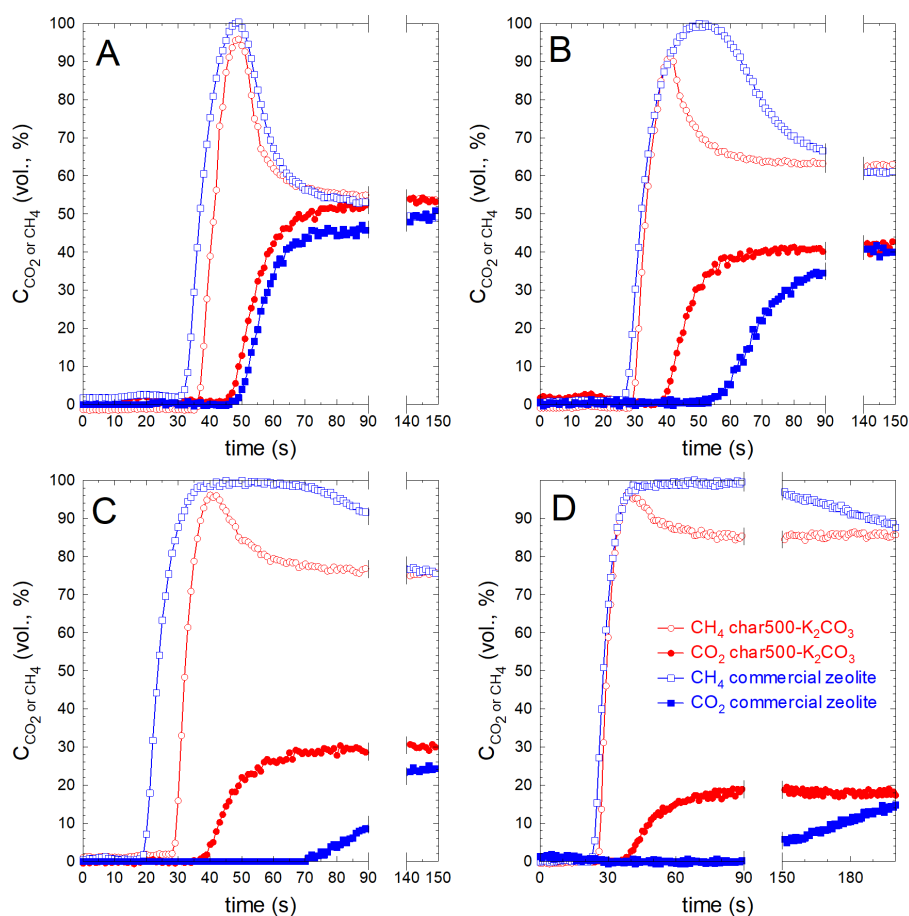


Figure 3.26. Breakthrough curves CO_2 and CH_4 with char500- K_2CO_3 and commercial zeolite under different CO_2/CH_4 (v/v) mixtures, 50/50 (A), 40/60 (B), 30/70 (C) and 20/80 (D)

Table 3.24. Adsorption parameters evaluated from breakthrough curves of CO₂ and CH₄ with char500-K₂CO₃ under CO₂/CH₄ mixtures

Material	CO ₂ /CH ₄ (v/v)	CO ₂				CH ₄				Y _{CH₄} (mmol g ⁻¹ min ⁻¹)	CH ₄ Purity (%)	CH ₄ Recovery (%)
		t _{break} (s)	t _{sat} (s)	R (%)	q (mg g ⁻¹)	t _b (s)	t _{ex} (s)	R (%)	q (mg g ⁻¹)			
Char500-K ₂ CO ₃	50/50	46	74	73.3	86.4	37	42	94.4	23.6	0.146	94.3	6.5
	40/60	39	77	64.8	59.3	30	36	88.7	22.8	0.163	80.4	6.1
	30/70	39	83	74.7	46.9	27	34	87.2	25.4	0.360	93.4	11.5
	20/80	38	84	62.0	34.5	26	33	87.5	27.5	0.653	93.8	18.3
Zeolite 13X	50/50	47	99	60.9	98.8	32	36	89.1	19.6	0.243	99.7	10.9
	40/60	54	104	61.7	94.5	27	33	89.0	21.0	0.550	99.8	20.5
	30/70	72	169	57.6	112.5	19	26	84.5	18.3	1.166	99.9	37.3
	20/80	126	250	70.2	114.9	24	32	82.8	27.7	2.367	99.8	66.3

Figure 3.26 depicts that the plastic-based activated char500-K₂CO₃ displays very close profiles to the commercial zeolite formula used in biogas upgrading when feeding 50/50 mixtures. In this case, the difference in breaking times between CH₄ and CO₂ is 9 s of the char500-K₂CO₃ versus the 15 s provided by the commercial zeolite. Bearing in mind that the plastic-based adsorbent was prepared from a valorized residue, the different adsorption mechanisms as a molecular sieve, and the higher cost of the zeolite, the prepared material seems very competitive for the upgrading application. At a higher proportion of CH₄ in the feeding gas, the zeolite was demonstrated to be more effective than the carbonaceous material, enlarging the breaking time between CH₄ and CO₂, and therefore the operating time. From the textural properties of the zeolitic molecular sieve and the comparison with the char500-K₂CO₃, see **Figure 3.27**, it is appreciated that the zeolite exhibits lower total surface area than the plastic-based activated carbon, i.e. 446.3 versus 803.7 m² g⁻¹, respectively. Additionally, the micropore volume of the carbon material is also higher, 0.221 (zeolite) versus the 0.307 cm³ g⁻¹ (char500-K₂CO₃). However, from the pore size distribution, the zeolite clearly states a narrower frequent ultramicropore size centered at 0.371 nm, an aspect of paramount importance that strongly impacts the CO₂ uptake, reaching values at 100 kPa of 218.9 mg g⁻¹ (273 K) and 162.5 mg g⁻¹ (298 K). The narrow pore size effectively acts as a molecular sieve and impedes the penetration of CH₄ molecules of bigger size than CO₂; subsequently, the CH₄ uptake is lower than the registered with the carbon-based material, sky-rocketing the selectivity towards CO₂, i.e. around 48 a 1000 kPa. However, the high cost of zeolites makes carbonaceous materials competitive although it implies a reduction of selectivity, the comparison of the char500-K₂CO₃ CO₂/CH₄ selectivity of 3.2 is quite close to the 4.7 reported for commercial formulas that display similar micropore size, i.e. 0.8 nm, prepared by activated by physical methods [100].

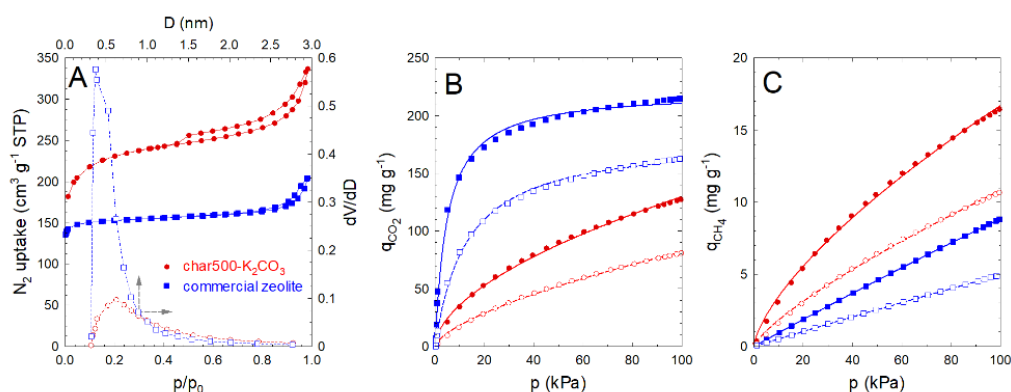


Figure 3.27. Comparison of commercial formulas and char500-K₂CO₃ for biogas upgrading. N₂ adsorption-desorption isotherms and micropore size distribution (A), CO₂ isotherms, and CH₄ isotherms (B) at 273 K (filled symbols) and 298 K (empty symbols). Connecting lines of subfigures B and C represent the fitting to Freundlich (char500-K₂CO₃) and Langmuir (zeolite) models

The tendency observed in the enlarged breaking times at raising the CH_4 at the inlet stream evidences a rising value of the CH_4 yield, see **Table 3.23**. This fact evidences the lower CH_4 yield reached at rising the CH_4 concentration fed to the column. Comparing the yield performed by the zeolite to the plastic-based activated carbon, the values are over 3-folded. The performance of novel activated carbon is still lower than that of commercial zeolite. However, if compared to the values reported in the literature with other carbon materials, the char500- K_2CO_3 exhibits a very similar value to activated carbon prepared from biomass precursors, such as cherry stone [47] and coconut shell [100], or commercial activated carbon formulas [101].

This CH_4 enrichment capability of our plastic-based activated carbons has potential implications and applications in the energy transition through renewable fuel production since it can lead to the production of biomethane. The qualities and applications of biomethane gas are like those of natural gas, making it a versatile and easy-to-store fuel that doesn't require natural gas equipment and device settings to be changed. It can be utilized for both residential and industrial purposes, including direct power generation in hydrogen or biomethane fuel cells, feedstock for Fischer-Tropsch fuel manufacturing processes, and thermal and power generation [102].

Recycling and regeneration of char500- K_2CO_3 was also evaluated since it is important for successfully commercializing new adsorbent materials. **Figure 3.28** depicts the CO_2 and CH_4 capacity and the CO_2 recovery of char500- K_2CO_3 after five adsorption-desorption cycles. The adsorption capacities were constant on the first five regeneration cycles. The constant adsorption capacities after regeneration can be ascribed to the successful adsorbent regeneration. It has been reported that some other common adsorbent materials such as activated carbons and zeolites maintain good adsorption performance up to or more than five regeneration cycles [103–107].

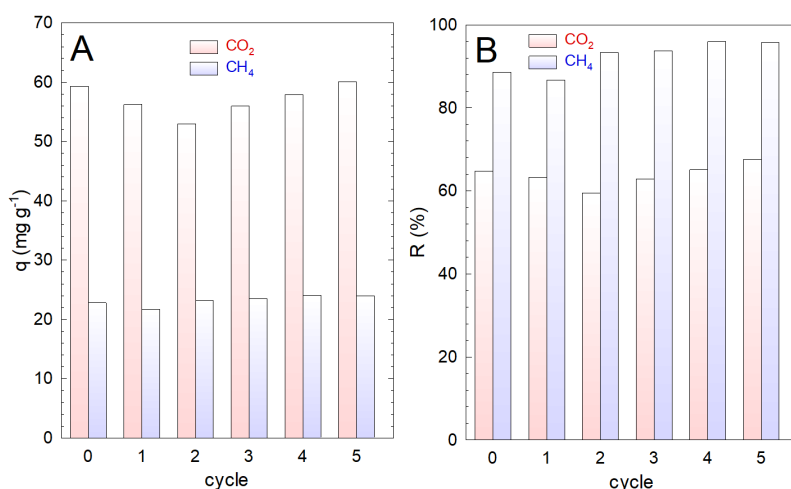


Figure 3.28. Adsorption parameters during sequential cycles with char500-K₂CO₃ under a CO₂/CH₄ mixture 40/60

3.2.1.5. Conclusions

This work proves the feasibility of valorisation of plastic waste of mixed polymers unsuitable for mechanical recycling. The carbonization temperature at which the plastic char was obtained exerted a positive effect on the second stage of activation, being the results attained at 500 °C better than at 450 °C. From the different chemical activating agents studied, the use of less toxic K₂CO₃ displayed better results than KOH either on the textural properties and CO₂ adsorption capacity. The sodium salts lead to poorer results if compared to their potassium counterparts. ZnCl₂ and FeCl₃ failed in the development of textural properties and CO₂ uptake. All the activating agents lead to micropores of an average size centered at roughly 0.75 nm. The percentage of ultramicropores and oxygenated surface groups were well-correlated with the CO₂ uptake, being the highest value obtained with K₂CO₃ either in static and dynamic adsorption experiments, with respective values at 25 °C of 82.1 and 79.5 mg g⁻¹.

The breakthrough curves over CO₂/CH₄ mixtures of 50/50 (v/v) depicted close behavior to commercial materials such as zeolites, although at higher CH₄ proportion the higher selectivity of the zeolite due to the molecular sieve mechanism with micropores of lower than 0.5 nm that allows the insertion of CO₂ nor CH₄ launched the benefits if compared to the plastic-based activated carbon. However, if the results are compared to other carbon formulas, either commercial or prepared from other precursors such as biomass, the results of the valorized plastic waste are very competitive, reaching comparable CH₄ production yield in the obtention of a CH₄ stream enriched at 95 %.

Recycling and regeneration of char500-K₂CO₃ were also evaluated after five adsorption-desorption cycles. The constant adsorption capacities after regeneration can be ascribed to the successful adsorbent regeneration.

Some future strategies to improve the performance of plastic-based activated carbons include: i) develop a comprehensive roadmap for implementing new precursors and technologies in activated carbon production; ii) incorporate new techniques and technologies to improve the production process and increase efficiency; iii) investigate the performance of plastic-based activated carbon in other applications.

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3.2.1.6. References

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Chapter 4. Char Produced from Biomass and Landfill Waste at Industrial scale

4.1 Liquid and gas effluent treatment: chemical activation

4.1.1. Paper 4: Promoting the circular economy: Valorization of a residue from industrial char to activated carbon with potential environmental applications as adsorbents

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Ledicia Pereira, Ventura Castillo, Mónica Calero, Sergio González-Egido, M. Ángeles Martín-Lara, Rafael R. Solís

4.1.1.1. *Abstract*

Pyrolysis of residues enriched with carbon, such as in agroforestry or industrial activities, has been postulated as an emerging technology to promote the production of biofuels, contributing to the circular economy and minimizing waste. However, during the pyrolysis processes a solid fraction residue is generated. This work aims to study the viability of these chars to develop porous carbonaceous materials that can be used for environmental applications. Diverse chars discharged by an industrial pyrolysis factory have been activated with KOH. Concretely, the char residues come from the pyrolysis of olive stone, pine, and acacia splinters, spent residues fuel, and cellulose artificial casings. The changes in the textural, structural, and composition characteristics after the activation process were studied by N₂ adsorption-desorption isotherms, scanning electron microscopy, FTIR, elemental analysis, and XPS. A great porosity was developed, S_{BET} within 776-1186 m² g⁻¹ and pore volume of 0.37-0.59 cm³ g⁻¹ with 70-90 % of micropores contribution. The activated chars were used for the adsorption of CO₂, assessed by thermogravimetry analysis, leading to CO₂ maximum uptakes of 90-130 mg g⁻¹. There was a good correlation between the CO₂ uptake with microporosity and oxygenated surface groups of the activated chars. Moreover, their ability to adsorption of contaminants in aqueous solution was also evaluated. Concretely, there was studied the adsorption of aqueous heavy metals, i.e., Cd, Cu, Ni, Pb, and Zn, and organic pollutants of emerging concern such as caffeine, diclofenac, and acetaminophen.

Keywords: char; activated carbon; adsorption; carbon dioxide; heavy metals; pharmaceuticals

4.1.1.2. Introduction

The growing recognition of the environmental challenges faced by our planet has led to a heightened focus on understanding and mitigating two critical issues: the excessive release of carbon dioxide into the atmosphere [1] and water scarcity [2]. The presence of pollutants in water bodies such as heavy metals [3] or anthropogenic organic contaminants of emerging concern [4] like pharmaceuticals and or personal care products hazards the reuse of wastewater effluents [5]. These issues have significant implications for the health of ecosystems, human well-being, and the sustainability of our natural resources [6]. All these pollutants pose a significant threat to water and air quality, putting the well-being of both wildlife and human populations on the line. It is imperative to mitigate their release and decontaminate them to uphold a state of optimal health among the population and lessen the global mortality rates attributed to air and water pollution. In 2019 alone, air pollution was responsible for approximately 6-7 million premature deaths worldwide, while water pollution contributed to 1-4 million premature deaths [6].

The worldwide energy-related CO₂ emissions were reported to have stayed constant at 36.1 Gt [7] but had a significant impact on the global annual average of atmospheric CO₂ concentration, leading to a rise of approximately 2.6 parts per million in 2020 [8]. Strategies for reducing atmospheric CO₂ concentrations include the use of renewable energy sources [9], energy optimization [10], growing natural forests [11], and sequestration by diverse processes, in which absorption using amine-based solvents is currently the most used technique [12]. However, the adsorption technique is emerging as an economical and greener alternative for capturing and storing the emitted CO₂ from industrial activity [12,13].

On the other hand, anthropogenic and intensified industrialization activities exert a direct influence on the contamination of water bodies by heavy metals and organic pollutants. Heavy metal contamination predominantly originated from direct effluent emissions into rivers and lakes coming from industrial discharges, power generation, mining operations, battery manufacturing facilities, paper mills, petrochemical industries, paint manufacturing units, and similar sources [14,15]. These heavy metals encompass cadmium, copper, zinc, lead, nickel, and chromium [15]. Various techniques exist for the elimination of harmful metallic ions, such as ion exchange, inverse filtration, precipitate separation, adsorption, coagulation, and extraction [16–19]. In addition, organic dyes, pharmaceuticals, and personal care products, along with others related to modern life are also prevalent in wastewater as a result of human activities [20]. For instance, caffeine has been found in Italian and German natural waters at maximum concentrations, respectively, of 124 ng L⁻¹ [21] and 640 µg L⁻¹ [22]. Diclofenac, a widely spread anti-inflammatory pharmaceutical, is consumed at a rate of approximately 1000 tons annually and has

been detected in surface, ground, and drinking water at concentrations ranging from ng/L to $\mu\text{g/L}$ [23]. Diclofenac is considered a prevalent environmental contaminant in various regions worldwide, including Switzerland, Spain, Sweden, and the Baltic region [23]. Acetaminophen is a pharmaceutical compound used as a painkiller, for fever reduction, and analgesic purposes. The global consumption of acetaminophen exceeded 149.3 kilotons in 2014, and it has frequently been detected in water sources [24,25].

Adsorption processes have emerged as a greener alternative that avoids the use of toxic solvents for capturing CO_2 from gas effluents [13,26] and the removal of water contaminants [27,28]. These processes have garnered attention for their remarkable effectiveness, respect for the environment, ease of implementation, affordability, and exceptional efficiency [29,30]. The most utilized adsorbents include carbon materials, and zeolites, as well as recently metal-organic frameworks (MOFs) and ionic liquids, among others. MOFs are highly porous materials constructed from metal ions or clusters coordinated with organic ligands [31]. Although MOFs exhibit exceptional adsorption capacities, their synthesis often involves complex and costly procedures. Moisture can hinder the accessibility of adsorption sites within zeolitic structures, limiting their effectiveness [32]. Ionic liquids, characterized by their liquid state at room temperature, possess unique properties that make them attractive for the absorption of gases such as CO_2 [33]. Their high cost and difficulty in managing and utilizing ionic liquids can hinder their widespread implementation [34]. Therefore, carbon materials emerge as the most favorable alternative for the removal of both CO_2 and water pollutants due to their well-established properties, low cost, effectiveness, and versatility in adsorption processes [35,36]. Notably, residual biomass and non-recyclable plastics hold remarkable potential as sources of carbon for producing biochar through pyrolysis processes [26]. These materials are abundantly available in nature, stemming from agricultural, forestry, and human-related activities, making them valuable renewable sources of carbon with environmentally friendly characteristics [29–31]. Diverse residues rich in carbon content have been successfully transformed into carbonaceous adsorbents. Just to cite some examples, winery wastes [37], residues from the mushroom production chains [38], sludge from urban wastewater treatment [39], sludge from the brewery industry [40], or agroforestry residues [41–43].

This work deals with the assessment of the adsorption effectiveness of porous activated carbon materials prepared from the chemical activation of industrial char that utilize newly developed processed plastics and forestry residues as effective strategies for the removal of CO_2 and water decontamination. Diverse industrial chars discharged after the pyrolysis process to obtain biofuels were considered. In particular, the chars came from the pyrolysis of forestry residues such as olive stone,

pine, and acacia splinters, solid recovered fuel (SRF), and cellulose artificial casings. Olive stones proceeded from the olive oil industry; pine and acacia splinters were residues from agroforestry activities; the SRF comes from the dehydration of solid waste, typically consisting of combustible components of municipal solid waste; and cellulose artificial casings are artificial viscose casings widely used in the food industry. These residues were pyrolyzed in a local factory to prevent them from being landfilled, which led to obtaining added-value biofuels. In the process, also a char was obtained, which was the object of this investigation. Hence, the valorization of this pyrolysis residue into an activated carbonaceous material enables to closing of the recycling loop.

Diverse chemical agents have been lately researched to activate carbon precursors, paying special attention to low hazardous substances [44]. Nonetheless, KOH is the most popular studied to date due to its superior reactivity towards carbon [45], leading, therefore, to utmost performance in developing microporosity [46]. The activated chars were fully characterized and their properties were analyzed by N₂ physisorption, FTIR, and elemental analysis. The activated chars were then examined for the adsorption of CO₂ from gaseous streams, removal of aqueous heavy metals (Cd, Cu, Ni, Pb, and Zn), and organic pollutants of emerging concern (caffeine, diclofenac, and acetaminophen).

4.1.1.3. Experimental section

Activation of the industrial chars

The industrial chars were obtained from local factories that produce syngas and biofuels from the pyrolysis of municipal, industrial, and agroforestry residues. Five different chars of different natures were provided, i.e. olive stone (OS), industrial first-transformation agroforestry waste products like pine or acacia splinter, and industrial wastes such as the solid recovered fuel (SRF) or cellulose artificial casings. The five collected chars were dried overnight at 120 °C. The activation was carried out with KOH due to the highest textural properties developed [47]. The thermal activation started by placing in an inert crucible the char and KOH at a mass ratio of 1:1 based on the conditions studied in previous work [47]. The thermal treatment was carried out under inert N₂ fed at 200 mL min⁻¹. The char-KOH mixture was heated from room temperature to 300 °C at a rate of 10 °C min⁻¹. After, the temperature was held for 1 h at 300 °C to melt the activating agent. Next, the temperature rose from 300 °C to 800 °C at a rate of 10 °C min⁻¹. Then, the temperature was kept for 1 h at this temperature. Finally, the sample was cooled to room temperature. The cooled samples were then washed with 1 M HCl and dried at 120 °C overnight. The dried solid was ground and sieved to < 250 µm. The final activated chars were named OS-AC (from olive stone), Pine-AC (from pine splinters), Acacia-AC (from acacia splinters), SRF-AC (from spent residue fuels) and

Cellulose-AC (from cellulose artificial casings). The yield of the activated carbon during their preparation was 79 % for OS-AC, 75 % for Pine-AC, 72 % for Acacia-AC, 41 % for SRF-AC, and 78 % for Cellulose-AC. A commercial powder-activated carbon purchased from Panreac AppliChem has been used for comparison purposes.

Characterization of the chars

The textural properties were studied by N₂ physisorption. The adsorption-desorption isotherms with N₂ at 196 °C were obtained in a Sync 200 device from 3P Instruments©. The samples were degassed overnight at 150 °C under a vacuum in a J4 prep degasser station of 3P Instruments©. The specific surface area was obtained by the Brunauer-Emmett-Teller method (S_{BET} , relative standard deviation RSD < 1 %), and the total specific pore volume (V_{T}) was calculated from the N₂ uptake at $p/p_0 \sim 0.99$. The t-plot method was used for the estimation of the specific surface of micropores (S_{MP}) and the micropore volume (V_{MP}). The micropore size distribution was obtained by CO₂ adsorption isotherms carried out at 0 °C, considering the Horvath-Kawazoe (HK) method for the calculation [48,49].

The proximate analysis was applied to quantify the percentages of moisture, volatiles, fixed carbon, and ash in the samples by thermogravimetric analysis in a Perkin-Elmer STA 6000 thermobalance (RSD < 5 %). The sample was first kept at 30 °C under N₂ (20 mL min⁻¹). Next, the temperature was risen to 110 °C (heating rate, 40 °C min⁻¹) and maintained for 10 min at this temperature. Then, the temperature was raised to 875 °C (heating rate, 40 °C min⁻¹) and kept at this temperature for 10 min. Finally, the N₂ was changed into O₂ (20 mL min⁻¹) at 875 °C for another 10 min. The determination of each of the constituents was completed by quantifying the weight loss in each step, and the fixed carbon by the difference.

The morphology of the particles was observed by Scanning Electron Microscopy (SEM) in a FEI Quanta 400 device (30 kV, 3.5 nm resolution).

The content of carbon, hydrogen, nitrogen, and sulfur was determined by elemental analysis in a Thermo Scientific Flash 2000 device (RSD values, 0.5 % for C, 1 % for H, and 0.6 % for N). Oxygen was estimated by the difference with the other elements after the removal of the ash content from the proximate analysis. For the chemical composition of the surface, X-ray Photoelectron Spectroscopy (XPS) was carried out in a Kratos AXIS Ultra-DLD device using an X-ray source from Al K α . All the spectra were corrected to the C1s peak of adventitious carbon to 284.6 eV. For the processing and deconvolution of the peaks, the software XPSpeak 4.1® was used, considering a Shirley background correction.

Adsorption tests

Adsorption of CO₂

The adsorption of CO₂ was assessed in terms of thermodynamics and kinetics. The thermodynamics of CO₂ adsorption was carried out through physisorption in a Sync 200 device from 3P Instruments©. As done with N₂ isotherms, the samples followed the same procedure. The adsorption isotherms were conducted at 0 °C and 25 °C and the data obtained fitted to a Freundlich isotherm, in which the CO₂ uptake (q_{CO_2} , mg g⁻¹) is described as a function of the CO₂ pressure (p) as follows [50]:

$$q_{\text{CO}_2} = K_F p^{1/n_F} \quad (4.1)$$

where K_F (mg g⁻¹ kPa^{-n_F}) and n_F are, respectively, the Freundlich constant and exponent. The CO₂/N₂ selectivity during the CO₂ process was calculated from their respective isotherms conducted at 25°C, applying the Henry's law, by dividing the initial slopes of CO₂ and N₂ adsorption isotherms [51]. The isosteric heat of CO₂ adsorption (ΔH_{ads}) was obtained as a function of the CO₂ uptake (q_{CO_2}) applying the Clausius–Clapeyron equation [52,53]:

$$\Delta H_{\text{ads}} = -R \ln \left(\frac{P_2}{P_1} \right) \frac{T_1 T_2}{(T_2 - T_1)} \quad (4.2)$$

Fixing a value for the CO₂ uptake, the pressure (p_1 and p_2) was obtained using the parameters obtained with the Freundlich model at $T_1=0$ °C and $T_2=25$ °C, leading to the obtention of the isosteric adsorption calculation.

The kinetics of adsorption of CO₂ was assessed in thermobalance (Perkin-Elmer, STA 6000) assays following a three-step program. The first step consisted of a drying step by heating the sample from room temperature to 200 °C, and kept for 1 h, under 50 mL min⁻¹ of N₂. The second step was a cooling of the sample from 200 °C to 30 °C under 50 mL min⁻¹ of N₂. Finally, the isothermal CO₂ adsorption of the dried sample was conducted under 50 mL min⁻¹ of CO₂ for 2 h, until a constant sample mass was reached. During the adsorption of CO₂, the mass of the sample increased from the initial mass of the dried sample. This increase lets the determination of the adsorbed CO₂ capacity over time (q_{CO_2}). The CO₂ adsorption kinetics have been adjusted to two models that are usually applied to physisorption processes [54,55]. Lagergren's pseudo-first order model supposes that the rate of CO₂ adsorption is directly proportional to the difference between the saturation concentration and the mean concentration within the particle, describing the evolution of the adsorbed CO₂ capacity (q_{CO_2} , mg g⁻¹) as follows [56]:

$$q_{\text{CO}_2} = q_1 (1 - e^{-k_1 t}) \quad (4.3)$$

where q_1 (mg g^{-1}) means the CO_2 adsorption capacity at saturation conditions of the pseudo-first order model and k_1 (min^{-1}) is the pseudo-first order rate constant. The Avrami model is a three-parameter modification of the first-order kinetics that was originally proposed to model the phase transitions and crystal growth of materials [57] but has been recently applied to the study of CO_2 adsorption onto functionalized activated carbon [58–60]. The Avrami model predicts the adsorption evolution by a fractal modification of the pseudo-first order of the adsorbed CO_2 as follows:

$$q_{\text{CO}_2} = q_A (1 - e^{-(k_A t)^{n_A}}) \quad (4.4)$$

where q_A (mg g^{-1}) means the CO_2 adsorption capacity at saturation conditions of the Avrami model, k_A (min^{-1}) is the Avrami kinetic constant and n_A (dimensionless) is the Avrami exponent.

Adsorption of aqueous heavy metals and contaminants of emerging concern

The batch adsorption experiments of heavy metals were conducted in 100 mL Erlenmeyer flasks at room temperature (25 °C). Different solutions of Pb, Zn, Ni, Cd, and Cu within approximately 10–300 mg L^{-1} with an adsorbent dose of 2.0 g L^{-1} and 160 rpm in an orbital stirrer until reaching the equilibria. The samples were filtered with syringe filters (Millipore Millex-GV PVDF, 0.45 μm), and the concentration of the metal was analyzed by Atomic Absorbance (AA) spectrometry in a PerkinElmer® PinAAcle 500 Flame device. The initial concentration of the metallic adsorbate solution before adding the adsorbent and after reaching the equilibria was analyzed for the determination of the adsorption uptake.

The batch adsorption experiments of the organic contaminant of emerging concern followed the same procedure conducted with the heavy metals. Different solutions of caffeine (CAF), diclofenac (DCF), and acetaminophen (ACE) within 10–500 mg L^{-1} with an adsorbent dose of 0.2–2.0 g L^{-1} and 200 rpm of magnetic stirring. The concentration of the organic was quantified by High-Pressure Liquid Chromatography (HPLC) in an Alliance e2695 HPLC device from Waters™ coupled to a 2998 photodiode array UV-visible detector. The stationary phase used for the separation was a Zorbax Bonus-RP column (4.6×150 mm, 5 μm). For the analysis of CAF and DCF, isocratic methods were carried out. A mixture of acetonitrile (A) and acidified water with 0.1 % (vol.) of trifluoroacetic acid (B) was pumped at a rate of 1 mL min^{-1} with an A:B ratio of 15:85 for CAF and 65:35 for DCF. In the case of ACE, a gradient method was applied from 20:80 to 60:40 in 7 min. The quantification was conducted at 275 nm for CAF, 247 nm for DCF, and ACE.

The isotherms of aqueous contaminants, either metals or organic pollutants of emerging concern, were fitted to different models [61]. It was the three-parameter model such as the Sips equation, which better fitted to the experimental data than the two parameters Freundlich [50] or Langmuir [62] model. Sips's equation describes the isotherm as follows [63]:

$$q_e = \frac{q_s(K_s C_e)^{n_s}}{1 + (K_s C_e)^{n_s}} \quad (4.5)$$

where q_e (mg g^{-1}) and q_s (mg g^{-1}) are the adsorbed amount in the equilibria and the maximum, respectively; K_s ($\text{mg}^{-1} \text{L}$) is the Sips's constant and n_s (dimensionless) the Sips's exponent.

The adsorption kinetics of the aqueous contaminants have been adjusted to two models that are usually applied to physisorption processes [64]. From all of them, the pseudo-second order was selected due to the best-fitting results achieved. The Ho's pseudo-second order assumes that the sorption uptake is proportional to the number of active sites occupied on the sorbent modeling the temporal adsorbed contaminant (q_t , mg g^{-1}) as follows [65]:

$$q_t = \frac{k_2 q_2^2 t}{1 + k_2 q_2^2 t} \quad (4.6)$$

where q_2 (mg g^{-1}) means the contaminant adsorption capacity at saturation conditions obtained by the pseudo-second order and k_2 ($\text{mg}^{-1} \text{g min}^{-1}$) is the pseudo-second order rate constant.

4.1.1.4. Results and discussion

Characterization of the activated chars

The analysis of the textural properties was considered the key proof of the activation of the chars and the building of a porous material with empowered adsorption properties. The main results of N_2 isotherms at 77 K are provided in **Table 4.1** and **Figure 4.1A** depicts the adsorption-desorption isotherms of the activated materials. The raw materials, which means the chars before activation, were non-porous, BET areas reached a maximum of $12 \text{ m}^2 \text{ g}^{-1}$ (Acacia-char) or $23 \text{ m}^2 \text{ g}^{-1}$ (SRF-char) or even below. The activation with KOH provided a great porosity, raising the surface area from $779 \text{ m}^2 \text{ g}^{-1}$ (Pine-char) to over $1000 \text{ m}^2 \text{ g}^{-1}$ (OS-AC and acacia-AC). These results are similar to the porosity reported in the literature by KOH for biochars [66] and other residues based on plastics [26], which are very competitive to commercial formulas such as the show in **Figure 4.1A** with roughly $713 \text{ m}^2 \text{ g}^{-1}$. The N_2 isotherms can be identified, according to IUPAC's classification [67], as Type I for all the samples except for SRF-AC, defining a concave inflection point at $p/p_0 \sim 0.1$. Type I is ascribed to microporous materials,

having pore size distributions over a broad range since the inflection point is displaced from $p/p_0=0.1$ [67,68]. The sample SRF-AC described a mixed isotherm of Types I and IV, providing evidence of certain mesoporosity [68]. The samples that defined a Type I isotherms did not describe any hysteresis loop since the desorption step overlaps the adsorption curve. However, the SRF-AC sample did perform a type H4 hysteresis, characteristic of micro-mesoporous carbon materials [68], also associated with narrow slit mesopores [69]. The microporosity was high in all the samples, much more important than the commercial formula (only 33 % of micropores), as the proportion of micropore volume to the total was around 90 %, except for SRF-AC which provided only 71 % of micropores. Regarding the size of the micropore, the HK method was applied to the CO_2 adsorption isotherms carried out at 0 °C, leading to the size distribution depicted in **Figure 4.1B**. As observed, the micropore size most frequently was around 0.5-0.7 nm which is consonant with the activation of KOH according to the literature [70].

Table 4.1. Textural properties obtained from N_2 adsorption-desorption isotherms

Sample	S_{BET}	S_{MP}	V_{T}	V_{MP}	$V_{\text{MP}}/V_{\text{T}}$
	($\text{m}^2 \text{ g}^{-1}$)	($\text{m}^2 \text{ g}^{-1}$)	($\text{cm}^3 \text{ g}^{-1}$)	($\text{cm}^3 \text{ g}^{-1}$)	(%)
OS-char	<0.1	0	<0.001	0	0
Pine-char	0.4	0	0.002	0	0
Acacia-char	12.3	0	0.024	0	0
SRF-char	22.7	1.4	0.062	0	0
Cellulose-char	1.4	0	0.005	0	0
OS-AC	1186.8	1131.5	0.646	0.595	92.1
Pine-AC	778.7	718.6	0.424	0.373	87.9
Acacia-AC	1030.1	973.1	0.562	0.511	90.9
SRF-AC	824.6	732.6	0.539	0.384	71.2
Cellulose-AC	966.0	919.8	0.531	0.484	91.1
Commercial AC	712.8	396.3	0.625	0.204	32.6

S_{BET} : total specific surface area by BET method; S_{MP} : micropore surface area by t-plot method; V_{T} : total pore volume from N_2 uptake at $p/p_0 \sim 0.99$; V_{MP} : micropore volume by t-plot method

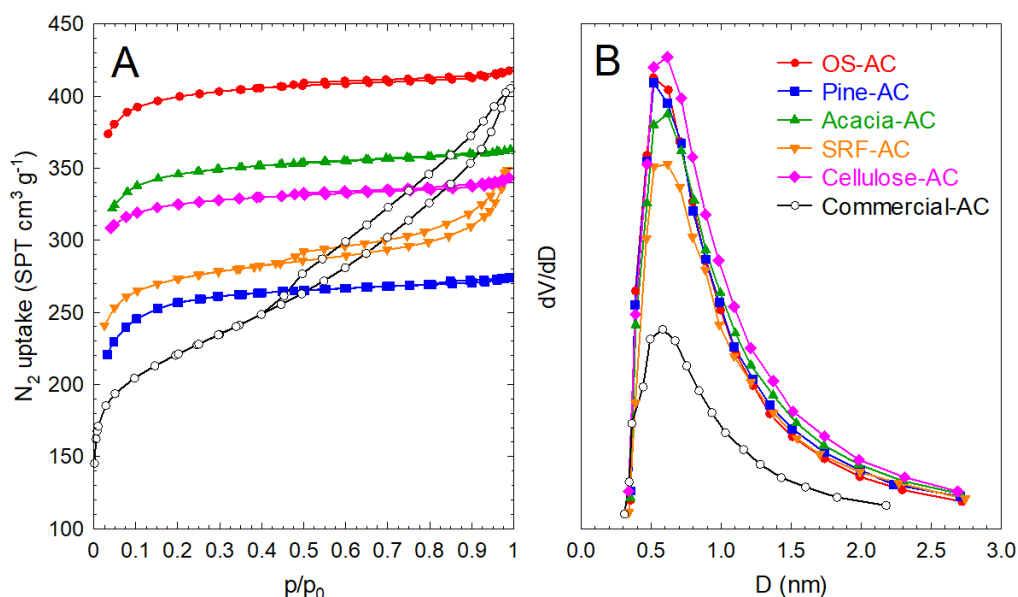


Figure 4.1. N_2 adsorption-desorption isotherms of the industrial chars after activation (A) and micropore size distribution obtained by the HK method from CO_2 adsorption isotherms (B)

The textural morphology of the particles after activation was visually confirmed by SEM micrographs. **Figure 4.2** illustrates a selection of the pictures taken for the five activated chars. The images provide evidence of the porosity developed in the material. Due to the vegetal origin of olive stones, pine, and acacia splinters, the structure of the activated chars still resembles their origin. In the case of olive stone, a porous structure resembling a sponge is envisaged. For pine and acacia, a brick shape is identified in which long organized, and repeated slits are defined. The action of KOH during activation promotes the formation of additional cavities, as observed in the case of pine (**Figure 4.2C**) in which small holes are defined in the lateral wall of the particle, probably during the activation reaction of the organic content of the char and KOH. In the case of Cellulose-AC and SRF-AC, some cavities were also observed. In the case of the plastic cellulose casing, the activated material displayed cavities and holes as the result of a combination of plain surfaces. The SRF-AC was the material with the highest heterogeneity observed. Although a holey morphology is frequently observed, there were also appreciated wrinkled and granulated surfaces.

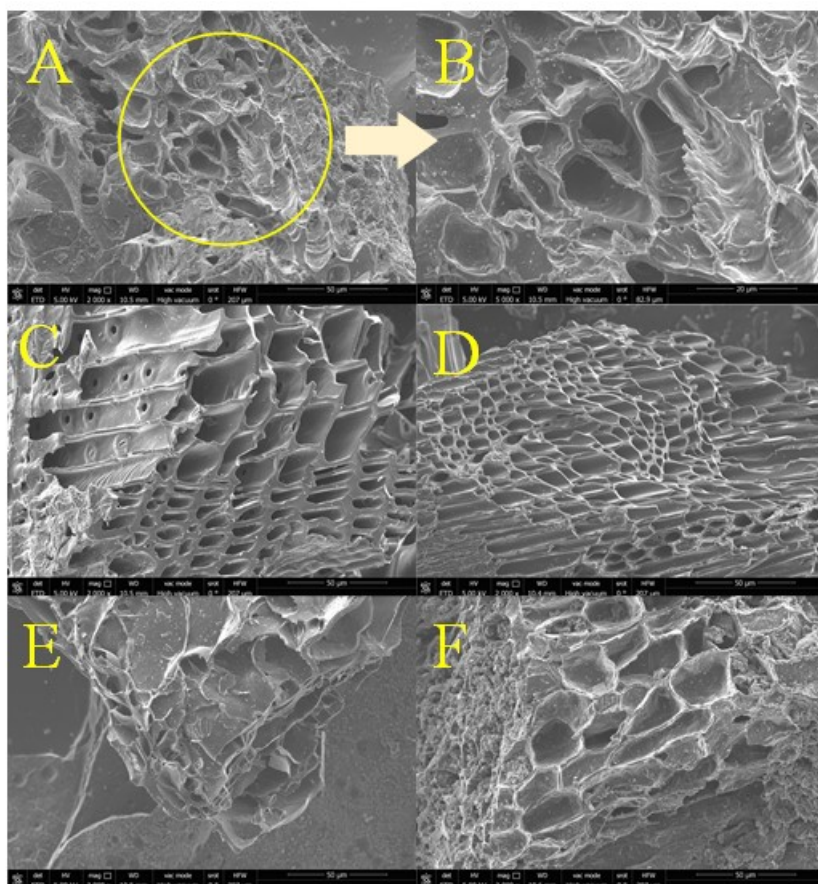


Figure 4.2. SEM pictures of the chars after activation: OS-AC (A and B), Pine-AC (C), Acacia-AC (D), Cellulose-AC (E), and SRF-AC (F)

The results of proximate and elemental analysis are provided in **Table 4.2**. The chars were characterized by a high carbon content in the case of Pine-char, Acacia-char, and Cellulose-char, as they are the result of a pyrolysis process of biomass precursors, leading to over 80 % of carbon content. Pine residues have been reported to lead the formation of char with over 89 % of C [71,72]; acacia wood usually leads to chars with C percentage up to 70 % [73], and in the case of cellulose the C content can reach values close to 90 % [74]. OS-char is frequently reported by a lower carbon content [75] as a consequence of the C percentage of the olive stones, frequently around 50 % [76]. SRF-char also displayed lower C content, due to its complex origin, with an important contribution of inorganic matter as the high ash content suggests. The content of nitrogen, if detected, was low in all the chars except the almost 2 % found in the SRF-char. The oxygen was obtained as the difference in the elemental analysis; leading to considerable percentages in OS-char and SRF-char. However, the high content of ash obtained in these samples suggests an

important content of inorganic matter. In general terms, there is a good relationship between the fixed carbon of proximate analysis and the carbon content obtained by elemental analysis, being the pine-char, acacia-char, and cellulose-char the most carbon enriched. The activation with KOH enriched the carbon content and reduced the ash proportion. KOH has been reported as capable of dissolving ash and other compounds during the activation [77], that were removed during the washing carried out after the activation [78].

Table 4.2. Proximate and elemental analysis of the chars before and after activation

Sample	Proximate analysis (wt. %)				Elemental analysis (wt.%)			
	Moisture	Volatile	Fixed carbon	Ash	N	C	H	O*
OS-char	1.4	12.9	81.4	4.3	0.2	60.3	16.2	19.0
Pine-char	3.1	15.8	77.5	3.6	-	85.9	4.4	6.1
Acacia-char	3.5	14.9	80.1	1.5	0.4	83.5	3.8	10.7
SRF-char	2.7	14.6	52.2	30.5	1.9	61.7	3.4	2.6
Cellulose-char	1.9	14.6	81.4	2.1	-	84.9	3.9	9.1
OS-AC	4.7	8.3	85.0	2.0	-	89.0	0.2	8.9
Pine-AC	3.1	13.0	81.2	2.7	-	84.3	0.3	12.7
Acacia-AC	5.4	11.0	81.9	1.7	0.6	86.4	0.3	11.0
SRF-AC	7.6	9.1	69.5	13.8	0.9	74.8	0.4	10.2
Cellulose-AC	8.9	12.6	78.5	0	0.2	88.6	0.2	11.0
Commercial-AC	0.7	5.3	93.2	0.8	0.1	88.1	0.6	10.4

*Obtained as the difference after removing the ash content

The chemical composition of the surface was assessed by the XPS technique. **Table 4.3** summarizes the results of elemental composition and the characterization of the chemical environment of C, and O, i.e. the nature of the functional groups on the surface. Some differences are stated when comparing the results obtained by XPS and elemental analysis. For instance, the contribution of C is lower in the case of XPS. Bearing in mind the superficial character of the XPS technique, this effect provides evidence of the presence of oxygen groups, concentrated onto the surface. The O percentages provided by XPS were higher than those tentatively estimated by elemental analysis. The chemical nature of the elements at the surface was assessed by deconvolution of the high-resolution XPS spectra. Regarding the C_{1s} spectrum, the following contributions were considered for deconvolution: C=C (284.6 eV), C-C (285.3 eV), C-O (286.6 eV), C=O (288.0 eV), and O=C-OR (289.9

eV) [79]. The O_{1s} region was fitted to quinone (530.7 eV), C=O (531.5–532.0 eV), and C-O (~533 eV) [80]. The N, although detected, was not deconvoluted due to the low proportion at which it appeared. **Table 4.3** also summarizes the elemental composition of the surface of the activated chars. In this table, it can be observed that the carbon content decreased in the order Cellulose-AC > OS-AC ~ Pine-AC > Acacia-AC > SRF-AC. The carbon content varies from the values obtained by elemental analysis; nevertheless, the XPS analysis accounts only superficially, not the whole bulk of the particle as in elemental analysis. The deconvolution analysis of the C_{1s} region is depicted in **Figure 4.3**, in which it can be appreciated a similar distribution of functional groups with some exceptions such as the lack of C-O in OS-AC and Pine-AC or the high proportion of carboxylic groups in Cellulose-AC, Acacia-AC, and OS-AC. However, due to the different content of carbon in each sample, the comparison should be taken with caution. For an accurate evaluation of the percentage of oxygenated carbonaceous groups, the sum of percentages of the area of the peaks regarding oxygenated groups, i.e. C-O, C=O and COO^- , from C_{1s} region was multiplied by the carbon content. According to this calculation (see C_{XPS-Ox} column in **Table 4.3**), the percentages of C_{XPS-Ox} decreased in the order Cellulose-AC > Acacia-AC > OS-AC > Pine-AC ~ SRF-AC. The O_{1s} region was also deconvoluted, considering that the oxygen is linked to carbon exclusively. However, as pointed out in **Table 4.3**, the amount of metal content cannot be considered negligible. These metals are expected to be metal oxides. For this reason, the results of O_{1s} deconvolution (see **Figure 4.3**) are just a mere qualitative comparison between functional groups, out of any feasible quantification. Interestingly, in the case of OS-AC the presence of quinonic groups was not observed. Acacia-AC and Cellulose-AC displayed an equilibrated proportion of quinonic, C-O and C=O groups. In the case of Pine-AC and SRF-AC, the proportion of functional groups was C=O > C-O > quinonic groups.

Table 4.3. Surface chemical composition of the activated chars by XPS

Sample	C _{XPS}	O _{XPS}	N _{XPS} (wt.%)	OthersXPS	C _{1s}			O _{1s}			
					Type	BE (eV)	% Peak	C _{XPS} -O _x (wt.%)	Type	BE (eV)	% Peak
OS-AC	73.9	15.9	3.5	4.0 (Fe) 1.2 (Si) 1.1 (Ca) 0.3 (Zn)	C=C	284.6	47.0	17.1	quinone	530.7	0.0
					C-C	285.2	30.5		C=O	531.7	58.3
					C-O	286.5	0.6		C-O	533.4	41.7
					C=O	287.9	14.1				
					COO-	290.0	8.5				
Pine-AC	71.3	22.4	0.4	2.8 (K) 2.6 (Ca) 0.2 (Si)	C=C	284.6	49.2	15.6	quinone	531.0	9.7
					C-C	285.4	29.2		C=O	531.7	52.3
					C-O	286.6	0.0		C-O	533.5	38.1
					C=O	288.5	21.9				
					COO-	289.9	0.0				
Acacia-AC	67.3	23.2	0.9	3.1 (Fe) 2.4 (Ca) 2.4 (K)	C=C	284.5	58.5	18.0	quinone	531.0	22.1
					C-C	285.2	14.7		C=O	531.8	38.1
					C-O	286.5	8.8		C-O	533.3	39.7
					C=O	288.5	10.0				
					COO-	289.9	8.0				
SRF-AC	48.9	28.1	1.4	7.9 (Si) 4.5 (Fe) 3.5 (Ti) 2.7 (K) 1.5 (P)	C=C	284.5	60.3	15.1	quinone	530.8	12.7
					C-C	285.7	8.7		C=O	532.1	44.3
					C-O	286.5	10.8		C-O	533.0	43.9
					C=O	288.5	15.8				
					COO-	289.9	4.3				
Cellulose-AC	80.6	14.0	0.6	4.4 (Fe) 0.5 (Ca)	C=C	284.5	64.2	21.2	quinone	530.8	23.4
					C-C	285.4	9.5		C=O	532.0	37.9
					C-O	286.2	9.3		C-O	533.4	38.7
					C=O	288.1	6.6				
					COO-	289.5	10.4				
Commercial-AC	94.5	5.5	-	-	C=C	284.6	64.0	24.6	quinone	530.7	10.6
					C-C	285.7	9.9		C=O	532.1	26.3
					C-O	286.4	6.4		C-O	533.5	63.1
					C=O	288.5	5.5				
					COO-	290.0	14.1				

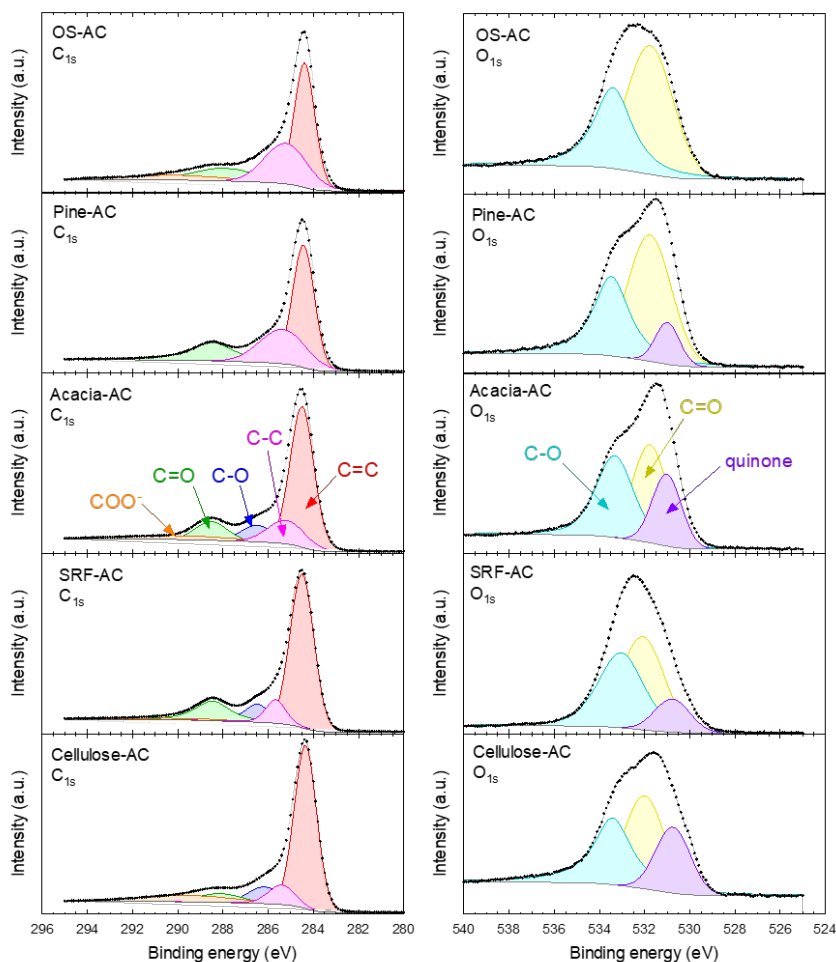


Figure 4.3. XPS deconvolution of the C_{1s} (left) and O_{1s} (right) regions of the activated chars

Adsorption of CO_2

The thermodynamics of CO_2 adsorption was first studied at different pressures up to 100 kPa at two different temperatures, i.e. 0 °C and 25 °C, see the results depicted in **Figure 4.4A**. The continuous growth tendency of the CO_2 uptake until 100 kPa suggests a good fitting to the Freundlich isotherms that lack the definition of a plateau, confirmed by the good correlation coefficient ($R^2 > 0.99$, see results in **Table 4.4**). The Freundlich model is an empirical model that assumes a non-ideal and reversible process of plausible multilayer adsorption on a heterogeneous surface [50], due to the presence of certain heterogeneity in the surface of the material [81]. If the CO_2 uptake at the two temperatures is compared, an exothermic behavior is

deduced since the increase in the temperature led to a decrease in the CO₂ uptake. The Freundlich constant (K_F) decreased with the temperature due to the exothermic nature; and the exponent was higher than the unit in all the cases, which is characteristic of a physisorption process [82]. The efficiency in terms of CO₂ uptake followed the order Cellulose-AC > Acacia-AC ~ Pine-AC > OS-AC > SRF-AC. According to the pore size distribution, all the samples depicted the same HK profile, with no difference among the micropore size most abundant (0.5-0.7 nm). The differences among the samples may originate from the micropore volume and the presence of oxygenated functional groups able to capture CO₂ molecules. The presence of oxygenated groups, specifically carboxyl and hydroxyl, plays an important role in promoting the adsorption performance due to the predominant interaction by electrostatic interaction [83,84]. According to the characterization by XPS, those materials with the highest CO₂ uptake displayed an important presence of carboxylic groups in the C_{1s} spectra.

Table 4.4. Freundlich parameters of CO₂ adsorption, CO₂/N₂ selectivity at 25 °C, and isosteric adsorption heat

Sample	T (°C)	Freundlich isotherm			q _{CO2} (mg g ⁻¹) at 1 bar	CO ₂ /N ₂ Selectivity ² (%)	-ΔH _{ads} ³ (kJ mol ⁻¹)
		q _{CO2} = K _F p ^{1/n_F}					
		K _F ¹	n _F	R ²			
OS-AC	0	15.64	1.901	0.994	176.3	13.5	21.5
	25	7.04	1.628	0.997	119.1		
Pine-AC	0	14.79	1.828	0.997	183.7	13.3	18.7
	25	7.98	1.672	0.998	125.4		
Acacia-AC	0	12.35	1.688	0.998	189.0	11.1	20.0
	25	6.01	1.501	0.998	129.2		
SRF-AC	0	10.36	1.663	0.997	165.2	22.7	19.4
	25	5.03	1.508	0.998	106.6		
Cellulose-AC	0	15.07	1.747	0.997	210.3	25.6	19.8
	25	7.51	1.554	0.998	145.4		
Commercial-AC	0	12.23	1.977	0.997	125.6	1.3	12.6
	25	5.40	1.682	0.998	83.4		

¹ K_F in mg g⁻¹ kPa^{- n_F} .

²Selectivity obtained at 25 °C.

³Isosteric adsorption heat at $q_{CO_2} = 100$ mg g⁻¹

Similar CO₂ capacities at room temperature (25°C) have been reported in the literature with chars activated with KOH [85], although the comparison should be taken with caution since the experimental procedure of the activated carbon may vary on the activation temperature or the KOH-char ratio. Olive stone has been the most widely biochar studied to date, with CO₂ uptakes of 88 mg g⁻¹ [86], 110 mg g⁻¹ [87] and 123 mg g⁻¹ [88]. In the case of pine, pyrolyzed slash pine led to a CO₂ uptake of 136 mg g⁻¹ [89]. For pine, also a higher value has been reported, i.e. 220 mg g⁻¹, over twice the obtained in this work (91 mg g⁻¹), probably due to the higher micropore volume achieved as a consequence of the KOH-char ratio (2:1), higher than the used in this work (1:1) [90].

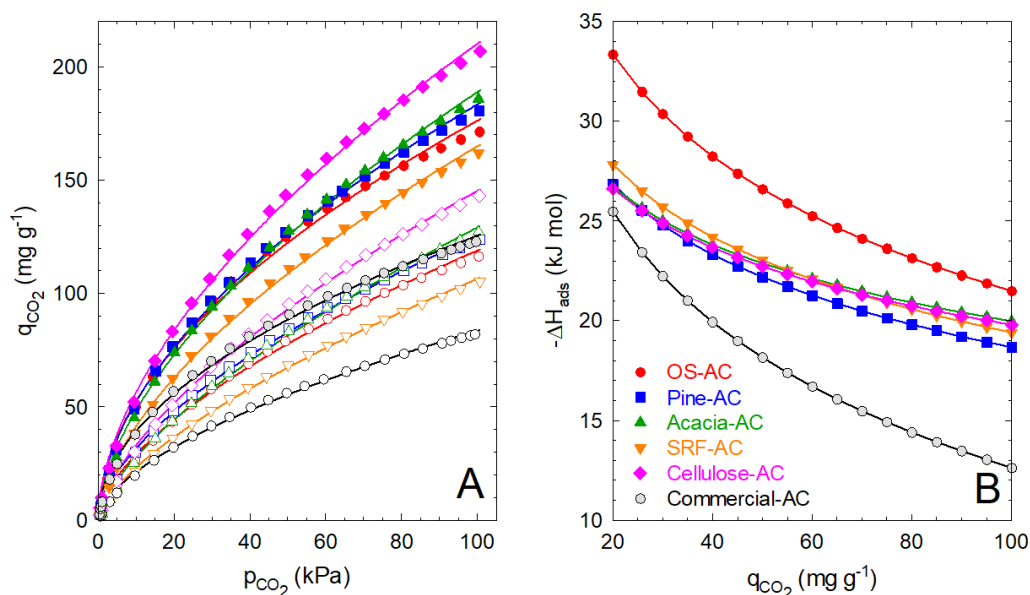


Figure 4.4. (A) CO₂ adsorption isotherms at different pressures at 0 °C (filled symbols) and 25 °C (empty symbols). (B) Isosteric heat of adsorption (ΔH_{ads})

The isosteric heat of adsorption was estimated with the Clausius-Clapeyron equation, and the results are illustrated in **Figure 4.4B**. This figure shows that all the activated chars defined a decreasing isosteric heat of adsorption with the coverage degree of adsorbed CO₂. This common response is associated with the heterogeneity of the surface that entails a preferable linkage to certain active sites, leading to higher exothermicity than the rest. This response is a direct consequence of the good fitting to the Freundlich model, which considers that the adsorption energy logarithmically decreases with the degree of coverage of active sites [81]. Considering a coverage of 100 mg CO₂ g⁻¹ the obtained values are within 18.7–21.5 kJ mol⁻¹. Since values below 40 kJ mol⁻¹ are considered physisorption, and values over 80 kJ mol⁻¹ are considered strong enough to be chemisorption [91], the adsorption CO₂ process with the activated char takes place via physisorption. All

the samples displayed a very similar profile for the isosteric heat, except for OS-char which defined a curve moved to higher values, but still at low values and considered as physisorption. The commercial-AC performed the weakest interaction with CO₂ molecule.

Regarding the selectivity of the process in CO₂-N₂ mixtures, as displayed in **Table 4.4**, the values are within 10-17, Acacia-AC > SRF-AC > Pine-AC > Cellulose-AC > OS-AC. The values obtained among the samples are quite similar in the same order of magnitude.

The CO₂ adsorption onto the chars before and after activation was assessed by thermogravimetric analysis, see **Figure 4.5A**. The non-activated char performed a moderate CO₂ uptake, within 13.3 mg g⁻¹ (SRF-char) and 44.1 mg g⁻¹ (OS-char). After activation, the adsorbed CO₂ uptake was increased 2-3 times, depending on the material, giving CO₂ uptakes of within 76.8 mg g⁻¹ (SRF-AC) and 129.8 mg g⁻¹ (Cellulose-AC). These values are slightly lower than the obtained in the physisorption isotherms for the pressure of ~1 bar, probably due to the gas diffusional limitations inside the crucible during the assay carried out in the thermobalance if compared to a gas pycnometer device as used for the construction of the CO₂ isotherm [92,93]. Furthermore, the lack of vacuum in the analysis, and the plausible adsorption of N₂, although limited due to the high selectivity to CO₂, may contribute to further explain the differences.

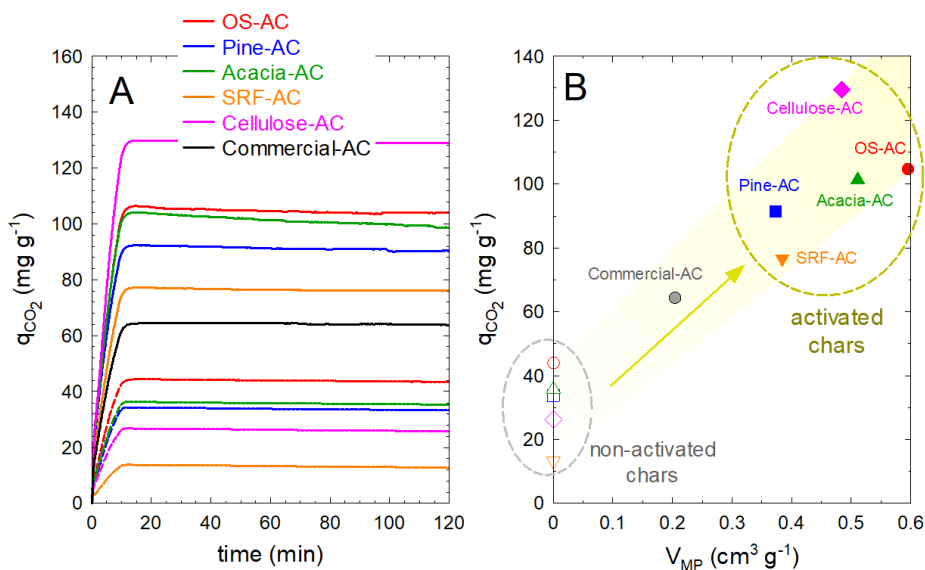


Figure 4.5. (A) Temporal evolution of adsorbed CO₂ with the industrial chars before (dashed line) and after activation (solid line). (B) Relationship between the CO₂ uptake (thermobalance) and the microporous volume

As shown in **Figure 4.5A**, the CO₂ adsorption kinetics described a rapid process in a short time with no induction period. The kinetics of the process were studied by fitting the temporal data to pseudo-empirical models [54]. Due to the physisorption nature of the process [55,94], Lagergren's pseudo-first order and the fractal Avrami version were those which best described the experimental data, see results in **Table 4.5**. The Avrami model slightly improved the fitting values of R². The rate constants of all the chars were within 0.20-0.25 min⁻¹ either before or after activation. These values are similar to the already reported for the adsorption of CO₂ onto carbonaceous microporous materials, whose pseudo-first order kinetic values are within 0.10-0.30 min⁻¹ [56,95–97]. That suggests a lack of influence of the microporosity developed onto the kinetics of the process, affecting only the saturation value, i.e. the thermodynamics.

Table 4.5. Kinetic model parameters of CO₂ adsorption with the industrial chars before and after activation

Sample	Pseudo-first order			Avrami			
	$q_{CO_2} = q_1(1 - e^{-k_1 t})$			$q_{CO_2} = q_A(1 - e^{-(k_A t)^{n_A}})$			
	q_1	k_1	R ²	q_A	k_A	n_A	R ²
	(mg g ⁻¹)	(min ⁻¹)		(mg g ⁻¹)	(min ⁻¹)		
OS-char	44.1	0.228	0.978	44.0	0.215	1.266	0.988
Pine-char	33.9	0.239	0.973	33.8	0.225	1.274	0.984
Acacia-char	35.9	0.243	0.975	35.8	0.230	1.226	0.983
SRF-char	13.3	0.247	0.944	13.3	0.227	1.339	0.960
Cellulose-char	26.4	0.251	0.970	26.3	0.238	1.203	0.977
OS-AC	104.9	0.231	0.976	104.8	0.218	1.242	0.984
Pine-AC	91.5	0.247	0.979	91.4	0.238	1.149	0.983
Acacia-AC	101.6	0.246	0.964	101.4	0.231	1.241	0.973
SRF-AC	76.7	0.230	0.979	76.6	0.219	1.213	0.986
Cellulose-AC	129.8	0.213	0.978	129.5	0.201	1.315	0.990
Commercial-AC	64.5	0.227	0.985	64.4	0.220	1.158	0.989

q_1 and q_A (mg g⁻¹) are the adsorption at saturation conditions; k_1 (min⁻¹) and k_A (min⁻¹) are the pseudo-first order and Avrami rate constants

The improved adsorption performance after activation can be explained based on the textural properties created. The adsorption efficiency of CO₂ has been strongly correlated to the microporosity developed in the material [98,99] although it depends also on the nature of the functional groups present on the surface [100].

It has been reported that activated carbons enriched with micropores, especially pores with diameters inferior to 1 nm were found to show a high CO₂ uptake [46]. The presence of micropores favors the diffusion of CO₂ in the materials, improving the kinetics of the process [101]. **Figure 4.5B** shows the relationship between the CO₂ uptake and the micropore volume, reflecting a proportional effect between the two variables. The sample with the lowest CO₂ uptake, that is the SRF-AC, also led to the less developed microporosity percentage, 71 %, whereas the rest of the chars displayed around 90 %. The commercial-AC also follows the relationship between CO₂ uptake and the microporosity, with only a ~64 mg g⁻¹ of CO₂ were captured due to the low ~33 % of micropores present in the sample.

The greater performance of activated carbons has not only been attributed to textural properties such as the presence of larger micropore volume and the presence of narrow micropores but also to the chemistry of the surface, i.e. the presence of oxygenated functional groups [102]. Although **Figure 4.5B** suggests a certain correlation between the CO₂ uptake and the number of micropores, especially when comparing the chars before and after activation, it does not fully explain why Cellulose-AC outstands from the rest, because the micropore volume is slightly higher in the case of Acacia-AC and OS-AC, which provided less adsorption capacity towards CO₂. For that reason, it was studied a plausible relationship between the oxygenated groups on the surface and the CO₂ uptake. **Figure 4.6** illustrates this relationship considering the amount of C_{XPS} that is linked to oxygen as calculated from the C_{1s} region (see C_{XPS}-Ox column in **Table 4.3**). As appreciated in this figure, there is a good linear correlation between the two variables ($R^2=0.97$), explaining the CO₂ uptake among the samples. Therefore, it is proved that, besides the microporosity developed, the presence of oxygenated carbon groups also plays a crucial role in the CO₂ uptake. This fact has been reported in the literature previously, in which the raise of oxygenated groups in carbon materials has been objective to enhance the efficiency of the material [103]. For instance, the modification of commercial coconut shell-activated carbon aimed at the raise of oxygenated groups has been demonstrated to be efficient in raising the CO₂ uptake, suggesting that the process entails the adsorption within the pores and adsorption onto the oxygen-containing functional groups [83].

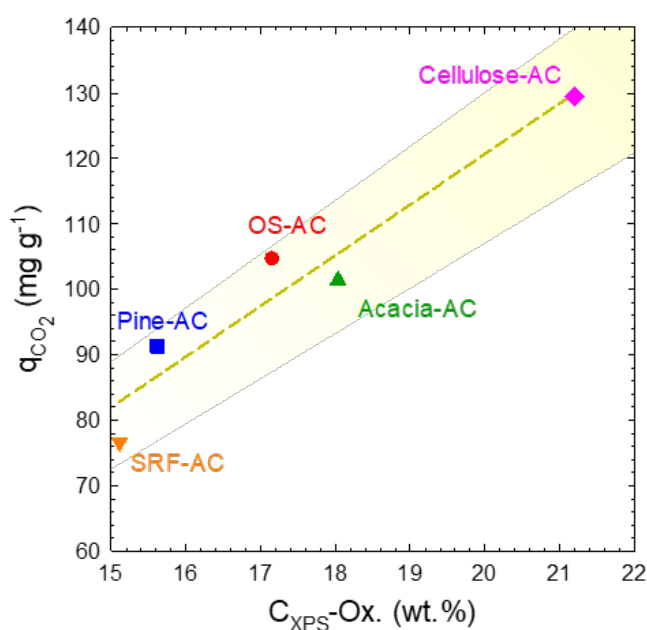


Figure 4.6. Relationship between the CO₂ uptake (thermobalance) and the amount of superficial carbon accounting for oxygenated groups ($C_{XPS-Ox.}$).

Adsorption of aqueous heavy metals in water

The activated chars were also tested for the removal of heavy metals, i.e. Pb^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} , and Cu^{2+} . The experimental data were fitted to diverse models available in the literature [61], such as the classic models of two-parameters, i.e. Freundlich [50] and Langmuir [62], or the three-parameter models such as the of Sips [63], which provided the best adjustment.

The adsorption isotherms are illustrated in **Figure 4.7**. In general terms, comparing the adsorption uptake, regarding the metal the order observed was $Pb^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$. It should be highlighted that in the case of Ni^{2+} , the saturation plateau was not reached. If the different activated chars are compared, it can be stated in general terms that the efficiency followed the order Pine-AC > Acacia-AC > SRF-AC > Cellulose-AC > OS-AC. The adsorption isotherms were fitted to diverse models, giving a better fitting of the three-parameter models, such as the Sips (see results in **Table 4.6**), than the two-parameter models of Langmuir or Freundlich. Except for Ni^{2+} , the adsorption reaches a stable plateau and the saturation adsorption uptake could be obtained. For Ni^{2+} , the Sips model extrapolates outside the experimental conditions tested. The adsorption of heavy metals takes place over the mesopores [104]. This may explain why the char with the lowest microporosity proportion gave the highest metal adsorption uptake

regardless of the type of metal. The presence of mesopores is important but not the only requirement for good adsorption performance. The mechanism of adsorption of metals takes place by electrostatic interaction, ion exchange between metal cations and H^+ ions present in acidic groups, and interaction with the oxygenated surface groups, mainly [105].

In general terms, the metal uptake was lower than the reported values available in the literature [105]. There are numerous examples of biochars with higher adsorption uptake of diverse metals before than after chemical activation [106]. The development of microporosity and modification of the functional groups of the surface may result in the detriment of the adsorption performance. The presence of mesoporosity and high electrostatic charge results in decisive efficiency [107]. The use of apricot stone after activation with H_2SO_4 has reported a Pb uptake of 21.4 mg g^{-1} [104], close to the 27 registered by Pine AC. Apple pulp was activated with $ZnCl_2$ and capable of capturing 10.5 mg g^{-1} of Pb^{2+} and 9.3 mg g^{-1} of Zn^{2+} [106].

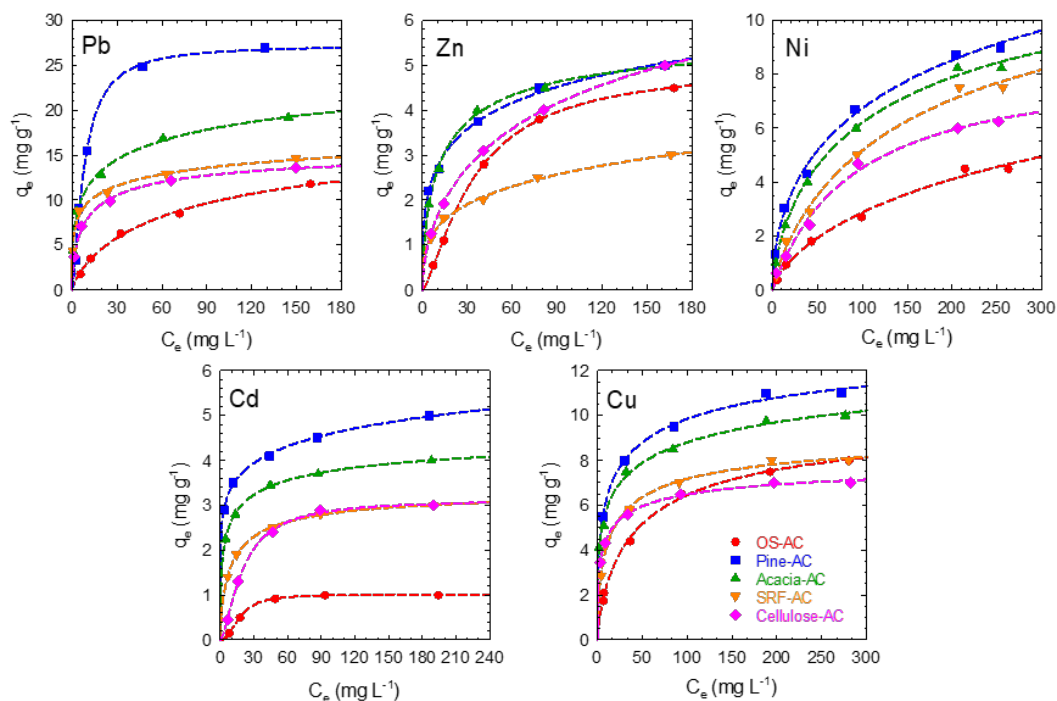


Figure 4.7. Metal adsorption isotherms with the activated chars. The dashed lines represent the fitting to the Sips model. Experimental conditions: $C_{\text{metal},0}=5\text{-}300 \text{ mg L}^{-1}$; $C_{\text{adsorbent}}=2.0 \text{ g L}^{-1}$; $T=20^\circ\text{C}$

Table 4.6. Fitting parameters of metal isotherms to the Sips model

Metal	Sips parameters	Activated char				
		OS-AC	Pine-AC	Acacia-AC	SRF-AC	Cellulose-AC
Pb ²⁺	q _s	18.91	27.31	23.46	23.58	16.34
	K _s	1.16·10 ⁻²	1.24·10 ⁻¹	1.60·10 ⁻²	2.99·10 ⁻²	8.88·10 ⁻²
	n _s	0.782	1.394	0.363	0.310	0.607
	R ²	0.996	0.992	0.996	0.994	0.994
Zn ²⁺	q _s	5.02	11.02	5.89	12.24	10.01
	K _s	2.88·10 ⁻²	3.77·10 ⁻³	7.54·10 ⁻²	2.06·10 ⁻⁴	6.15·10 ⁻³
	n _s	1.375	0.335	0.678	0.333	0.583
	R ²	0.999	0.994	0.998	0.995	0.999
Ni ²⁺	q _s	12.51	20.47	14.05	13.48	8.64
	K _s	1.84·10 ⁻³	2.67·10 ⁻³	7.15·10 ⁻³	5.63·10 ⁻³	1.10·10 ⁻²
	n _s	0.715	0.539	0.696	0.823	0.994
	R ²	0.992	0.995	0.997	0.993	0.991
Cd ²⁺	q _s	1.01	21.70	4.94	3.40	3.13
	K _s	5.75·10 ⁻²	2.95·10 ⁻⁶	1.43·10 ⁻¹	9.63·10 ⁻²	5.01·10 ⁻²
	n _s	2.259	0.161	0.440	0.703	1.504
	R ²	0.999	0.998	0.999	0.999	0.998
Cu ²⁺	q _s	10.10	15.11	15.90	9.51	8.46
	K _s	2.10·10 ⁻²	4.39·10 ⁻²	1.90·10 ⁻²	6.34·10 ⁻²	1.31·10 ⁻¹
	n _s	0.762	0.422	0.334	0.605	0.131
	R ²	0.998	0.994	0.993	0.993	0.459

q_e (mg g^{-1}) refers to the amount of adsorbed metal at equilibrium; C_e (mg L^{-1}) is the solute concentration at equilibrium; q_s (mg g^{-1}) is the adsorption capacity of Sips model; K_s (L mg^{-1}) is the Sips constant; and n_s (dimensionless) means the exponent of the Sips model.

Adsorption of aqueous contaminants of emerging concern

The adsorption of the activated chars was evaluated by selecting three organic contaminants of emerging concern due to their high occurrence in wastewater, such as acetaminophen, caffeine, and diclofenac. The adsorption isotherms are plotted in **Figure 4.8**. In many cases a stable value plateau was reached, enabling the estimation of the saturation capacity. Among the vast number of isotherms models available in the literature [61], the data was fitted to the classic models such as the two-parameter Freundlich [50] and Langmuir [62] and the three-parameter model of Sips [63]. The best fitting was achieved with the Sips model (see **Table 4.7**), probably due to its hybrid character, suitable for the prediction of the adsorption behavior of the heterogeneous surface, and avoiding the restriction of the increasing concentration of adsorbate that Freundlich isotherm supposes [61]. **Figure 4.8** depicts the high adsorption capacity of the activated materials. There are no observed great differences among the contaminants tested is the saturation adsorption uptake if visually compared in **Figure 4.8**, being the saturation uptake in all the materials with the three selected pollutants within roughly 200-500 mg g^{-1} , according to the experimental interval of conditions studied. It is observed the same behavior when comparing the adsorbents with the three pollutants. The Pine-AC displayed less saturation uptake, i.e. 200-250 mg g^{-1} in the interval of C_e studied. The activated char most active was OS-AC, with a performance of briefly 400-500 mg g^{-1} . The other three activated char, i.e. Acacia-AC, SRF-AC, and Cellulose-AC, described an intermediate adsorption uptake, with isotherms profiles very similar among them in the case of CAF and DCF, and more differentiated with ACE. The adsorption mechanism of CECs onto activated carbon materials involves hydrogen bonding, hydrophobic and electrostatic interactions between the adsorbate molecule and the surface of the activated material [108]. The sample OS-char, which performed the highest surface area and a moderate presence of oxygenated groups, led to the highest CECs uptake which suggests that well-developed textural properties are decisive for the CECs retention.

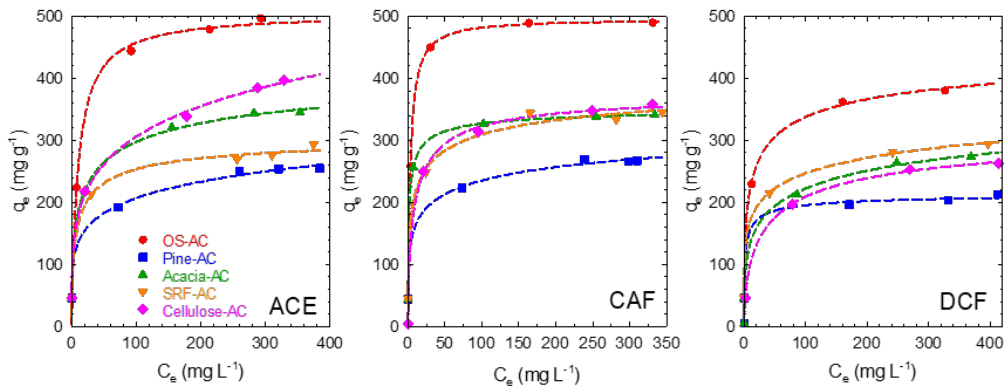


Figure 4.8. Adsorption isotherms with the activated chars with acetaminophen (ACE), caffeine (CAF), and diclofenac (DCF). The dashed lines represent the fitting to the Sips model. Experimental conditions: $C_{CEC,0}=10\text{--}500\text{ mg L}^{-1}$; $C_{\text{adsorbent}}=0.4\text{--}2.0\text{ g}\cdot\text{L}^{-1}$; $T=20\text{ }^{\circ}\text{C}$

Table 4.7. Fitting parameters of CECs isotherms to the Sips model

CEC	Sips parameters	Activated char				
		OS-AC	Pine-AC	Acacia-AC	SRF-AC	Cellulose-AC
ACE	q_s	506.05	956.29	459.90	314.53	1328.41
	K_k	$1.02\cdot 10^{-1}$	$3.35\cdot 10^{-5}$	$3.99\cdot 10^{-2}$	$1.13\cdot 10^{-1}$	$1.48\cdot 10^{-4}$
	n_s	0.966	0.226	0.437	0.588	0.287
	R^2	0.998	0.997	0.999	0.996	0.999
CAF	q_s	496.24	421.61	356.84	433.54	381.51
	K_s	$3.24\cdot 10^{-1}$	$2.14\cdot 10^{-2}$	$7.35\cdot 10^{-1}$	$9.73\cdot 10^{-2}$	$1.14\cdot 10^{-1}$
	n_s	1.005	0.305	0.557	0.402	0.699
	R^2	0.999	0.998	0.999	0.994	0.999
DCF	q_s	482.35	217.77	471.76	559.98	330.76
	K_s	$7.00\cdot 10^{-2}$	$5.43\cdot 10^{-1}$	$7.19\cdot 10^{-3}$	$3.97\cdot 10^{-3}$	$2.46\cdot 10^{-2}$
	n_s	0.435	0.544	0.350	0.258	0.602
	R^2	0.996	0.997	0.997	0.999	0.999

q_e (mg g^{-1}) refers to the amount of meal adsorbed at equilibrium; C_e (mg L^{-1}) is the solute concentration at equilibrium; q_s (mg g^{-1}) is the adsorption capacity of Sips model; K_s (L mg^{-1}) is the Sips constant; and n_s (dimensionless) means the exponent of the Sips model.

The sample OS-char performed the highest value of contaminant uptake at saturation conditions within the interval of equilibria concentration studied. This value is very competitive if compared to the reported values in the literature for similar biochar precursors activated with KOH. For instance, using durian seed it has been reported a maximum ACE adsorption capacity of 304 mg g^{-1} [109] or 330 mg g^{-1} after activation of Jatoba bark [110]. A value in the same order as the OS-AC of this work has been reported with tree Bark residues, 571 mg g^{-1} [111]. This work

also demonstrated that KOH displayed as an activating agent better textural properties and adsorption ability than ZnCl_2 (411 mg g^{-1}), ZnSO_4 (363 mg g^{-1}), and MgCl_2 (222 mg g^{-1}) [111]. Other activated carbons prepared with different chemical agents have provided good adsorption capacities, such 118 mg g^{-1} using as precursor orange peels with (activation with ZnCl_2) [112], 300 mg g^{-1} with lignin (activation with FeCl_3) [113], 200 mg g^{-1} with cork powder (activation with K_2CO_3) [114], 435 mg g^{-1} with pine wood (activation with K_2CO_3) [115], 204 mg g^{-1} with peach stones (activation with K_2CO_3) [114] or 113 mg g^{-1} with polyethylene terephthalate (activation with K_2CO_3) [114]. A commercial formula has reported a saturation capacity of 245 mg g^{-1} (Filtrisorb-400 from Chemvtron) [116], 117 mg g^{-1} (Norit PK 1-3) [116] or 221 mg g^{-1} [117]. All the activated chars prepared in this study improved the adsorption uptake of this commercial formula.

Regarding the maximum uptake reached for CAF, 496 mg g^{-1} , with OS-AC. Spent coffee capsules were activated with KOH and led to a CAF maximum uptake of 315 mg g^{-1} [118]. Plastic waste activated with KOH has reported 351 mg g^{-1} of CAF saturation capacity [119]. Regarding alternative activating agents, K_2CO_3 with pine wood led to 500 mg g^{-1} [115], 177 mg g^{-1} using açai seed activated with K_2CO_3 [120], 296 mg g^{-1} with residue from the biofuel production after treatment with K_2CO_3 [121], $260\text{--}270 \text{ mg g}^{-1}$ for peach stones activated with H_3PO_4 [122], 367 mg g^{-1} with grape stalks after H_3PO_4 activation [123], pineapple leaves were activated with H_3PO_4 and led to 155 mg g^{-1} [124], or 118 mg g^{-1} with macrophytes plants activated with CO_2 [125]. Commercial formulas have provided maximum CAF uptakes of 270 mg g^{-1} (Calgon Filtrasorb 400) [126].

In the case of DCF, the maximum uptake of the OS-AC is estimated, according to **Figure 4.9**, almost 500 mg g^{-1} . This value is very competitive if compared to other activated carbonaceous materials prepared from biochars which usually provide low DCF uptakes [127]. Some exceptions are the use of sugar cane bagasse activated with ZnCl_2 which displayed a DCF uptake of 315 mg g^{-1} [128], the activation of Sycamore balls with ZnCl_2 and uptake of 179 mg g^{-1} [129], or the activation of sunflower seed with H_3PO_4 which reported an extraordinarily high DCF maximum uptake of 690 mg g^{-1} , attributed to the surface $-\text{P}_2\text{O}_7$, and $-\text{COOH}$ groups and acidity [130]. A study using tea waste as carbon precursor, and different chemical agents for the activation led to DCF adsorption capacities below 100 mg g^{-1} , i.e. 81 mg g^{-1} (ZnCl_2), 82 mg g^{-1} (K_2CO_3), and 75 mg g^{-1} (KOH) [131]. Commercial formulas have provided much lower DCF uptake than any of the prepared activated carbon. For instance, WG-12 (Gryfskand, Poland), F-300 (Chemvtron Carbon), and ROW 08 Supra (Norit) have led to DCF uptakes of, respectively, 89 mg g^{-1} , 108 mg g^{-1} and 90 mg g^{-1} [132].

The kinetics of the adsorption process of the CECs over the activated chars was studied due to the paramount importance of the selection of the retention time at

real scale-up applications. As the adsorption behavior of the three selected CECs was very similar to the activated chars, ACE was selected for the study of the kinetics of the process, aimed at the comparison among the materials rather than the behavior with other contaminants. **Figure 4.9** illustrates the temporal evolution of the ACE uptake over the five activated chars. As observed, the adsorption process of ACE is very fast, reaching the maximum adsorption capacity of roughly 10 min. Noteworthy, it should be mentioned that the sample at 120 min did not display any detectable peak in the HPLC. The kinetics of the process were modeled to diverse models, such as Lagergren's pseudo-first order, Ho's pseudo-second order, intraparticle diffusion, or Elovich's diffusional model [51,133]. It was the pseudo-second order that led to the best fitting of the experimental data. The results are shown in **Table 4.8**. The driving force assumed by the pseudo-second order model provided the best fitting. The comparison of the k_2 -values confirmed that the kinetics was faster according to the order Cellulose-AC > SRF-AC > Pine-AC ~ Acacia-AC > OS-AC. This kinetic constant value, although affected by diffusional effects related to the design of the crucible, was compared to the reported in the literature. The Cellulose-AC displayed a second-order rate constant, $k_2=5.127 \cdot 10^{-1} \text{ mg}^{-1} \text{ g min}^{-1}$, a high value if compared to the reported in the literature. Similar kinetics have been described with commercial formulas of activated carbon [134] or considerably faster than other carbonaceous materials under research such as activated carbon prepared from the activation of lignin char with FeCl_3 [113,135].

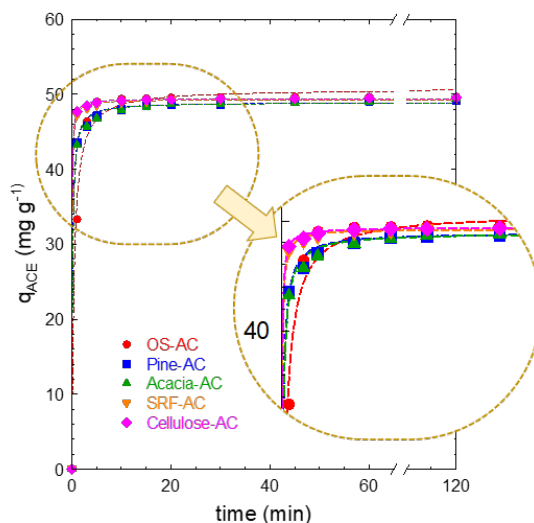


Figure 4.9. Kinetic adsorption of ACE onto the activated chars. The dashed lines represent the fittings to the pseudo-second order model. Experimental conditions: $C_{ACE,0}=100 \text{ mg L}^{-1}$; $C_{adsorbent}=2.0 \text{ g L}^{-1}$; $T=25 \text{ }^{\circ}\text{C}$

Table 4.8. Adsorption kinetics of ACE with the activated chars. The dashed lines represent the fittings to the pseudo-second order model. Experimental conditions as shown in Figure 4.9

Sample	$q_{ACE} = \frac{k_2 q_2^2 t}{1 + k_2 q_2 t}$		
	q_2	$k_2 \cdot 10^2$	R^2
OS-AC	50.7	4.53	0.992
Pine-AC	48.9	14.96	0.982
Acacia-AC	48.9	13.97	0.999
SRF-AC	49.3	42.50	0.999
Cellulose-AC	49.4	51.27	0.999

q_2 (mg g⁻¹) refers to the amount of ACE adsorbed at equilibrium; k_2 (mg⁻¹ g min⁻¹) is the Sips constant, and n_s (dimensionless) means the exponent of the Sips model.

4.1.1.5. Conclusions

The activation of chars obtained from agroforestry and industrial activities possess interesting properties that make them good candidates for the preparation of activated carbons. Thus, it is given a solution for a residue currently produced in diverse pyrolysis factories. The valorization of this carbon-enriched residue through chemical activation led to the production of highly microporous materials which display diverse potential applications in the depuration of gas and liquid effluents.

Considering the adsorption of CO₂, the overall adsorption uptake was explained in terms of the microporosity developed after the activation with KOH, which led to carbonaceous solids in which over 80 % of the pore volume accounts as micropore (most frequent size around 0.5 nm). Not only does the presence of narrow micropores enhance the performance of CO₂ adsorption, but also the surface chemistry, i.e. the oxygen-containing function, which explains the adsorption performance among the activated chars. The higher the content of oxygenated groups, the larger the CO₂ uptake.

Regarding the efficiency of the adsorption of heavy metals, it was observed a moderate adsorption capacity, due to the limited presence of mesopores. Hence, the best performance was recorded for the removal of Pb, saturation uptake ~20 mg g⁻¹. Better results were achieved in the adsorption of organic contaminants of emerging concern, i.e. acetaminophen, caffeine, and diclofenac. Depending on the nature of the char activated the contaminant uptake was within 200-500 mg g⁻¹, which makes them very competitive for a real application. More interestingly, the kinetics of the process was described as a pseudo-second order process with fast kinetics which enables them for a real practical alternative.

As a future outlook, further investigation of the activation process at a larger scale close to industrial production should be conducted, validating the results already obtained at a lab scale. Moreover, detailed research should be conducted to address the regeneration of the spent adsorbent after submitted to an aqueous application.

Acknowledgments

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4.1.1.6. References

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4.2. Liquid and gas effluent treatment: physical activation

4.2.1. Paper 5: On the physical activation of biomass and urban waste chars for water treatment and CO₂ adsorption

Submitted to publication

Ledicia Pereira, Mónica Calero, Gabriel Blázquez, Sergio González-Egido,
María González-Lucas, M. Ángeles Martín-Lara, Rafael R. Solís

4.2.1.1. *Abstract*

Different industrial chars, a subproduct result of the valorization of agroforestry, urban, and industrial residues by pyrolysis, were valorized using them as carbon precursors of activated carbons. The char derived from olive stones, acacia, pine residues, artificial cellulose, and spent recovered fuel (SRF, mixed urban waste, paper, and plastics) were submitted to physical activation with CO₂ (800°C and 1 h). The activation led to materials with moderate surface area, i.e. 340-370 m² g⁻¹, except for the SRF (136 m² g⁻¹), and high micropores contribution (up to 83 % with olive stones). The chemical composition was characterized by elemental analysis, X-ray photoelectron spectroscopy, and ammonia temperature programmed desorption, which corroborated the presence of carbonyl and quinone groups. The activated samples were efficient in the adsorption of CO₂ from post-combustion gases (maximum uptake, 121 mg g⁻¹ at 273 K and 100 kPa), strongly dependent on the micropore's contribution. The best sample displayed stable CO₂ uptake in dynamic cycles of adsorption-desorption. The activated samples were also evaluated as potential candidates for adsorption in lead and caffeine water decontamination. The best Pb uptake was obtained with the activated SRF char (25.5 mg g⁻¹) whereas the best result in caffeine removal was reported by the activated char of pine (17.1 mg g⁻¹). Dynamic assays of Pb and caffeine adsorption in fixed-bed columns demonstrated stable adsorption and regeneration after the first cycle of stabilization. Overall, the achieved results suggest that physical activation with CO₂ is suitable for activating chars with environmental applications.

Keywords: physical activation; char; water treatment; CO₂ adsorption; waste recovery

4.2.1.2. *Introduction*

The ceaseless growth of population and the associated economic development to human beings embrace diverse drawbacks such as natural resources sought, the release of incessant polluting emissions, and the generation of wastes, among them, urban wastes that without alternative are landfilled [1]. The deep concern of current societies about sustainable development and migration from carbon-based energy

sources has been manifested internationally with diverse agreements signed under the United Nations negotiations.

The European Union is devoted to tackling more sustainable solid waste management based on a circular economy, minimizing landfilled residues [2]. In this sense, those residues that are not suitable for physical recycling are eligible for chemical valorization [3]. Pyrolysis is an irreversible thermochemical transformation of carbon-enriched precursors at high temperatures (500-700°C) under an oxygen-free atmosphere, promoting the lysis of larger chains which triggers the formation of an oil, a syngas, and a solid residue named char [4]. The operational conditions, mainly temperature, holding time, heating rate, and inert gas flow rate, define the yield and nature of each fraction. Although the valorization purpose is mainly focused on the maximization of oil and syngas phases, the applications for the char are still not well addressed, especially in those cases in which the residue comes from plastic or urban waste residues.

The chars obtained during thermochemical methods display poor textural properties [5,6]. For that reason, post-activation methods are required, in which physical and chemical activation can be stated [7]. Although chemical activation has been stated as the most effective to boost textural properties, the impact of chemical substances, their hazard, and the further compulsory washing steps to remove the non-reacted chemicals compromise the cost and the environmental impact [8]. Although more responsible activation agents may alleviate some concerns [9], physical activation emerges as a plausible alternative. Physical activation relies on the thermochemical transformation at high temperatures, i.e. 700-900°C, in the presence of reactive conditions, water, or CO₂ steam [10]. Between them, CO₂ has been widely used due to its higher ability to develop micropores whereas H₂O steam triggers the formation of larger mesopores [11]. For carbon capture and utilization applications, microporosity is largely preferred [12]. During the activation process, volatile substances are released and occluded pores in the original char are opened and connected with others. Moreover, the gasification reactions of CO₂, which selectively react with the most reactive carbon, widen the microporosity of the surface [13]. Multiple biomass-based biochars have been activated with CO₂ previously in the literature, including diverse residues of agroforestry activities [14].

Anthropogenic CO₂ emissions are one of the biggest challenges that humans face [15]. Carbon-based materials with a well-developed porosity can be potential candidates for carbon capture and storage. The advantages they display overcome the limitations of other materials, concretely carbon materials benefit from low cost, simple synthesis, tunable design of porous and surface functional groups, fast kinetics, competitive selectivity towards certain adsorbates such as CO₂, etc. [16]. Besides, the treatment of water effluents for the adsorption of anthropogenic contaminants, either inorganic such as metals [17] or organic origin such as

contaminants of emerging concern [18], is a mature and well-established technology in water treatment facilities, for both drinking water and sewage [19].

This paper investigates the potential of physical activation for processed chars of different origins, including agroforestry residues (acacia and pine splinters), food industry (artificial cellulose used as packing agent and olive stones), and urban waste (recovered organic fractions including cardboard, paper, and plastics) for their valorization as activated carbons with adsorption properties. After activation with CO_2 , the textural and chemical properties were evaluated such as N_2 and CO_2 physisorption, immediate and elemental analysis, X-ray photoelectron spectroscopy, and ammonia temperature programmed desorption. The application of the activated chars was evaluated in two different scenarios, i.e. for CO_2 adsorption and storage in the gas phase, and water treatment for the removal of Pb as a representative inorganic pollutant, or caffeine, an organic pollutant of emerging concern.

4.2.1.3. Experimental section

Preparation of the activated chars

The chars used in this work were of industrial origin from pyrolysis plant that obtain biofuel and syngas from urban, industrial, and agroforestry wastes. Five resulting chars obtained from the thermochemical valorization of very different wastes were considered, concretely olive stones (OS), acacia and pine splinters, artificial cellulose used in the food industry for packing purposes, and an industrial waste named as the solid recovered fuel (SRF) made of urban wastes, paper, cardboards, and non-recyclable plastics. The chars, after the reception, were dried overnight at 120°C . Next, they were submitted to physical activation with CO_2 at 750°C . Firstly, N_2 (200 mL min^{-1}) was fed until reach 750°C (heating rate, $10^\circ\text{C min}^{-1}$). Next, the gas was switched with CO_2 (200 mL min^{-1}) and the temperature kept at 1 h and then natural cooled. This temperature and holding time were selected based on the ample information available in the literature that reports them as the average optimum for this process [20].

Characterization of the chars

The characterization of the textural properties was conducted by physisorption techniques. The N_2 adsorption and desorption isotherms were carried out by the standardized method at 77 K. A sync 200 physisorption device from 3P© instruments was used. The samples were outgassed overnight at 110°C under a vacuum atmosphere. The total surface area was calculated through the BET method (S_{BET}). The total pore volume was determined from the N_2 consumption at a high relative pressure ($p/p_0 \sim 0.99$). The microporosity was quantified by the t-plot method, leading to the obtention of the micropore surface (S_{MP}) and volume (V_{MP}). The micropore size distribution was calculated from the CO_2 isotherms carried out

at 273 K. The Horvath–Kawazoe (HK) method was applied for the determination of the pore size distribution [21,22].

The carbon content was determined in a first approach by proximate analysis. The relative proportions of moisture, volatiles, fixed carbon and ash was quantified by thermogravimetry analysis under inert atmosphere. A PerkinElmer STA 6000 thermobalance was used, raising the temperature and the sample from room temperature to 110°C (40°C min⁻¹) under 20 mL min⁻¹ of N₂, and holding for 10 min to calculate the moisture. Then, the temperature was raised to 875°C (40°C min⁻¹) to quantify the volatile contribution. Next, the N₂ flow was exchanged by O₂ (20 mL min⁻¹) to promote the combustion of the fixed carbon. Finally, the sample was cooled leaving to the obtention of the ashes. The content of C, H, N, S, and S was measured by elemental analysis in a Thermo Scientific Flash 2000 device. The contribution of O was tentatively estimated by difference and removing the ashes contribution. The chemical composition of the surface was studied by X-ray Photoelectron Spectroscopy (XPS). The analysis was conducted in a Kratos AXIS Ultra-DLD device irradiated with an X-ray source from Al K α . The spectra were corrected to 284.6 eV in the C_{1s} peak with Shirley background correction. The spectra were processed with the software XPSpeak 4.1. The analysis of the surface was completed with Chemisorption analysis, and conduction Thermal Programmed Desorption (TPD) with NH₃ to compare the acidity of the materials and the surface functional groups. The device used was an AMI-300Lite chemisorption station from Altamira Instruments® coupled to Thermal Conductivity Detection (TCD). About 100 mg of the sample was placed in a quartz ‘U’ shape reactor and submitted. After drying at 110°C with He (25 mL min⁻¹), the adsorption step was carried out with NH₃ (10 % NH₃ in He, 25 mL min⁻¹) under 100 °C for 1 h. Finally, a temperature program from 100 °C to 1000 °C was applied under He (25 mL min⁻¹) and the TCD signal was recorded.

Carbon dioxide adsorption experiments

The CO₂ adsorption experiments were carried out in two different setups. Firstly, characterization tests of the CO₂ adsorption process were conducted under static conditions in a sync 200 physisorption device from 3P© instruments. The CO₂ isotherms were obtained at two different temperatures, i.e. 273 and 298 K. These two isotherms were used to calculate the CO₂ isosteric adsorption heat (ΔH_{ads}) as a function of the CO₂ uptake coverage. Hence, the equation of Clausius–Clapeyron was considered in combination with the Freundlich isotherms [23–25].

The CO₂:N₂ selectivity at 298 K was calculated considering the Ideal Adsorbed Solution Theory (IAST) [26]. An isotherm of N₂ at 298 K was obtained. Both, CO₂ and N₂ isotherms were fitted to the Freundlich model to predict the volume gas

uptake with pressure, and the selectivity as a function of the pressure for a typical post-combustion mixture of 15:85 CO₂:N₂ was calculated as follows [27,28]:

$$S = \frac{\frac{V_{\text{CO}_2}}{P_{\text{CO}_2}}}{\frac{V_{\text{N}_2}}{P_{\text{N}_2}}} = \frac{V_{\text{CO}_2}}{V_{\text{N}_2}} \frac{85}{15} \quad (4.7)$$

where V_i means the gas uptake (STP cm³ g⁻¹) at a certain pressure and p_i is the partial pressure of the i component in the mixture.

Dynamic tests of CO₂ adsorption were conducted in a lab-made jacketed Pyrex glass column (10 cm high and 1 cm internal diameter). The bed temperature was controlled by pumping refrigerant through the annular space of the column. The column was loaded with 1 g of activated carbon, which was retained with the aid of inert glass balls. Two mass flow controllers produced a gas mixture of CO₂ and N₂ (100 mL min⁻¹) at different proportions, the CO₂ concentration ranging from 10-40 %. A continuous Non-Dispersive InfraRed (NDIR) detector (NDIR Edinburgh Instruments Ltd.) was placed at the column exit to monitor the CO₂ concentration leaving the column. The adsorbed CO₂ was calculated from the area below the removed CO₂, from the initiation of the test until reaching the saturation time (95 % of the fed CO₂):

$$q_{\text{CO}_2} = \frac{v C_{\text{inlet}}}{m_{\text{sample}}} \int_0^t \left(1 - \frac{C_t}{C_{\text{inlet}}}\right) dt \quad (4.8)$$

where v (L s⁻¹) is the volumetric flow rate, C_{inlet} (mol L⁻¹) stands for the inlet CO₂ concentration, and m_{sample} (g) means the loaded mass of activated carbon in the column.

Adsorption tests in the aqueous phase

The adsorption capacity of the physically activated carbon was assessed by the obtention of the adsorption isotherms, conducted in 100 mL flasks under batch mode at 25 °C. The adsorbent was added at a dose of 2 g L⁻¹ in 50 mL solutions of different concentrations of Pb²⁺ (10-320 mg L⁻¹) or caffeine (10-640 mg L⁻¹). The slurry was kept under vigorous stirring until reaching the equilibria. Samples before and after adsorption were withdrawn for analysis and filtered with commercial syringe filters (Millipore, Millex-GV PVDF, 0.45 µm). The concentration of Pb²⁺ was quantified by Flame Atomic Absorbance spectrometry in a PinAAcle 500 spectrometer from PerkinElmer®. The concentration of caffeine was analyzed by High-Pressure Liquid Chromatography (HPLC), coupled with molecular absorbance spectrophotometric detection. The chromatograph used was an Alliance e2695 apparatus from Waters™ in which a 2998 photodiode array UV-visible module was connected. The analyte separation was carried out in a Zorbax Bonus-

RP column (4.6×150 mm, $5 \mu\text{m}$). The mobile phase, pumped at a rate of 1 mL min^{-1} was a mixture of acetonitrile (A) and acidified water with 0.1% (vol.) of trifluoroacetic acid (B) with a constant A: B ratio of 15:85. The absorbance at 275 nm was selected for the quantification. The concentration was measured in each flask before and after adding the adsorbent to determine the adsorbate uptake and the resulting isotherms were successfully fitted to the three-parameter Sips's model [29].

The dynamic behavior was tested in a fixed-bed column. The set-up consisted of a jacketed column (11 cm height, 1.5 cm internal diameter), thermostated at 25°C . The column was loaded with 0.5 g of activated carbon, sieved at $355\text{--}500 \mu\text{m}$ to avoid bed compaction, and retained with glass spheres and wool. The column was operated in continuous pumping of Pb^{2+} (20 mg L^{-1}) or caffeine (20 mg L^{-1}) at an average rate of 2 mL min^{-1} . For the desorption experiments, a solution consisting of aqueous HCl 1 M in the case of desorption of Pb^{2+} and methanol in the case of caffeine was fed at the same flow rate.

4.2.1.4. Results and discussion

Characterization of the activated materials

The main goal of the activation process relies on the improvement of the textural properties, enlarging the porosity of the carbonaceous char. For this purpose, N_2 adsorption-desorption isotherms were carried out, illustrated in **Figure 4.10**. The original chars displayed negligible surface area, i.e. values below $1 \text{ m}^2 \text{ g}^{-1}$ (OS, pine, and cellulose), or very low, i.e. inferior to $25 \text{ m}^2 \text{ g}^{-1}$ (acacia and SRF). The activation with CO_2 raised the porosity of the samples, see **Table 4.9** with values in the range of $340\text{--}370 \text{ m}^2 \text{ g}^{-1}$, except for the SRF- CO_2 , $136 \text{ m}^2 \text{ g}^{-1}$, probably due to the recalcitrance nature of this residue for the reaction with CO_2 . The surface areas are less impressive than the reported chemical activation with alkali [23,30] or carbonates [31]. Nonetheless, the values obtained are at the same level as other char feedstocks [10]. The activation with CO_2 of char obtained in the pyrolysis with N_2 of pine sawdust has been reported to reach $336 \text{ m}^2 \text{ g}^{-1}$ (activated at 800°C , 1.5 h) [32], very close to the $367 \text{ m}^2 \text{ g}^{-1}$ of this work. For olive stone, the activation of a char with an initial surface is higher than the one reported in this study, i.e. $209 \text{ m}^2 \text{ g}^{-1}$, which led to a rise after CO_2 activation (850°C , 1 h) to $572 \text{ m}^2 \text{ g}^{-1}$ [33], which means an increase of $363 \text{ m}^2 \text{ g}^{-1}$ during the activation, the same as the one obtained in this work. In other work, a hydrochar derived from olive stones generated during hydrothermal treatment was also activated under CO_2 steam (750°C , 1 h), leaving a porous material of $449 \text{ m}^2 \text{ g}^{-1}$ [34]. The CO_2 activation of acacia residues has reported very similar values, $395 \text{ m}^2 \text{ g}^{-1}$ [35]. Residues of cellulose, submitted to pyrolysis and after a second step of CO_2 activation (600°C , 1 h) were reported to reach a value of $434 \text{ m}^2 \text{ g}^{-1}$, slightly higher than the $359 \text{ m}^2 \text{ g}^{-1}$ obtained in this work. SRF is a complex

mixture based on spent residues fuel with an important contribution of plastic waste, whose activation may be like plastic char that after activation have exhibited an area of around $100 \text{ m}^2 \text{ g}^{-1}$ [36].

Table 4.9. Characterization of the textural properties by N_2 physisorption at 77 K

Sample	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	S_{MP} ($\text{m}^2 \text{ g}^{-1}$)	V_{T} ($\text{cm}^3 \text{ g}^{-1}$)	V_{MP} ($\text{cm}^3 \text{ g}^{-1}$)	V_{UMP} ($\text{cm}^3 \text{ g}^{-1}$)	$V_{\text{MP/VT}}$ (%)
OS-CO ₂	363.2	328.1	0.203	0.170	0.121	83.7
Acacia-CO ₂	341.8	291.2	0.193	0.142	0.123	73.6
Pine-CO ₂	367.9	286.7	0.225	0.139	0.095	60.4
Cellulose-CO ₂	359.7	341.6	0.204	0.155	0.137	76.0
SRF-CO ₂	136.1	61.7	0.207	0.031	0.039	15.0

S_{BET} : total surface area by BET method; S_{MP} , micropore surface; V_{T} , total pore volume from $p/p_0 \sim 0.99$ uptake; V_{MP} , micropore volume; V_{UMP} , ultramicropore volume ($< 0.7 \text{ nm}$)

According to the IUPAC's classification [37], the isotherms of the activated samples, except for SRF-CO₂, are described as Type I. This shape embraces the strong presence of narrow micropores, i.e. $< 1 \text{ nm}$ [38]. After filling the micropores at low relative pressures, a plateau is reached. In contrast, the sample SRF-CO₂ defines a Type II isotherm with the definition of a knee, characteristic of mesoporous materials [39]. The determination of the micropore contribution by the t-plot method corroborates these facts in the values obtained for the microporous surface and pore volume and their contributions. As a matter of fact, the microporosity understood as the ratio in terms of pore volume was high, over 60 %, in all the samples except for SRF-CO₂. Remarkably high was the ratio defined by the sample OS-CO₂, i.e. 83 %. Instead, the SRF-CO₂ displayed mostly mesoporosity, accounting for only 15 % of micropores. Regarding the hysteresis loop in the desorption step, it can be observed that the most porous samples did not define a clear loop. Only the sample pine-CO₂ timidly described an H4 loop, which is consistent with the lowest microporosity, 60 %, the group among these samples. The SRF-CO₂ performed a very different behavior, with an H3 loop. **Figure 4.10** also illustrates the pore size distribution, confirming the presence of micropores whose average size is centered at approximately 0.4-0.6 nm. It is also deduced that the sample SRF-CO₂, the more mesoporous, accounted for micropores presence much less than the rest.

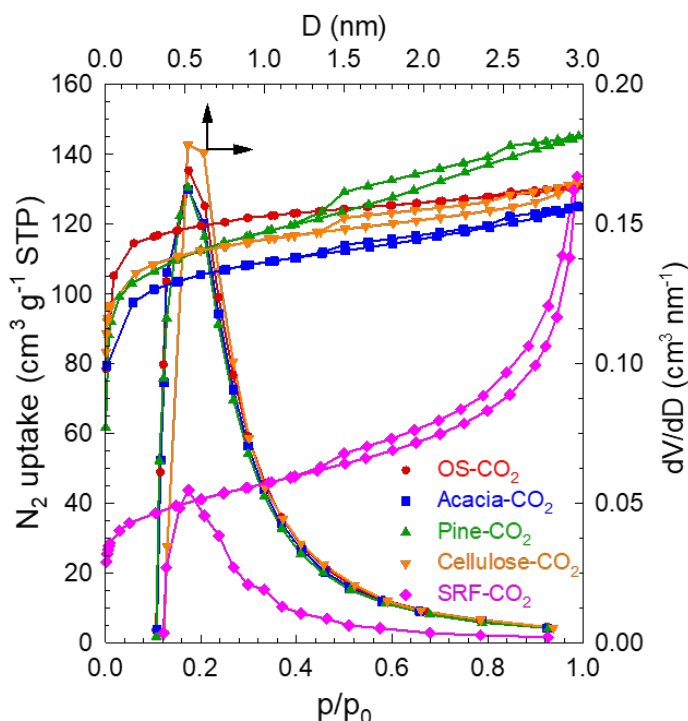


Figure 4.10. Textural characterization by physisorption analysis of the CO₂-activated chars with N₂ adsorption-desorption isotherms at 77 K and the micropore size distribution obtained from CO₂ adsorption isotherm at 273 K with the HK method

The composition and carbon content were analyzed by proximate and elemental analysis and XPS techniques, respectively. The results achieved are summarized in **Table 4.10** and **Figure 4.11**. In general, when comparing the samples, it is evidenced that the activated carbon obtained from acacia, pine, and cellulose displayed the highest carbon content, as both the fixed carbon and the C percentage from elemental analysis corroborate. The lignocellulosic origin of their char provides them with an elevated carbon content [23]. The olive stone displayed a particular behavior. Although fixed carbon suggests a high carbon content, the elemental analysis verified 55 %, which is consistent with the origin of the olive stones [40], which usually displays around 50 %. After the activation reaction, some active superficial carbon reacts with the CO₂ triggering the formation of CO [41], leaving a similar composition in terms of the bulk [23,42]. The sample SRF is the result of a char obtained from solid recovered fuel, mainly composed of organic waste, paper, and cardboard, mixed with non-recyclable plastic, which makes it a solid with poorly enriched carbon [23]. This fact explains why after activation the content was lower than the other samples whose origin was lignocellulosic.

Table 4.10. Proximate and elemental analysis of the chars physically activated with CO₂

Sample	Proximate analysis (%)				Elemental analysis (%)		
	Moisture	Volatile	Fixed carbon	Ash	C	H	O*
OS-CO ₂	3.6	8.4	85.2	2.8	55.1	1.1	43.8
Acacia-CO ₂	6.9	7.0	85.7	0.4	88.4	1.2	10.4
Pine-CO ₂	4.6	6.2	85.5	3.7	84.4	1.2	14.4
Cellulose-CO ₂	4.1	6.2	87.7	2.0	71.0	1.2	27.8
SRF-CO ₂	2.9	5.9	68.2	23.0	60.0	0.8	36.7

*From the difference after subtraction of the ashes. N content was negligible in all the samples.

The surface chemical composition was evaluated by the XPS technique due to its relevance for practical applications such as adsorption. **Figure 4.11** depicts the surface composition obtained by XPS, the contribution to the deconvoluted peaks of C_{1s} and O_{1s} for all the samples, and the high resolution of C_{1s} and O_{1s} regions of one of the samples, i.e. OS-CO₂. The surface composition, although different from the bulk values obtained by elemental analysis, conserves the same relative behavior among the samples. The activation of acacia, pine, and cellulose led to over 90 % of surface C. The O content was the lowest in these three samples, 7.0-8.5 %. The difference between surface and bulk was more remarkable in the cases of OS-CO₂ (85 %) and SRF-CO₂ (77 %). Moreover, these two samples performed the highest O content on their surface, i.e. 13.4 % in OS-CO₂ and 16.7 % in SRF-CO₂. This latter material corroborated the presence of Si and Al at roughly 2 %, evidencing the complexity of the waste used for the preparation. The high-resolution spectrum of C_{1s} was explained based on the contributions of sp² C=C (284.4 eV), sp³ C-C (285.3 eV), C-O (286.5 eV), C=O (288.5 eV), and O-C=O (290.0 eV) [43]. The O_{1s} region was deconvoluted in quinone (531.0 eV), C=O (532.0 eV), and C-O (533.0 eV) [44]. According to the deconvolutions, the two most oxygenated samples, i.e. OS-CO₂ and SRF-CO₂, displayed the highest content of C-O bonds to the detriment of sp³ C-C. The activated chars prepared from acacia, pine, and cellulose were the most enriched in carboxylic acids. From the O_{1s} region, it is evidenced that all the predominant oxygenated group was the C-O. The SRF-CO₂ displayed the highest contribution of quinones, and the cellulose-CO₂ outstanding the content of C=O.

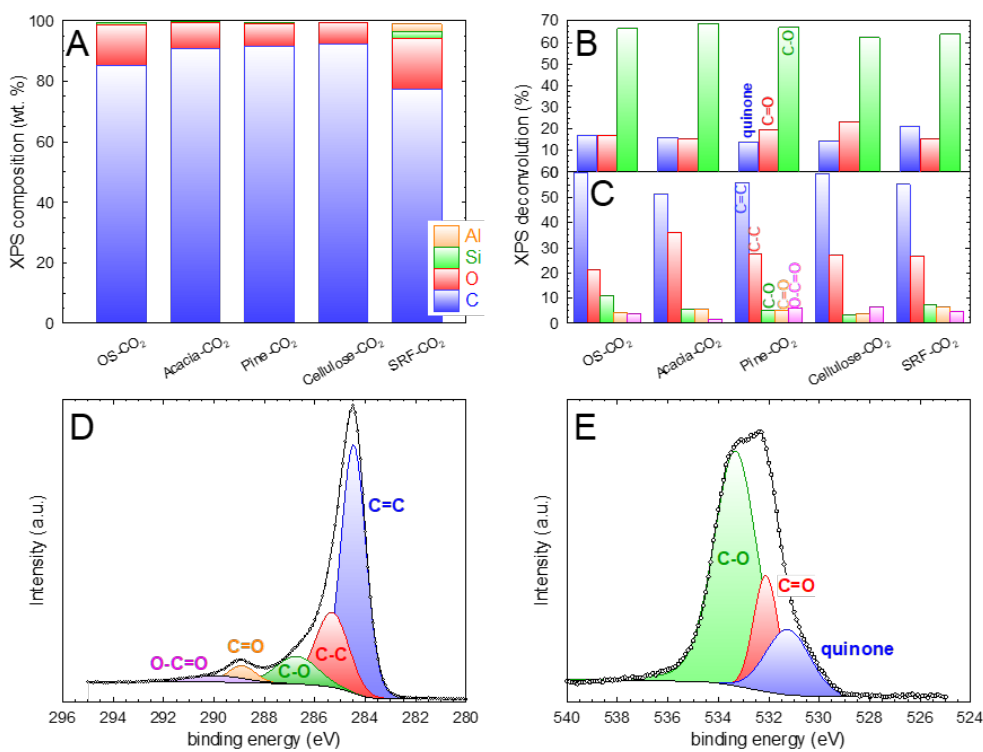


Figure 4.11. Characterization of the activated chars by XPS. Surface composition (A), deconvoluted contributions obtained in C_{1s} (B) and O_{1s} (C) regions, and example of deconvolution of the C_{1s} (D) and O_{1s} (E) regions of OS-CO₂

The surface was further characterized by chemisorption analysis with ammonia TPD. The desorption TPD profiles are illustrated in **Figure 4.12**. The acidity and the nature of the oxygenated groups were further corroborated by chemisorption analysis. For the interpretation of the TPD profiles, the temperature at which different bands appeared were classified as follows: carboxyl below 450°C, anhydride at 350-600°C, phenol at 500-750°C, and carbonyl-quinones at 750-1000°C [45–47]. According to the TPD areas below the curves, the acidity followed the order of Cellulose-CO₂ > Acacia-CO₂ > Pine-CO₂ > OS-CO₂ >> SRF-CO₂. As stated by the deconvolution of O_{1s} of XPS, the desorption profiles proved a major contribution of carbonyl and quinones in all the samples, in the order described previously. Only the samples OS-CO₂ and Acacia-CO₂ defined a timid shoulder in the region of carboxylic acids. The sample SRF-CO₂ did not perform any substantial acidity character and the TPD profile barely suggests a minor presence of carbonyl/quinones and phenolic groups.

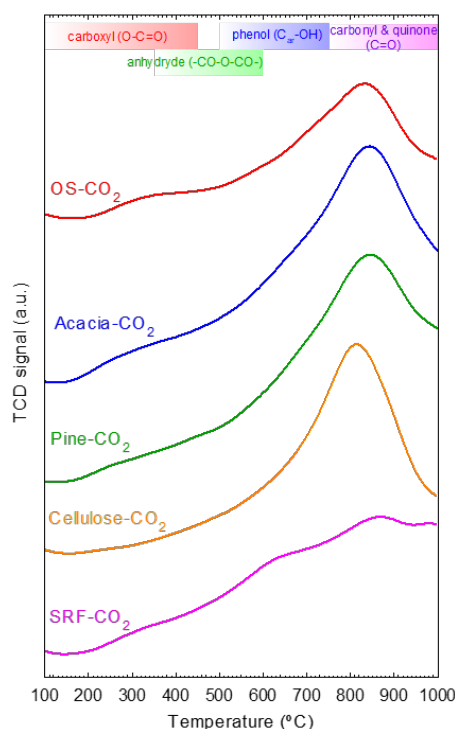


Figure 4.12. Chemisorption characterization with TPD-NH₃ of the chars activated with CO₂.

Carbon dioxide adsorption

The adsorption capability of the physically activated chars was analyzed by conducting static physisorption isotherms up to 100 kPa with CO₂ at two temperatures, 273 and 298 K. The results are depicted in **Figure 4.13A**. The CO₂ isotherms, see **Figure 4.13A**, whose profile depicts the typical Freundlich isotherm due to the reversibility, non-ideality, and plausible multilayer adsorption of CO₂ onto activated carbons. The values at 273 K and ambient pressure followed the order OS-CO₂ (121 mg g⁻¹) > Acacia-CO₂ (115 mg g⁻¹) = Cellulose-CO₂ (115 mg g⁻¹) ~ Pine-CO₂ (112 mg g⁻¹) and >> SRF-CO₂ (36 mg g⁻¹). The dependency of the CO₂ uptake and the micropore volume is illustrated in **Figure 4.13B**, leading to a linear tendency that can presumably be assumed as proof of the importance of micropore development. The textural properties play an essential role during CO₂ adsorption. The presence of micropores is of paramount importance for capture at low pressures [48], concretely ultramicropores, in the range of 0.5-0.9 nm [49], which serve as the optimum active sites for effective interaction. Furthermore, the existence of an adequate functional group results in enhanced selectivity of CO₂ compared with other gases. The adsorbed CO₂ at 273 K and ambient pressure is high if considered the micropore volume. The adsorbed CO₂ per unit of micropore

volume ranged from 715-812 mg cm⁻³. These values are high if compared to the reported in the literature. In a previous work of these materials activated with KOH, the values were 300-500 mg cm⁻³ [23]. For olive stone activated with CO₂, this ratio has been reported as 466 mg cm⁻³ (activation at 1000°C, 30 min), lower than the material of this study [50]. A value of 410 mg cm⁻³ has been published for olive stones activated for 6 h at 800 °C [51]. For instance, pine sawdust submitted to pyrolysis and CO₂ activation (800°C, 1.5 h) led to 663 mg cm⁻³ [32]. In the case of cellulose, a value of 552 mg cm⁻³ has been reported (activation 800°C, 1 h) [52].

The isotherms were obtained at two different temperatures, i.e. 273 and 298 K, registering a decay of CO₂ uptake, as the result of the exothermicity of the process, more important in the samples prepared from acacia, pine, and cellulose. This behavior evidence not only the exothermicity of the process but also a plausible influence of the oxygenated groups in the thermodynamics of the process, as the samples OS-CO₂ and SRF-CO₂ displayed higher surface oxygen, and their CO₂ uptakes were less affected by the decrease of the temperature, i.e. less exothermic. The CO₂ isosteric adsorption heat versus the CO₂ coverage is illustrated in **Figure 4.13C**. An asymptotic trend with the CO₂ uptake degree was performed by all the materials, as the consequence of the heterogeneity of the surface in which the most preferred active sites are covered at low pressures. The heat tends to ~20 kJ mol⁻¹ for acacia-CO₂, pine-CO₂, and cellulose-CO₂, whereas for SRF-CO₂ led to ~10 kJ kmol⁻¹, and OS-CO₂ led to a null value. These values prove the higher interaction of the three former materials, although labeled as a physisorption interaction due to the low values [53]. The results are within the expected in the literature for other biochars physically activated with CO₂ [51,54].

Finally, the characterization behavior in static experiments was completed with the estimation of the selectivity at 25°C by the IAST method for a post-combustion mixture of 15:85 proportion of CO₂:N₂. As depicted in **Figure 4.13D**, all the samples performed quite similar trends, a logarithmic curve whose asymptote tends to selectivity value of 28 (Cellulose-CO₂)-38 (Acacia-CO₂). These values were higher than the reported previously in the literature for pine sawdust at similar conditions, either activated with CO₂ or KOH, 17 and 12 respectively [32].

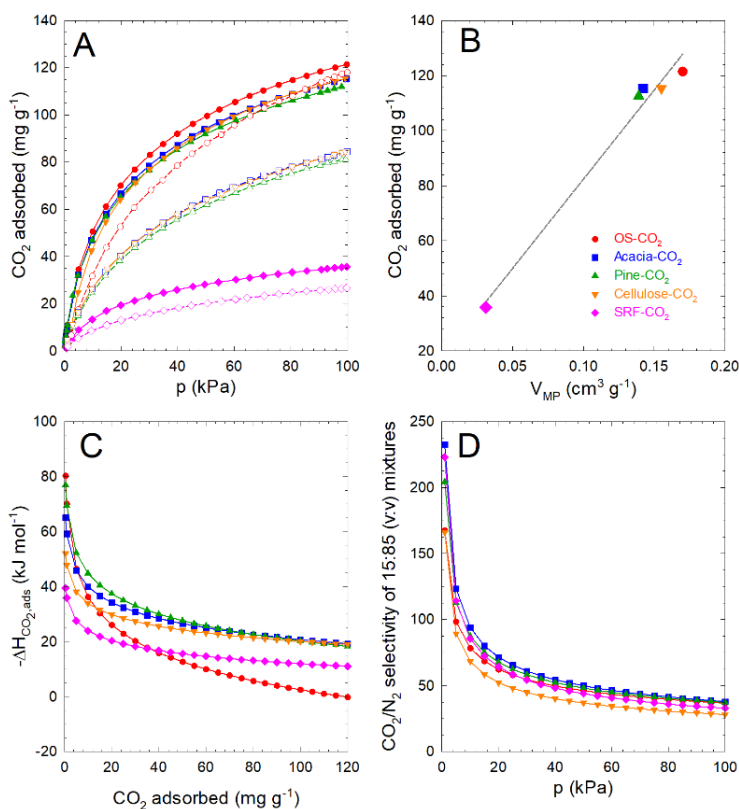


Figure 4.13. Adsorption of CO₂ of the activated chars. CO₂ isotherms at 273 K (filled symbols) and 298 K (empty symbols) (A), the relationship of the CO₂ uptake at 273 K and the micropore volume (B), the isosteric adsorption heat (C) and the selectivity of a post-combustion CO₂/N₂ mixture of 15:85 (v/v) (D)

Based on the higher performance of the sample OS-CO₂, further analysis under dynamic adsorption tests of CO₂-N₂ mixtures was performed. The influence of the inlet CO₂ concentration was evaluated in the range of 10–40 % during three consecutive cycles, as depicted in **Figure 4.14**. Regardless of the inlet CO₂ concentration, the breakthrough time was barely affected by the inlet CO₂ concentration, around 60 s. The CO₂ uptake during the adsorption cycle increased as the inlet concentration was raised, i.e. the average values during the three cycles were 31.9 ± 0.5 mg g⁻¹ (10 %), 61.5 ± 0.4 mg g⁻¹ (20 %), 93.3 ± 1.5 mg g⁻¹ (30 %), and 92.6 ± 0.4 mg g⁻¹ (40 %). This effect can be ascribed to the increased probability of interaction between the adsorbate and the surface of the adsorbent. Moreover, the established CO₂ gradient is larger when the inlet concentration is raised; therefore, the mass resistance opposed to the transfer is diminished [55–57]. These values were inferior to those obtained in the static test (121 mg g⁻¹). These differences may be attributed to diffusion limitations during the gas flow in the bed

for which the presence of mesopores may help as a first shuttle to the micropores where CO_2 is retained [58]. The material displayed great stability during the reutilization in sequential adsorption-desorption cycles at the four inlet CO_2 concentrations tested, as visible in **Figure 4.14B** at different inlet CO_2 concentrations.

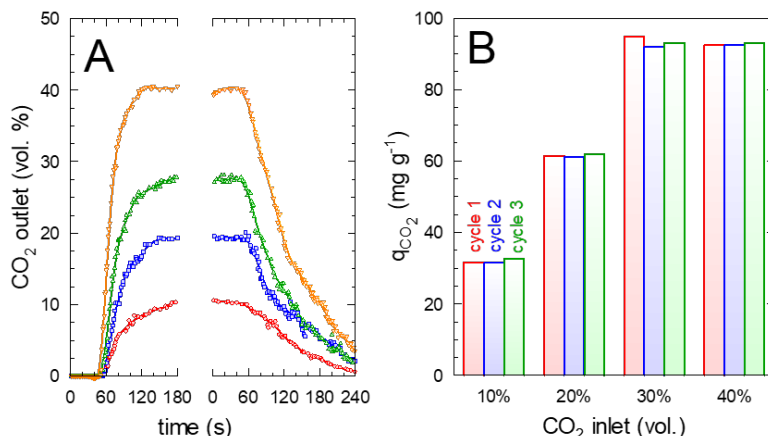


Figure 4.14. CO_2 adsorption and desorption breakthrough curves at different inlet concentrations (10–40 %) with OS- CO_2 . An example of a cycle of adsorption and desorption breakthrough curve (A) and the CO_2 saturation capacity in three consecutive cycles (B)

Adsorption of pollutants in water

The performance of the CO_2 -physical activated chars was evaluated for water treatment applications. Two different pollutants were selected based on their ubiquitous presence either in industrial or urban wastewater, i.e. lead [59] and contaminants of emerging concern such as caffeine [60–62]. Firstly, equilibria batch tests were conducted with all the activated materials, leading to the adsorption isotherms of Pb and caffeine depicted in **Figure 4.15**.

The adsorption of Pb was moderate if compared to other materials, with maximum adsorption uptakes, in the range of study, following the order SRF- CO_2 (25.5 mg g^{-1}) > Cellulose- CO_2 (18.5 mg g^{-1}) > Acacia- CO_2 (15.5 mg g^{-1}) > OS- CO_2 (13.5 mg g^{-1}) > Pine- CO_2 (11.0 mg g^{-1}). The isotherms were successfully fitted to the Sips model, see **Figure 4.15A** and **Table 4.11**, with no definition of a clear plateau although the concentration in the equilibrium was high. Consequently, it should be taken into account that the estimation is valid in the concentration range of the study, and any extrapolation outside, such as the predicted saturation capacity (q_s), must be considered with caution. The Sips model combines Freundlich and Langmuir models in which the parameter n_s stands for the deviation among them [63]. The value of n_s indicates the affinity of the adsorbate to the adsorbent and the

number of occupied sites by each adsorbate molecule [64]. The sample SRF-CO₂ was the one that provided the lowest n_s value below the unit, indicating a high efficiency at low concentrations range. Moreover, it was the least microporous, evidence of a process not reigned by microporous development. The adsorption process of metals takes place by surface covering and further diffusion of ions into the pores. The radius of hydrated Pb²⁺ is around 0.401 nm, a value very close to the dominant micropore size of the samples, whose activation built micropores of around 0.5 nm [65], which may compromise the diffusion of the hydrated metal to the active adsorption sites. Besides, the mechanism involved includes surface complexation, electrostatic attraction of the surface and the hydrated metal, and precipitation [66], i.e. in the case of Pb²⁺, it starts to precipitate as Pb(OH)₂ at pH over 6.0 [67]. The enriched oxygen content and the presence of important mesoporosity of SRF-CO₂ may explain the higher Pb²⁺ uptake.

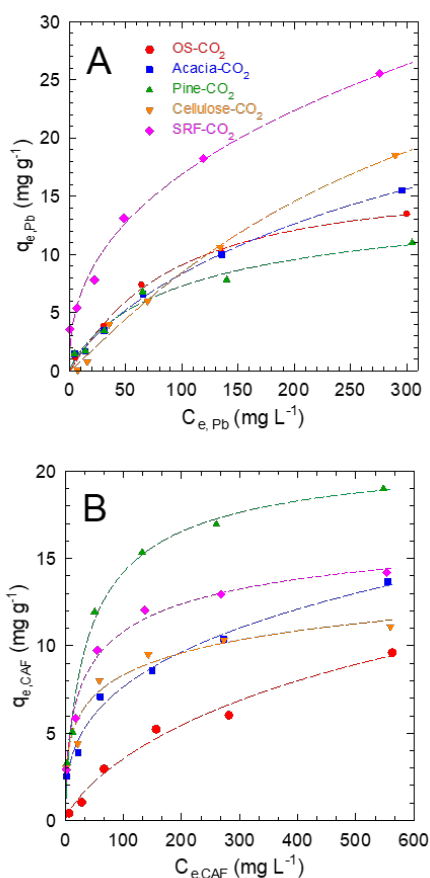


Figure 4.15. Adsorption isotherms of physically activated chars for removing Pb²⁺ (A) and caffeine (B). The dashed lines represent the fit to the Sips model. Experimental conditions: $C_0=10\text{-}650$ mg L⁻¹; $C_{adsorbent}=2$ g L⁻¹; $T=25$ °C

The adsorption capability of caffeine with the activated samples led to the order pine-CO₂ (19.0 mg g⁻¹) > SRF-CO₂ (14.2 mg g⁻¹) ~ Acacia-CO₂ (13.7 mg g⁻¹) > Cellulose-CO₂ (11.0 mg g⁻¹) > OS-CO₂ (9.6 mg g⁻¹). In this case, the plateau uptake of the isotherm was almost defined although the concentration at which they appear was high, see **Figure 4.15B**. The experimental data was successfully fitted to the three-parameter Sips model [29], leading to the parameters presented in **Table 4.11**. Most of the fitting led to a Sips exponent inferior to the unit, which indicates that the adsorption process is favorable at low adsorbate concentration [64]. According to the literature, caffeine adsorption is highly influenced by the pore volume [68,69]. All the activated chars displayed a pore volume in the range of 0.192-0.225 cm³ g⁻¹ which may explain great differences between their adsorption uptakes. These values might be labeled as low-moderate and not impressive if compared to the much higher values of astonishingly porous carbon materials [68], based on a more aggressive activation process, generally KOH [23].

Table 4.11. Fitting parameters to the Sips model of the adsorption isotherms of Pb²⁺ and caffeine

Material	q _{exp} [*] (mg g ⁻¹)	q _e = $\frac{q_s(K_sC_e)^{n_s}}{1 + (K_sC_e)^{n_s}}$			R ²
		q _s (mg g ⁻¹)	K _s (L mg ⁻¹)	n _s	
Adsorption of Pb ²⁺					
OS-CO ₂	9.6	16.75	1.166·10 ⁻²	1.115	0.996
Acacia-CO ₂	13.7	40.03	1.917·10 ⁻³	0.809	0.995
Pine-CO ₂	19.0	15.81	8.269·10 ⁻³	0.846	0.984
Cellulose-CO ₂	11.1	39.45	3.066·10 ⁻³	1.103	0.994
SRF-CO ₂	14.2	541.4	2.820·10 ⁻⁶	0.420	0.985
Adsorption of caffeine					
OS-CO ₂	13.5	24.15	9.963·10 ⁻⁴	0.764	0.984
Acacia-CO ₂	15.5	191.3	1.070·10 ⁻⁶	0.347	0.985
Pine-CO ₂	11.0	21.56	2.820·10 ⁻⁶	0.768	0.992
Cellulose-CO ₂	18.5	20.43	3.550·10 ⁻³	0.359	0.982
SRF-CO ₂	25.5	18.87	1.772·10 ⁻²	0.513	0.984

*Highest experimental uptake

The behavior under dynamic conditions was tested selecting for each contaminant the adsorbent with the best performance according to the highest experimental adsorption uptake, in the case of Pb²⁺ it was SRF-CO₂ and in the case of caffeine, it was pine-CO₂. **Figure 4.16** illustrates three consecutive adsorption and desorption cycles in each case. In the case of Pb²⁺, pictured in **Figure 4.16A-B**, it is appreciated that the column performance losses efficiency from the first cycle to the second, as the Pb²⁺ capacity dropped from 4.67 (1st run) to 2.96 mg g⁻¹ (2nd run), being almost constant in the following reusing cycles, i.e. 3.11 mg g⁻¹ (3rd run) and 3.05 mg g⁻¹ (4th run). This partial loss after the first cycle can be ascribed to a

partial fixation of Pb^{2+} that is not subsequently released in the desorption step, blocking part of the active sites as reported commonly in Pb^{2+} adsorption with other biochar formulas [70]. The first desorption cycle released 3.14 mg g^{-1} , which equals 67 % of desorption efficiency and after this cycle, the desorbed amount was roughly 90 %. Other works have reported modification of the textural properties during the regeneration with acid [71], which was not the case since the measured surface areas of the SRF- CO_2 material after the 4th run were very similar to the initial one, concretely 136 vs $181 \text{ m}^2 \text{ g}^{-1}$, before and after utilization respectively. In the case of caffeine, similar behavior has been recorded, see **Figure 4.16C-D**. The adsorption uptakes were 2.74 (1st run), 1.06 (2nd run), 1.33 (3rd run), and 1.23 mg g^{-1} (4th run). A considerable retention decay was registered after the first run, despite recovering over 90 % in the first desorption rung. In this case, the regeneration with methanol may have affected the surface properties, leading to less effective adsorption centers. Overall, the fixed-bed column tests manifested that the material can be regenerated and used in sequential cycles, although a settling in the first cycle is required after the first regeneration step.

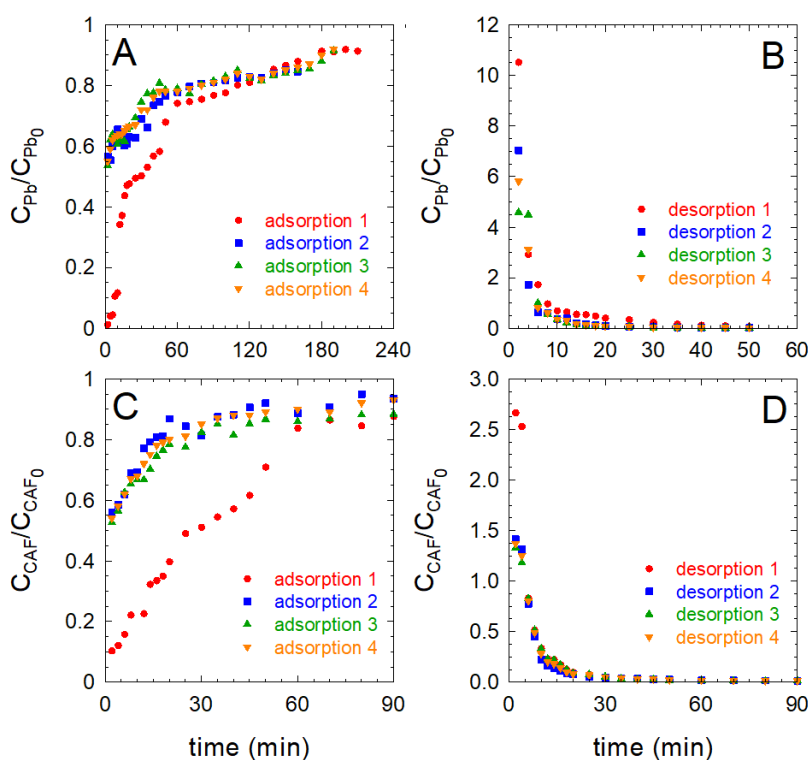


Figure 4.16. Breakthrough columns of adsorption and desorption cycles of Pb onto SRF- CO_2 (A and B) and caffeine with Pine- CO_2 (C and D). Experimental conditions: $C_0=20 \text{ mg L}^{-1}$; $m_{\text{adsorbent}}=0.5 \text{ g}$; $T=25^\circ\text{C}$, $Q=2 \text{ mL min}^{-1}$; desorption carried out with $\text{HCl } 1 \text{ M}$ for Pb and methanol for caffeine

4.2.1.5. Conclusions

Physical activation with CO₂ of chars recovered from pyrolysis valorization is a suitable technology for preparing porous materials; however, the porosity developed was moderate, with surface areas in the range 340-370 m² g⁻¹ and high microporosity contribution, of over 70 % in the best chars. XPS and chemisorption characterization evidenced the presence of carbonyl and quinone groups. Therefore, the material was very efficient for the adsorption of CO₂ which interestingly enables it for a practical application of CO₂ capture and storage such as in the post-combustion effluents, mainly ascribed to the high microporosity. However, physical activation did not perform activated carbon formulas as competitive for water treatment as those prepared under chemical activation, especially when using aggressive chemicals such as alkalis. The best Pb uptake was 25.5 mg g⁻¹ whereas the best result in caffeine removal was 17.1 mg g⁻¹. The performance in fixed-bed column assays showed that the regeneration step affects the uptake of the following cycle; however, after a first regeneration stabilization, it led to a stable behavior. Although these values may be labeled as low-moderate, depending on the nature of the polluted effluent, the physically obtained formulas may be suitable, since the concentration level at which the contaminants of emerging concern, usually in the range of ppb or lower, is still far from the saturation level uptake of the prepared adsorbents. These deterring limitations could be largely overcome by the benefits associated, such as the needless use of aggressive chemicals, like toxic alkalis, or additional washing steps for removing the chemical excess. Consequently, physical activation methods may be a potential alternative to boost a more respectful and sustainable activation process.

CRedit author statement

Ledicia Pereira: Conceptualization, Investigation, Visualization; **Mónica Calero:** Conceptualization, Investigation, Writing - Review & Editing, Project administration, Funding acquisition; **Gabriel Blázquez:** Investigation; **Sergio González-Egido:** Resources, Funding acquisition; **María González-Lucas:** Resources, Funding acquisition; **M. Ángeles Martín Lara:** Conceptualization, Investigation, Writing - Review & Editing, Supervision, Funding acquisition; **Rafael R. Solís:** Conceptualization, Investigation, Visualization, Writing - Original Draft, Supervision, Writing - Review & Editing.

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4.2.1.6. References

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Chapter 5. Scaling up the Production of Activated Char

5.1. Paper 6: Unravelling the lab-scaling up production of activated carbon from plastic-enriched waste

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Ledicia Pereira, Gabriel Blázquez, Ventura Castillo, Francisco Miguel González-Pernas, María González-Lucas, M. Ángeles Martín-Lara, Mónica Calero, Rafael R. Solís

5.1.1. Abstract

This work explores the preparation of activated carbon from the pyrolysis char residues in two different scale scenarios, i.e. a laboratory furnace and a scaled-up version in a lab-pilot plant rotatory furnace. As the activating method, K_2CO_3 was added to the carbonaceous precursor. The activation temperature (700-800°C) and the impregnation char: K_2CO_3 ratio (1:0.25-1:2) were modified in both setups, comparing the attained results of textural development and chemical composition by elemental analysis and XPS. The effect of the agitation during the activation process was also evaluated at the lab-pilot plant scale. The results pointed out a better definition of the textural properties at the lab-pilot plant scale, with an important influence on the agitation in the process. Thus, the optimum temperature was set as 750 °C, and the char: K_2CO_3 ratio as 1:0.5, leading to a material with an area of $\sim 1100 \text{ m}^2 \text{ g}^{-1}$, and a pore volume of $\sim 0.8 \text{ cm}^3 \text{ g}^{-1}$. The resulting activated carbon could adsorb up to 270 mg $CO_2 \text{ g}^{-1}$. Dynamic tests of CO_2 - CH_4 mixtures (from 20:80 to 40:60) were carried out with the optimized material prepared at the lab-pilot plant scale, demonstrating the suitability of the valorized residue as activated carbon for biogas upgrading, with high stability in sequential reusing assays.

Keywords: plastic waste; activated carbon; scale-up; lab-pilot plant

5.1.2. Introduction

Recently, there has been a growing concern about the uncontrolled generation of plastic waste, whose management is problematic in many cases. A wide variety of methods and technologies have been developed for the treatment of certain types of plastic waste, such as mechanical recycling processes, which allow raw materials to be recovered and cheaply for their re-use [1], or chemical recycling processes

involving thermochemical treatments, which enable monomers to be obtained and then used as raw materials in the manufacture of new plastics [2].

In this sense, the plastic pollution crisis has led to an increase in the research efforts on the valorization of plastic waste, which has become a hot topic, especially for those complex fractions that can no longer be mechanically recycled. Pyrolysis is one of the most widely studied thermochemical processes for the chemical valorization of complex plastic waste since it enables the treatment of highly variable composition residues, obtaining added-value products, such as pyrolysis oil, with a variable composition of light and heavy hydrocarbons, oxygenated and nitrogenous compounds. Although pyrolysis leads to the conversion of complex wastes into added-value chemicals for the petrochemical sector, a solid carbonaceous residue is also produced as a byproduct [3,4]. This non-porous carbonaceous material named char has a high potential in critical fields such as agriculture, construction, water decontamination, air depuration, and biogenic waste-derived biochar. Despite this, the raw biochar is scarcely porous [5], thus extra methods for improving textural properties via activation are required. Different strategies are commonly approached, including physical activation with N_2 , CO_2 , or water steam, and chemical activation using diverse substances [6]. Chemical activation has been postulated as more effective for scaffolding a porous structure than the physical processes [7], due to the greater reactivity the chemicals may have with the carbon content of the char [8], by selectively attacking the non-graphitic part of the char. In addition, the use of chemical agents also has a mild catalytic effect, reducing the activation temperature required for the enhancement of porosity [9]. From all the chemical agents available for this application, the activation with KOH has led to remarkable microporosity [10]; however, more sustainable derivatives [11,12], such as K_2CO_3 , have proven to conduct encouraging results with biomass-based carbon precursors [13–16]. The use of chemical agents that pose less hazard and safer operation conditions on a large scale is of utmost importance. Moreover, excessively aggressive chemicals such as alkalis may compromise the durability of the furnace components.

The use of plastic-based precursors for the synthesis of activated carbon has been demonstrated to be feasible and sustainable since it relies on the circular economy concept and is economically competitive with other biomass feedstocks [4,17,18]. The preparation of activated carbon from diverse residues has a large trajectory; nevertheless, the scaling-up assessment at high production has been poorly tackled. Not only can the production costs be affected [19], but also the textural properties may be altered. The limitations faced in limited lab-scale setups are often not overcome, providing non-realistic results. Moreover, although studies are available dealing with the preparation at a large scale [7], they rarely compare the results with lab-made installations, thus no clear conclusions can be made on the effect of

scaling-up on the activation process or the final properties of a given sample. Since most of the novel carbonaceous materials are first prepared at low productions, it seems interesting to compare the effects on the properties of the prepared material during the scaling-up.

The current literature regarding the valorization of plastic waste into activated carbon formulas is focused on one polymeric type. Little research has addressed real rejected fractions from the classification lines in plastic treatment plants. In this sense, this work is centered on the valorization of a second-generation residue, since the char released as a residue after the pyrolysis of a plastic-enriched waste is considered as the carbon precursor. Furthermore, the activation step has been addressed at lab-pilot plant scale, evaluating the influence of the operational variables during the scaling-up. Bearing in mind the lack of detailed studies comparing a lab-scaling in a pilot prototype for this kind of preparation, this work aims at the comparison of the same material in two different scenarios, i.e. a static laboratory tubular furnace with a limited loading capacity (100 mL space), with a lab-pilot plant rotatory furnace which enables the treatment of larger amounts (1250 mL space) under movement. An industrial char formula from spent residue fuel, enriched in carbon. This industrial residue is from the rejection fraction of recycling processes, leading to a mixture of paper, cardboard, and different plastics. After valorization via pyrolysis, a char is generated. Aimed at the loop-closing of this non-valuable fraction, this study pursues the activation under two approaches, using K_2CO_3 as a chemical activating agent. The influence of the activation temperature (700-800 °C) and the char-to-chemical agent impregnation ratio (1:0.25 to 1:2) was assessed in the two furnaces, comparing the impact of the setup on the development of the textural, chemical, and surface properties. The plausible influence of the rotatory agitation was also evaluated. Also, the application of activated char in biogas upgrading was tested in the present work, determining its performance in CH_4 purification in a variety of CH_4/CO_2 model mixtures.

5.1.3. *Experimental section*

Materials and preparation of the activated carbon

All the reagents used were analytical grade and used as received. Ultrapure water (18.2 $M\Omega \cdot cm$) from a Direct-Q®-UV device (Millipore®) was used for the preparation of all the solutions.

The raw char was provided by “*Grupo Layna Gestión de Residuos S.L.*”. The char was produced by pyrolysis of solid recovered fuel in a semi-industrial-scale continuous screw reactor, using moderate operating temperatures, with a residence time adequate for complete pyrolysis to occur. The solid recovered fuel was mainly

composed of paper, cardboard, and different plastics. The resulting char was used as the precursor for preparing activated carbons.

Two different experimental setups representing low production of activated carbon in a laboratory furnace and higher production in a lab-pilot plant rotatory furnace were considered and compared; see the scheme and detailed information regarding the dimensions of both setups in **Figure 5.1**. A tubular Nabertherm furnace was used at the laboratory scale, model R50/250/12, with an operating space of 100 mL. In this furnace, the temperature control applies to the inlet wall of the tube in which the sample is inserted into a metallic crucible. An amount of 10 g of sample was loaded, consisting of a mixture of char and K_2CO_3 at different mass ratios, varying from char: K_2CO_3 1:1 to 1:0.25. N_2 was fed at a rate of 0.1 L min^{-1} and the temperature was increased from room temperature a rate of $10 \text{ }^\circ\text{C min}^{-1}$ to 700-800 $^\circ\text{C}$, to be kept for 1 h. The operational variables, i.e. char: K_2CO_3 ratio and activation temperature, were set based on previous reports, limiting the K_2CO_3 to avoid excessive preparation costs and environmental impact [11]. For the production in the furnace in the lab-pilot plant, a hinged rotary tube kiln from Carbolite® Gero was used, model TS03 11/1000, with an operating space of 1250 mL. In this case, the loaded sample was 200 g, consisting of a mixture of char and K_2CO_3 at different ratios, the same as mentioned before. The sample was placed in the inlet of a rotatory quartz tube, in which a thermocouple was inserted, the sample being in direct contact with it. The carrier gas N_2 was fed at a rate of 2 L min^{-1} and the temperature program was the same as at the lab scale. In both cases, after activation accomplishment, the samples were naturally cooled down under N_2 . Then, the cooled samples were washed with HCl 1 M and dried at 120 $^\circ\text{C}$ overnight. All the resulting solids were ground and sieved to $<250 \text{ }\mu\text{m}$.

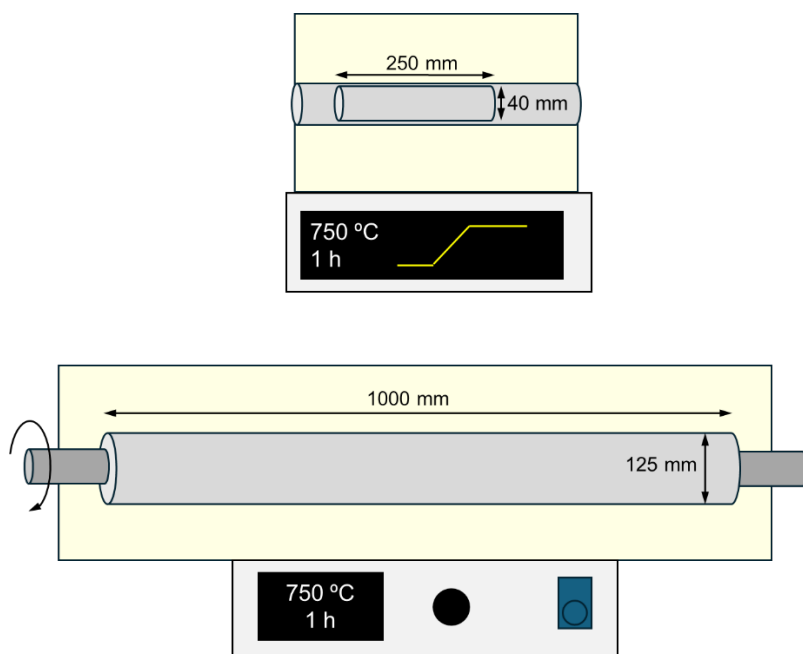


Figure 5.1. Scheme and dimensions of the laboratory furnace (top) and the lab-pilot plant rotatory kiln (bottom)

Characterization of the activated carbon

The textural properties were analyzed by physisorption techniques in a Sync 200 device from 3P Instruments© (Standard Deviation, $STD < 1\%$). The N_2 adsorption-desorption isotherms were carried out at $-196\text{ }^\circ\text{C}$. Previously, the samples were degassed overnight at $100\text{ }^\circ\text{C}$ under a vacuum in a J4 prep degasser station of 3P Instruments©. The total surface area was determined by the Brunauer-Emmett-Teller method (S_{BET}), and the total specific pore volume (V_T) was calculated from the N_2 uptake at $p/p_0 \sim 0.99$. The specific surface of micropores (S_{MP}) and the micropore volume (V_{MP}) were obtained from the t-plot method. The adsorption isotherm with CO_2 at 0°C was used to assess the micropore size distribution, considering the Horvath–Kawazoe (HK) method for the calculation.

The proximate analysis was conducted to determine the contribution of moisture, volatile matter, fixed carbon, and ash in the samples by thermogravimetric analysis in a PerkinElmer STA 6000 thermobalance. Firstly, the sample was submitted to $30\text{ }^\circ\text{C}$ under N_2 (20 mL min^{-1}). Next, the temperature was increased to $110\text{ }^\circ\text{C}$ (heating rate, $40\text{ }^\circ\text{C min}^{-1}$) and kept for 10 min at this temperature. Then, the temperature was raised to $875\text{ }^\circ\text{C}$ (heating rate, $40\text{ }^\circ\text{C min}^{-1}$) and maintained for 10 min. Finally, the N_2 was changed into O_2 (20 mL min^{-1}) at $875\text{ }^\circ\text{C}$ for another 10

min. The determination of each of the constituents was completed by quantifying the weight loss in each step, and the fixed carbon by the difference.

The chemical composition was analyzed by elemental analysis and X-ray Photoelectron Spectroscopy (XPS). The bulk composition C, H, N, and S was determined by elemental analysis in a Thermo Scientific Flash 2000 device (STD<1%). Oxygen was tentatively estimated as the difference with the other elements after removing the ash content from the proximate analysis. XPS technique was used for analyzing the superficial composition, in a Kratos AXIS Ultra-DLD device (sensitivity 0.1-1% atomic, STD<5%) using an X-ray source from Al K α . The spectra were corrected to the C_{1s} peak of adventitious carbon to 284.6 eV. The software XPSpeak 4.1® was used for the processing and deconvolution of the peaks, considering a Shirley background correction. Moreover, the nature and strength of the acid sited in the surface were further assessed by Thermal Programmed Desorption (TPD) with NH₃ on an AMI-300Lite chemisorption station from Altamira Instruments® equipped with a Thermal Conductivity Detector (TCD). Briefly, 100 mg of sample was loaded and submitted to adsorption with NH₃ (10 % NH₃ in He) under 100 °C and a temperature program from 100 °C to 1000 °C was applied.

Dynamic tests of biogas upgrading

The enrichment of biogas in CH₄ was studied under dynamic adsorption tests of CO₂-CH₄ mixtures between 20:80 and 40:60. The assays were conducted in a thermostatic fixed-bed column of 10 cm height and 1 cm internal diameter equipped with a porous ceramic plate at the base, operating at 30 °C and atmospheric pressure. In the middle 1 g of the adsorbent was placed inside and retained with glass balls inserted in the top. The adsorption tests were conducted by feeding CO₂/CH₄ mixtures ranging from 20:80, 40:60 and 80:20 (v/v). The concentration of CO₂ and CH₄ in the gas at the outlet was monitored with an INFRA.sens® AK5 device from Wi.tec-Sensorik, based on non-dispersive infrared (NDIR) analysis in a dual beam. The gas adsorption uptake, either for CO₂ or CH₄, was quantified from the breakthrough curves as the area below the adsorbed gas, which means the 1-C_t/C_{inlet} curve, being C_t and C_{inlet} the temporal concentration of the gas and the inlet value, respectively. The area was calculated from the initial time until the saturation time (t_{sat}), defined as the time in which C_{tsat}/C_{inlet}=0.95 [20]:

$$q = \frac{\vartheta C_0 \int_0^{t_{sat}} \left(1 - \frac{C_t}{C_0}\right) dt}{m_{AD}} \quad (5.1)$$

where ϑ means the volumetric flow rate (100 L min⁻¹), C₀ (mol L⁻¹) is the inlet CO₂ or CH₄ concentration, and m_{AD} (g) means the mass of adsorbent loaded in the column.

The selectivity was calculated from the results of dynamic tests as follows:

$$S_{CO_2/CH_4} = \left(\frac{q_{CO_2}}{q_{CH_4}} \right) \left(\frac{p_{CH_4}}{p_{CO_4}} \right) \quad (5.2)$$

where q_i is the gas uptake of the 'i' component at 298 K and atmospheric pressure, and ' p_i ' is the partial pressure.

The removal capacity (R) was calculated as the amount of gas, either CO_2 or CH_4 , retained in the column concerning the total fed amount:

$$R = \frac{q_i m_{AC}}{\theta C_0 t_{sat}} = \frac{\int_0^{t_{sat}} \left(1 - \frac{C_t}{C_0} \right) dt}{t_{sat}} \quad (5.3)$$

The performance of the CH_4 upgrading was verified by the calculation of some key parameters such as the productivity, CH_4 purity, and CH_4 recovery. The molar yield of CH_4 (Y_{CH_4} , mol $g^{-1} s^{-1}$) with a selected purity level (90 %) was determined from the integration of the molar flowrate profile of CH_4 at the gas outlet between the time defined as the time when CH_4 reaches the purity selected as 90 % [21,22]:

$$Y_{CH_4} = \frac{1}{m_{AD} t_{cycle}} \int_{t_1}^{t_2} F_{CH_4}(t) dt \quad (5.4)$$

where $F_{CH_4}(t)$ is the molar flow of CH_4 in the outlet stream, and t_{cycle} means the necessary time to reach the inlet conditions. Moreover, the CH_4 purity was calculated as the percentage of the CH_4 in the outlet gas as follows:

$$CH_4 \text{ purity} = \frac{\int_{t_1}^{t_2} F_{CH_4}(t) dt}{\int_{t_1}^{t_2} F_{CH_4}(t) dt + \int_{t_1}^{t_2} F_{CO_2}(t) dt} \quad (5.5)$$

The CH_4 recovery was estimated as the CH_4 extracted in the raffinate during the interval t_1 - t_2 concerning the amount fed during the cycle:

$$CH_4 \text{ recovery} = \frac{\int_{t_1}^{t_2} F_{CH_4}(t) dt}{\int_0^{t_{cycle}} F_{CH_4}(t) dt} \quad (5.6)$$

The adsorption-desorption cycles of reusing with a CO_2 - CH_4 mixture were carried out by swapping the inlet with pure N_2 at the same flow rate, i.e. 100 mL min^{-1} . The desorption cycle was concluded when the monitored CO_2 and CH_4 concentrations were negligible.

5.1.4. Results and discussion

Optimization of the activation temperature

The effect of the temperature during the activation process was assessed in the two defined scale-up stages, from 700 °C to 800 °C. The textural properties were analyzed by N₂ adsorption-desorption isotherms at -196 °C and CO₂ adsorption at 0 °C for the micropore size distribution. The results are depicted in **Figure 5.2**. In addition, **Table 5.1** summarizes the calculated results regarding the textural properties.

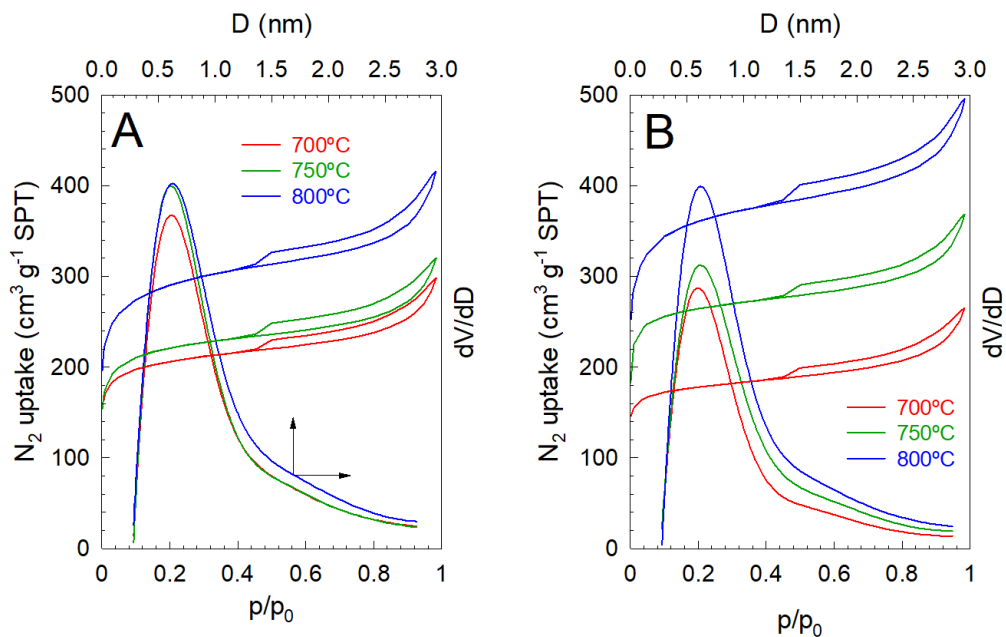


Figure 5.2. Effect of the temperature activation on the N₂ adsorption-desorption isotherms and micropore size distribution of the activated chars prepared with a K₂CO₃ ratio of 1:1 at laboratory (A) and lab-pilot plant scale (B)

Table 5.1. Effect of the activation temperature on the textural properties of the activated chars and CO₂ uptake

T (°C)	Reactor	S _{BET} (m ² g ⁻¹)	S _{MP} (m ² g ⁻¹)	V _T (cm ³ g ⁻¹)	V _{MP} (cm ³ g ⁻¹)	V _{MP} /V _T (%)	q _{CO2} (mg g ⁻¹) at 0°C and 1 bar
700	Laboratory	616	513	0.461	0.275	59.6	155.3
	Lab-pilot plant	527	440	0.410	0.238	58.0	161.9
750	Laboratory	661	551	0.495	0.295	59.6	162.8
	Lab-pilot plant	781	672	0.570	0.362	63.5	194.5
800	Laboratory	955	785	0.643	0.378	58.8	179.2
	Lab-pilot plant	1079	900	0.766	0.482	62.9	205.2

S_{BET}: total specific surface area by BET method; S_{MP}: micropore surface area by t-plot method; V_T: total pore volume from N₂ uptake at p/p₀~0.99; V_{MP}: micropore volume by t-plot method; V_{UMP}: volume of pore diameter inferior to 0.7 nm; q_{CO2}: CO₂ uptake at 100 kPa and 0 °C

The depicted N₂ isotherms described, according to IUPAC's classification [23], a mixed isotherm of Types I and IV, with a concave inflection point at around p/p₀~0.1 with provided evidence of certain mesoporosity [24] which is similar to the already reported for this spent residue fuel activated with KOH [25]. Concerning the hysteresis loop portrayed in the desorption step, a type H4 hysteresis is stated, which is characteristic of micro-mesoporous carbon materials [24], also associated with narrow-slit mesopores [26]. K₂CO₃ is a porogenic activating agent, milder than KOH, that leads to the development of micropores through a redox reaction in which K₂CO₃ oxidizes the carbonaceous matter to generate CO, the latter being responsible for the porosity created in the carbon solid [27]:



Moreover, potassium vapors enhance the formation of additional porosity by disrupting the carbon microstructure. As a result, the materials obtained by K₂CO₃ are primarily microporous with a certain contribution of mesopores [11]. According to the results, a temperature rise from 700 to 750 °C improved the microporosity developed in both activation scenarios, laboratory, and lab-pilot plant. However, although the total surface area is increased over 750 °C, the microporosity contribution is not further improved. This trend is explained based on a negative effect due to the sintering at temperatures higher than 900 °C and shrinkage of the carbon, the latter resulting in the narrowing and even closing of some of the pores [28]. If the material is devoted as an adsorbent for CO₂, whose efficiency mainly relies on the presence of micropores, the CO₂ uptake obtained did not report any

significant improvement at 800 °C respect to 750 °C, little justifying this extra energy consumption. The micropore size distribution portrays a maximum contribution of micropores of 0.5-0.6 nm, the ideal size for CO₂ adsorption. Concerning the effect on the furnace setup, although the temperature trend was quite similar, the scaling in the lab-pilot plant did not worsen the textural properties reached in the laboratory setup; actually, certain improvement was monitored, over 10 % of the extra surface at 750 °C and 800 °C.

The temperature effect on the chemical composition was tentatively analyzed by proximate analysis in a thermobalance to estimate the fixed carbon content, elemental analysis for the bulk composition, and XPS for surface analysis; see **Table 5.2**. According to the proximate analysis, the fixed carbon was higher in the lab-pilot plant than their counterparts prepared at the laboratory scale, roughly 66 % vs 54 %. In addition, the ashes content was lower in the lab-pilot plant. Regarding the influence of the temperature, a gradual increase of the fixed carbon is evidenced, especially in those samples prepared at the lab-pilot plant. Although the values of fixed carbon are different from the carbon content by elemental analysis, the temperature effect was further corroborated by the rise in the carbon proportion, as appreciated in the preparation of both furnaces either the bulk or surface content. The results suggest the presence of roughly 60 % of C content and low content of H. If the two set-up schemes are compared, the lab-pilot plant describes activated carbon with lower carbon content, at bulk and the surface. According to XPS, a superficial technique, around 20-30 % of superficial O was registered, the samples prepared at the lab-pilot plant being slightly more oxygenated. The temperature displayed a negative impact on the oxygen content. Although the carbon content rose with the activation temperature, the superficial oxygen was abated. This tendency has been previously reported, linked to the dehydration and elimination that occur during the carbonization reaction of K₂CO₃, releasing low molecular compounds via the cracking of chemical bonds [29].

Table 5.2. Effect of the activation temperature on the chemical composition of the activated chars

T (°C)	Reactor	Proximate analysis (%)			Bulk composition by EA (mass %)			Surface composition by XPS (mass %)			
		Volatile	Fixed Carbon	Ash	C	H	N	C	O	N	Others
700	Laboratory	11.8	52.8	35.4	65.7	2.0	1.4	60.4	23.9	2.4	6.4 (Si) 1.0 (Ti) 0.3 (Fe)
	Lab-pilot plant	12.0	64.7	23.3	58.5	1.5	1.0	51.4	30.0	1.4	7.5 (Si) 2.7 (Ti) 2.8 (Fe)
750	Laboratory	12.6	53.4	30.0	64.2	1.6	1.5	63.2	21.1	2.6	5.1 (Si) 1.2 (Ti) 2.1 (Fe)
	Lab-pilot plant	14.5	66.7	18.8	61.7	0.8	0.7	53.3	27.4	1.9	8.4 (Si) 1.0 (Ti) 4.2 (Fe)
800	Laboratory	11.5	53.8	34.7	63.5	1.4	1.3	64.6	25.7	1.8	8.8 (Si) 0.7 (Ti) 1.6 (Fe)
	Lab-pilot plant	14.1	67.0	18.8	61.7	1.0	0.0	55.6	23.6	3.3	5.3 (Si) 0.4 (Ti) 3.9 (Fe)

The chemical composition of the oxygenated groups at the surface was analyzed by deconvolution of the high-resolution XPS spectra. Concerning the C_{1s} spectra, the following contributions were considered for deconvolution: C=C (284.6 eV), C–C (285.3 eV), C–O (286.6 eV), C=O (288.0 eV), and O=C-OR (289.9 eV) [30]. In the case of the O_{1s} spectrum, it was fitted to quinone (530.7 eV), C=O (531.5–532.0 eV), and C–O (~533 eV) [31]. As illustrated in **Figure 5.3**, the temperature strongly impacted the presence of oxygenated groups. Concretely, the contribution of carbonyl groups (C=O) registered in the C_{1s} spectra increased over 750 °C, to the detriment of the presence of C–C bonds. In addition, the nature of the oxygenated groups was further analyzed by chemisorption technique with ammonia TPD. Different bands were identified according to the temperature in which they are expected to be released: carboxyl below 450°C, anhydride at 350-600°C, phenol at 500-750°C, and carbonyl-quinones at 750-1000°C [32–34]. The TPD profiles illustrated in **Figure 5.3** support the evidenced nature of the oxygenated group by XPS. It is observed that the major contribution of the groups is the sum of carbonyl and quinone. The presence of carboxylic acids was evidenced at the lowest temperature, i.e. the sample activated at 700 °C. A further rise until 800 °C contributed to eliminating these groups for the benefit of more carbonyl and quinone bonds and a slight contribution of phenolic groups, which is consistent with what was reported in the literature during the pyrolysis of carbon precursors [35].

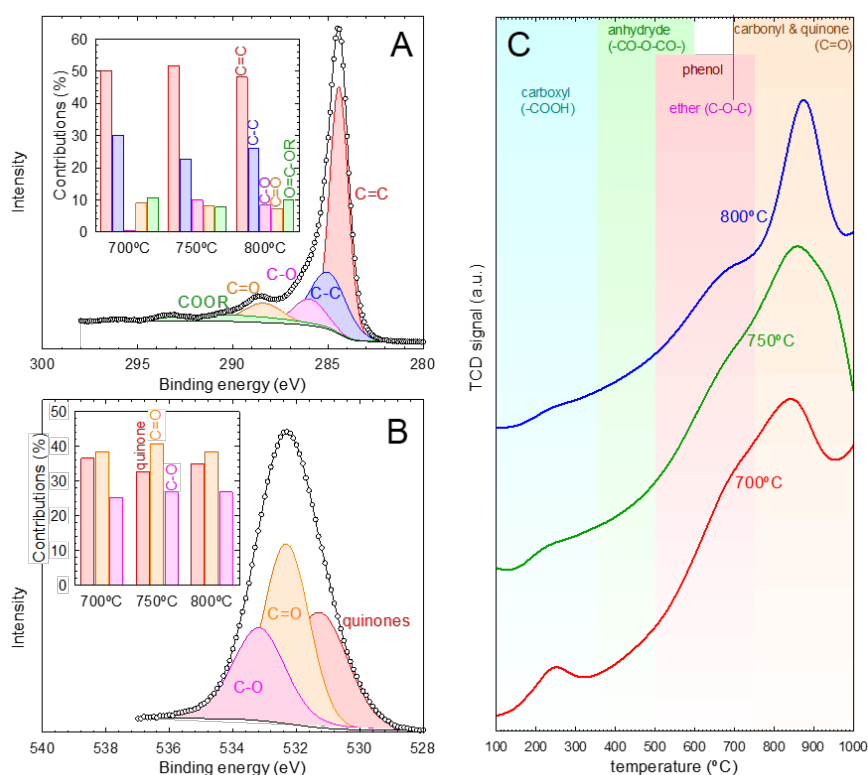


Figure 5.3. High-resolution XPS spectra of C_{1s} (A) and O_{1s} (B) of the sample prepared at the lab-pilot plant at 750°C with char: K₂CO₃ ratio of 1:1, the respective inlet figures depicting the effect of temperature on the deconvoluted contributions. TPD profiles of the prepared samples with a char: K₂CO₃ ratio of 1:1 at different temperatures (C)

Optimization of the activating ratio

After selecting 750 °C, as the optimal temperature for the activation with K₂CO₃, the influence of the proportion used in the process was assessed in both setups. The textural properties are depicted in **Figure 5.4**, and the characterization results are summarized in **Table 5.4**. Interestingly, while the laboratory furnace did not display any significant difference with the char: K₂CO₃ ratio used in the surface area and pore volume, it was not the case at the lab-pilot plant scale. During the preparation at a large scale, an outstanding difference in the definition of the total surface was observed when increasing the K₂CO₃ proportion from 1:0.25 to 1:0.50. After a further rise to 1:1. However, slight improvement was described, the little improvement appreciated does not justify the use of larger consumption of K₂CO₃. An excessive increase has been reported to have a detrimental effect on the formation of micropores as appreciated in the decrease of micropore volume under the ratio 1:2 [36].

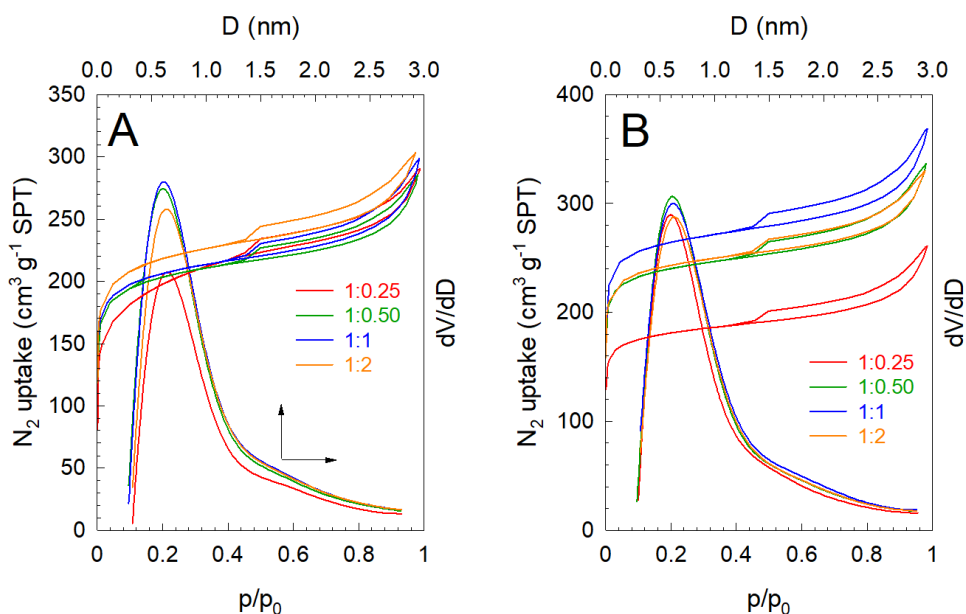


Figure 5.4. Effect of the char: K_2CO_3 ratio on the N_2 adsorption-desorption isotherms and micropore size distribution of the activated chars prepared at $750^\circ C$ at the laboratory (A) and lab-pilot plant scale (B)

Table 5.3. Effect of the char: K_2CO_3 ratio on the textural properties of the activated chars and CO_2 uptake

Char: K_2CO_3 ratio	Reactor	S_{BET} ($m^2 g^{-1}$)	S_{MP} ($m^2 g^{-1}$)	V_T ($cm^3 g^{-1}$)	V_{MP} ($cm^3 g^{-1}$)	V_{MP}/V_T (%)	q_{CO_2} ($mg g^{-1}$) at $0^\circ C$ and 1 bar
1:0.25	Laboratory	620	415	0.449	0.219	48.8	127.8
	Lab-pilot plant	631	477	0.404	0.246	60.9	160.9
1:0.5	Laboratory	640	538	0.441	0.272	61.7	154.9
	Lab-pilot plant	736	636	0.521	0.329	63.1	194.1
1:1	Laboratory	661	551	0.495	0.295	59.6	162.8
	Lab-pilot plant	781	672	0.570	0.362	63.5	194.5
1:2	Laboratory	669	556	0.469	0.290	61.8	152.7
	Lab-pilot plant	758	664	0.511	0.336	65.7	193.8

S_{BET} : total specific surface area by BET method; S_{MP} : micropore surface area by t-plot method; V_T : total pore volume from N_2 uptake at $p/p_0 \sim 0.99$; V_{MP} : micropore volume by t-plot method; q_{CO_2} : CO_2 uptake at 100 kPa and $0^\circ C$

The XPS results confirm the existence of a critical K_2CO_3 dosage in the oxygenation of the surface, as shown in **Table 5.4**. The detailed deconvoluted surface chemistry results prove that the oxygenated C percentage increased with a higher activating ratio, as reported in the literature [37]. Roughly, a proportion of K_2CO_3 higher than 1:0.5 led to 25 % for the preparation in the laboratory furnace. The oxygenated groups were more efficiently created at the larger production setup at the lab-pilot plant, i.e. 27 %, which was constant if the proportion was over 1:0.5. Since the surface properties of the prepared activated carbons are associated with oxidation-reduction reactions during the activation process, an increase in O, which is an electron donor, on the carbon surface will strongly affect the pore development of the carbon matrix [38]. The presence of C-O-K bound during the K_2CO_3 impregnation has been claimed to be reduced to C-K at the surface of the carbon precursor, followed by the generation of CO [39]. If the contribution of oxygenated species from C_{1s} analysis are compared, the rise of K_2CO_3 in the activation process seems to favor a higher formation of C-O and C=O, as portrayed in **Figure 5.5**. Moreover, the minimal proportion char: K_2CO_3 1:0.5 demonstrates from the deconvolution of O_{1s} groups to be limiting for the definition of a constant composition of their relative contributions. Regarding the results provided by the TPD technique, it is evidenced that the increase of K_2CO_3 during the activation enlarged the proportion of oxygenated species, concretely the carbonyl and quinone groups as reported in the literature when using KOH [40]. In addition, at an especially high ratio, i.e. 1:2, there is an important widening of the TPD profile to the temperatures corresponding to ethers and phenolic contribution.

Table 5.4. Effect of the char: K₂CO₃ ratio on the chemical composition of the activated chars

Char: K ₂ CO ₃ ratio	Reactor	Proximate Analysis (%)			Bulk composition by EA (mass %)			Surface composition by XPS (mass %)			
		Volatile	Fixed Carbon	Ash	C	H	N	C	O	N	Others
1:0.25	Laboratory	13.4	60.0	26.6	53.4	1.7	1.1	67.0	23.0	1.9	6.4 (Si) 0.4 (Ti)
	Lab-pilot plant	11.4	63.0	25.6	61.9	1.6	1.2	62.0	24.6	2.1	6.1 (Si) 0.4 (Ti) 1.8 (Fe)
1:0.5	Laboratory	12.1	57.1	30.8	63.5	1.7	1.2	63.4	24.5	1.9	7.1 (Si) 0.4 (Ti) 0.7 (Fe)
	Lab-pilot plant	10.0	63.1	26.9	66.6	1.4	1.3	56.2	27.2	2.2	7.8 (Si) 0.5 (Ti) 2.7 (Fe)
1:1	Laboratory	13.8	58.0	28.2	64.2	1.6	1.5	63.2	25.1	2.6	5.1 (Si) 1.2 (Ti) 2.1 (Fe)
	Lab-pilot plant	14.5	66.7	18.8	61.7	0.8	0.7	53.3	27.4	1.9	8.4 (Si) 1.0 (Ti) 4.2 (Fe)
1:2	Laboratory	12.5	59.3	28.2	57.0	1.6	1.3	61.9	25.2	2.5	6.5 (Si) 0.4 (Ti) 0.7 (Fe)
	Lab-pilot plant	9.5	71.1	18.8	60.8	71.4	1.0	58.2	27.1	2.1	7.1 (Si) 0.7 (Ti) 2.9 (Fe)

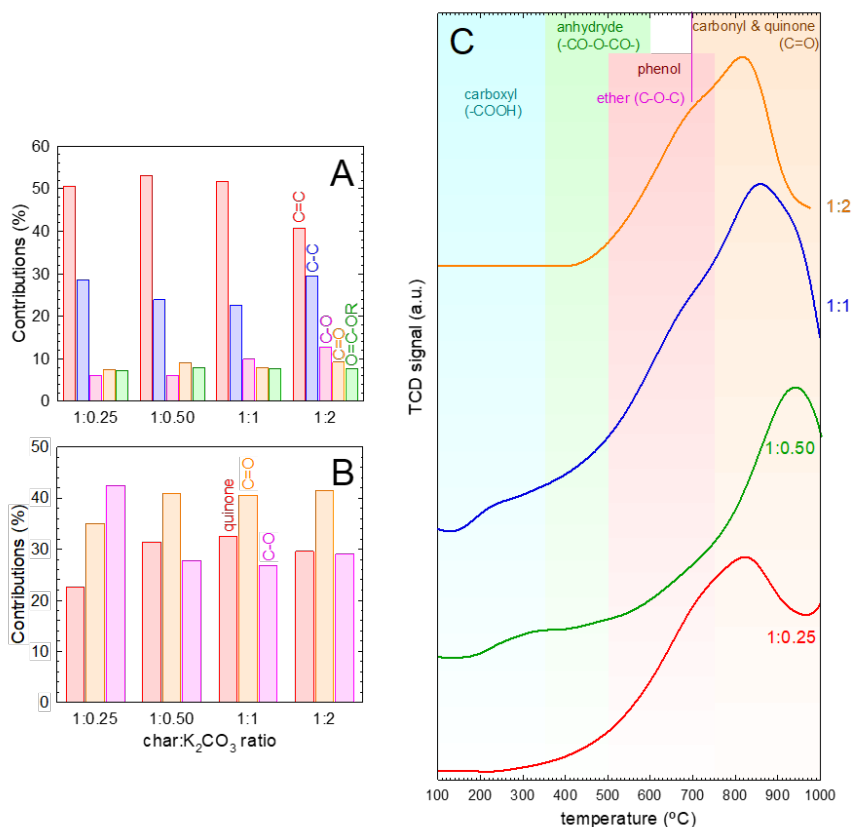


Figure 5.5. Effect of the char: K₂CO₃ ratio on the XPS surface contributions of C_{1s} (A) and O_{1s} (B) and the TPD profiles (C) of the samples prepared at 750 °C in the lab-pilot plant furnace

Influence of agitation

The effect of the agitation during the activation was evaluated in the lab-pilot plant furnace which displays the option of rotation at two different rates. The attained results, see **Table 5.5** and **Figure 5.6**, manifest a considerable improvement in the textural properties during the activation process. The speed of the agitation has been evidenced not to be of paramount importance since at the two tested speeds the BET area was roughly 1100 m² g⁻¹, which is an extra enlargement of 50 % of the static synthesis. Remarkably, this improvement did not mean a boosted micropore proportion, which was kept constant. The performance for CO₂ adsorption was impressively enhanced to circa 270 mg g⁻¹, in other words, an extra CO₂ adsorption of 40 %, ascribed to the larger surface area. This positive effect of mixture char-K₂CO₃ agitation can be explained based on the lack of melting of

K_2CO_3 below 900 °C [41]. Therefore, enhanced and intimate contact between the solid particles of char and K_2CO_3 is achieved under agitation.

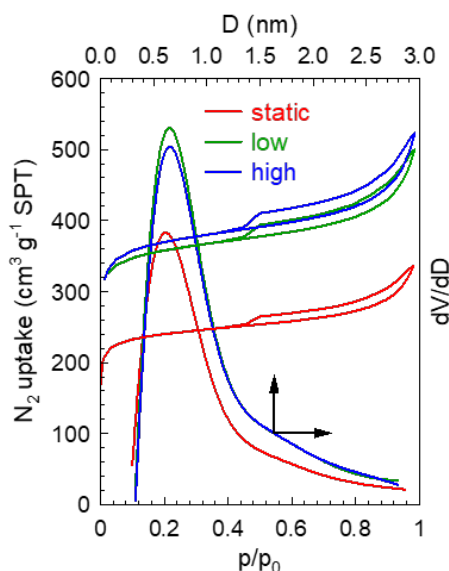


Figure 5.6. Effect of the agitation on the N_2 adsorption-desorption isotherms and micropore size distribution of the activated chars at the lab-pilot plant. Activation temperature: 750 °C, char: K_2CO_3 ratio, 1:0.50

Table 5.5. Effect of the agitation of lab-pilot plant furnace on the textural properties of the activated chars and CO_2 uptake

Agitation	S_{BET} ($m^2 g^{-1}$)	S_{MP} ($m^2 g^{-1}$)	V_T ($cm^3 g^{-1}$)	V_{MP} ($cm^3 g^{-1}$)	V_{MP}/V_T (%)	q_{CO_2} ($mg g^{-1}$) at 0°C and 1 bar
Static	736	636	0.521	0.329	63.1	194.1
Low	1096	953	0.773	0.492	63.6	271.9
High	1133	978	0.809	0.505	62.4	261.7

The agitation during the preparation in the lab-pilot plant furnace positively affected the oxygen content as suggested by XPS. The elemental analysis, see **Table 5.6**, indicates a decrease in the carbon proportion and the fixed carbon provided by the elemental analysis is also higher if the furnace was agitated. The rotation speed does not seem determinant as envisaged by the similar chemical characterization conducted by elemental analysis and XPS techniques. XPS and chemisorption techniques suggested an important contribution of carbonyl and quinone groups, as illustrated in **Figure 5.7**, followed in importance by acid carboxylic groups. The TPD profiles described an important maximum located at 900-950 °C, characteristic of carbonyl and quinone groups. This maximum is strengthened with the increase

of agitation during the activation process. Furthermore, to a much lesser extent, a timid peak regarding the contribution of carboxyl groups is defined in the TPD profile of the sample regardless of the presence of agitation in the preparation of the sample.

Table 5.6. Effect of the agitation on the chemical composition of the activated chars

Reactor	Proximate Analysis (%)			Bulk composition by EA (mass %)			Surface composition by XPS (mass %)			
	Volatile	Fixed Carbon	Ash	C	H	N	C	O	N	Others
Static	10.0	63.1	26.9	66.6	1.4	1.3	56.2	27.2	2.2	7.8 (Si)
										0.5 (Ti)
										2.7 (Fe)
Slow	11.6	75.4	13.0	72.3	0.1	1.3	56.5	26.2	2.8	7.2 (Si)
										4.2 (Fe)
										0.8 (Ti)
Fast	10.7	69.7	19.5	67.3	0.1	1.1	50.8	28.1	2.7	7.0 (Si)
										6.9 (Fe)
										1.3 (Ti)

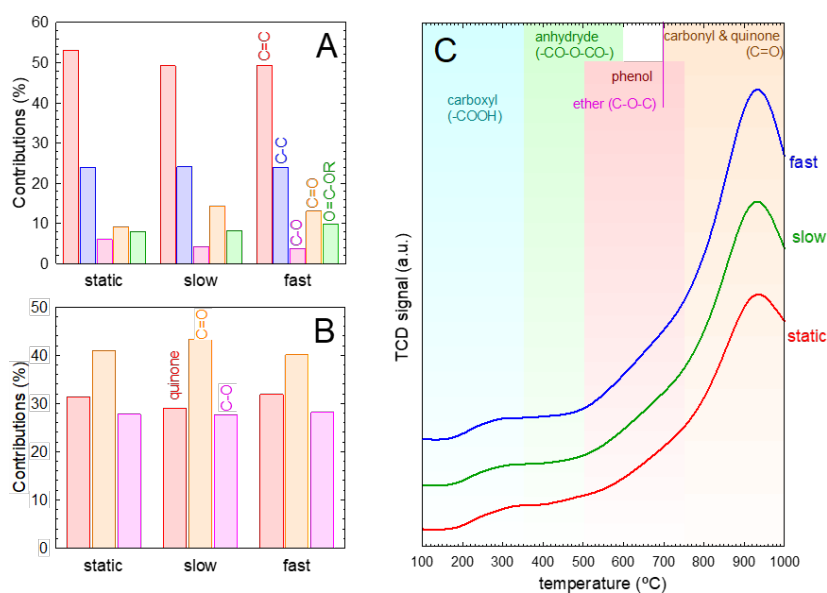


Figure 5.7. Effect of the agitation on the XPS surface contributions of C_{1s} (A) and O_{1s} (B), and the TPD profiles (C) of the samples prepared at 750 °C in the lab-pilot plant furnace

Effectiveness in the purification of biogas effluents

From the characterization results, the material char activated at 750 °C with a char: K_2CO_3 ratio of 1:0.5 prepared under slow agitation at the pilot plant scale was selected for further analysis as adsorbent in the purification of CH_4 in biogas mixtures. The behavior of CO_2 retention at different CO_2/CH_4 ratios was assessed in dynamic tests. **Figure 5.8** illustrates the breakthrough curves of CO_2 and CH_4 at a different ratio and the main characteristic parameters extracted from them are summarized in **Table 5.7**. The higher selectivity of activated carbon towards CO_2 defines first the appearance of CH_4 until the material is saturated with CO_2 . The selectivity of activated carbons to CO_2 is defined by a compromise of the textural, specifically enriched presence of microporosity, and chemical properties [42]. It has been claimed that some specific oxygenated functional groups prefer the adsorption of CO_2 over CH_4 molecules, which increases the selectivity of the material [43]. Specifically, the polar nature of these surface functionalities results in paramount importance for a boosted preference for CO_2 [44].

The difference in saturation times in the relative breakthrough curves for each component defines the operation time in which the material is saturated with CH_4 , albeit CO_2 is not. Therefore, a gas enriched with CH_4 is released. For a real practical application, the difference between both breaking times defines the operation time of the column. The released CH_4 in this period reaches a higher concentration than the inlet. **Figure 5.8** illustrates the breakthrough curves of the simultaneous adsorption of CH_4 and CO_2 . As the inlet proportion of CO_2 is raised, especially at 40 % and 80 %, the CH_4 curve does not reach a complete definition of 100 %, probably due to the limitation of the NDIR device which requires a minimum flow rate for a correct measurement. In addition, as depicted in **Figure 5.8**, the breakage times were shortened with the increase of the CO_2 concentration, affecting, especially, the CO_2 uptake which was considerably raised from 46.5 (20/80) to 83.6 $mg\ g^{-1}$ (40/60), 161.9 $mg\ g^{-1}$ (80/20). The selectivity of CO_2/CH_4 was not substantially altered, around 6. This value is within the typical range reported in the literature for commercial carbonaceous formulas, i.e. 4-6 [42,45,46], or other activated carbon prepared from biomass feedstocks [47].

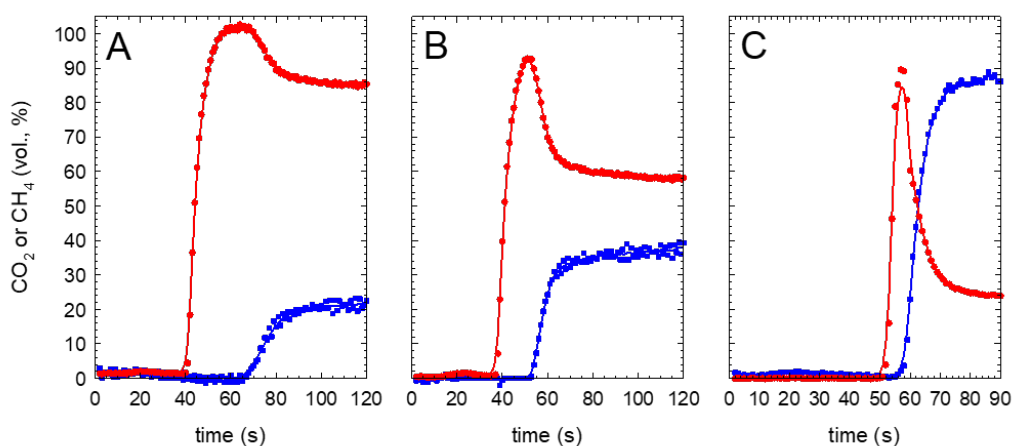


Figure 5.8. Breakthrough curves CO_2 and CH_4 with the material activated at 750°C , char: K_2CO_3 ratio 1:0.5 in the lab-pilot plant furnace under slow agitation for different CO_2/CH_4 (v/v) mixtures, 20/80 (A), 60/40 (B), and 80/20 (C)

Table 5.7. Adsorption parameters evaluated from breakthrough curves of CO_2 and CH_4 with the material activated at 750°C , char: K_2CO_3 ratio 1:0.5 in the lab-pilot plant furnace under slow agitation for different CO_2/CH_4 (v/v) mixtures

CO_2/CH_4 (v/v)	CO_2		CH_4		$S_{\text{CO}_2/\text{CH}_4}$	Y_{CH_4} ($\text{mmol g}^{-1} \text{min}^{-1}$)	CH_4 Purity (%)	CH_4 Recovery (%)
	R (%)	q (mg g^{-1})	R (%)	q (mg g^{-1})				
20/80	71.0	46.5	31.8	30.4	6.1	0.969	97.5	27.1
40/60	54.1	83.6	25.4	21.4	5.9	0.295	90.7	11.0
80/20	9.5	161.9	27.7	5.9	6.7	0.050	87.4	3.45

The effectiveness of the material was further assessed in adsorption-desorption cycles of reusing at the three CO_2/CH_4 proportions selected. The uptake of each component during each cycle is depicted in **Figure 5.9**. Generally, the material displayed a stable performance after four sequential reusing cycles at the three-proportion ratio tested. The CO_2 uptake was kept at $46.0 \pm 0.8 \text{ mg g}^{-1}$ (20:80), $83.9 \pm 1.0 \text{ mg g}^{-1}$ (40:60), and $163.8 \pm 1.9 \text{ mg g}^{-1}$ (80/20) in the fourth cycle. The CH_4 uptake was centered at the following average values: 29.5 ± 0.6 (20:80), $20.3 \pm 0.8 \text{ mg g}^{-1}$ (40:60), and $5.6 \pm 0.3 \text{ mg g}^{-1}$ (80/20). In all the cases the deviation was inferior to 5 %, which provides evidence of the great stability of the material. No significative loss of the adsorption uptake for CO_2 was registered in the sequential reusing cycles; therefore, the materials behave stable enabling it for industrial applications.

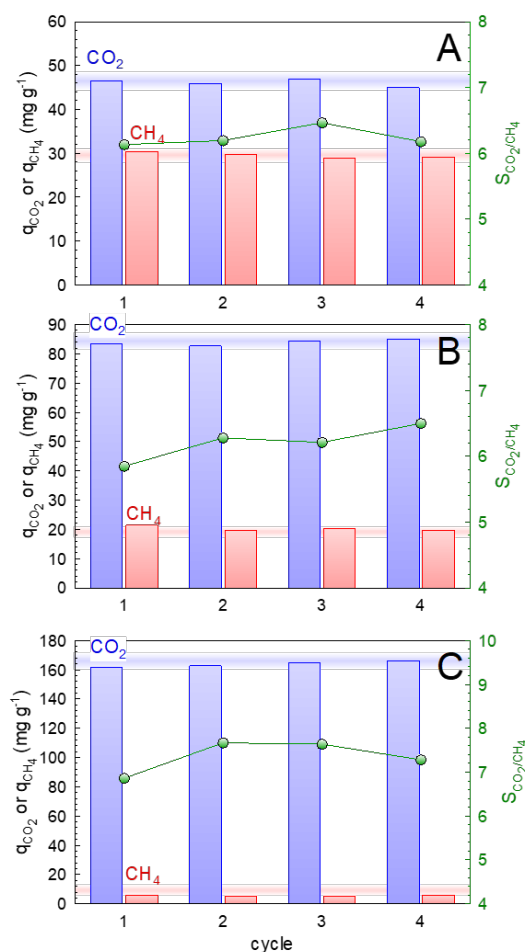


Figure 5.9. Stability of the material activated at 750 °C, char: K_2CO_3 ratio 1:0.5 in the lab-pilot plant furnace under slow agitation for different CO_2/CH_4 (v/v) mixtures, 20/80 (A), 60/40 (B) and 80/20 (C)

The selectivity values obtained for this activated carbon formula, obtained from the valorization of a char whose origin was based on plastic-enriched waste, provided selectivity values comparable to or even higher than the reported for other activated carbon formulas in the literature. **Table 5.8** summarizes the selectivity results reported in the literature for other activated carbon formulas. The value obtained for the optimum activated carbon of this work is within the most competitive values reported in the literature, i.e. 5.9. Although this selectivity is within the expected for carbon-based materials, other materials such as zeolites [48] or MOFs [49] perform better results. However, the use of activated carbon prepared from residues not only endorses the circular economy but also their preparation at a large scale is currently the most feasible at the lowest price.

The surface area and microporosity degree, as deduced from the disparity summarized in **Table 5.8**, are not the only factors that may explain the enhanced selectivity in CO₂/CH₄ mixtures, pointing out the need for chemical surface analysis. In the material prepared in this work, according to TPD and XPS analysis, carbonyl and quinone are the main oxygenated species.

Table 5.8. Comparison of CH₄/CO₂ selectivity of carbonaceous materials at atmospheric pressure

Sample	S _{BET} (m ² /g)	V _{MP} /V _T (%)	CO ₂ inlet (%)	S _{CO₂/CH₄}	T (K)	Ref.
Commercial (WV1050, MeadWestvaco)	1615	79.0	47.3	5.2	303	[50,51]
Commercial (Norit)	-	-	42	2.7	298	[52]
Commercial monolith (Mast Carbon)	483	-	50	2.0	299	[53]
Commercial (A35/4 CarboTech)	1393	-	50	3.4	293	[54]
Commercial (Desorex K43) impregnated with NaOH	815	78.9	45	2.1	298	[55]
Comercial granular (GAC 1240, Cabot Corporation)	982	62.4	50	2.7	303	[42]
Ordered mesoporous carbon	2255	-	50	3.0	298	[56]
Commercial (Desotec)	970	77.3	40	2.9	303	[57]
Plastic char activated with KOH-urea	385	44.2	40	5.0	293	[46]
Plastic char activated with K ₂ CO ₃	804	58.9	40	5.0	293	[48]
Plastic-enriched char activated with K ₂ CO ₃	1096	63.6	40	5.9	293	This work

5.1.5. Conclusions

This work demonstrates the feasibility and efficiency of chemical activation with a more sustainable agent such as K₂CO₃, much less corrosive than its traditional alkali counterpart, i.e. KOH. The resulting materials were defined by roughly 63% of microporosity. The influence of the activation temperature showed that an increase from 700 to 800 °C improved the surface area. However, the rise of the temperature negatively impacted the development of oxygenated functional groups, whose nature was carbonyl and quinonic groups. For a practical application of CO₂ adsorption, either the presence of micropores and oxygenated groups due to the electrostatic interaction between CO₂ and these groups was a crucial influence for an enhanced uptake; therefore, an intermediate temperature of 750°C (~780 m² g⁻¹ at the pilot plant kiln) was selected to define a compromise between them. The char:

K₂CO₃ ratio of 1:0.5 was selected as the minimum value for the definition of the optimum performance of the adsorbent. Higher proportions did not significantly improve the microporosity or the oxygen at the surface, being the CO₂ uptake quite similar. Hence, the minimum K₂CO₃ proportion was selected from an economic point of view. The results compared at the lab and pilot plant furnaces outlined a slight improvement at the larger scale. Interestingly, although K₂CO₃ was not melted in the working range of temperatures, the rotary agitation of the tubular kiln at the lab-pilot scale improved the surface area an extra ~50 % if compared to the static preparation, reaching values up to 1100 mg² g⁻¹. The optimum material was enabled as a potential candidate for gas adsorption applications such as the CH₄ upgrading in CO₂-CH₄ mixtures. The material displayed a selectivity value of around 6, the typical value reported in the literature for carbonaceous materials. This work proves the viability of the valorization of industrial chars from the pyrolysis of plastic-based residues at a large scale, leading to a competitive porous material for gas adsorption applications. For further consideration at the industrial scale, specific analyses including the material and the operational costs of the process during the adsorption-desorption steps require further research. Besides, from a technical point of view, the contact between the carbon precursor and K₂CO₃ salt should be optimized and the washing after activation is another critical aspect that requires further investigation.

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CRedit author statement

Ledicia Pereira: Methodology, Investigation; **Gabriel Blázquez:** Methodology, Investigation, Validation, Supervision; **Ventura Castillo:** Investigation; **Francisco Miguel González-Pernas:** Resources; Writing - Review & Editing; **María González-Lucas:** Project administration, Writing - Review & Editing; **M. Ángeles Martín-Lara:** Methodology, Investigation, Writing - Review & Editing; Project administration, Funding acquisition; **Mónica Calero:** Conceptualization, Methodology, Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition; **Rafael R. Solís:** Methodology, Formal analysis; Investigation; Supervision; Writing - Original Draft; Writing - Review & Editing.

5.1.6. References

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Chapter 6. Conclusions and Future Work

The conclusions for each section of this thesis are discussed in the following paragraphs.

The study entitled *Conversion of char from pyrolysis of plastic wastes into alternative carbons for heavy metal removal* confirms that activated carbons (ACs) derived from post-consumer mixed plastic waste exhibit strong adsorption capabilities for heavy metal removal from aqueous solutions. Among the tested activation agents, sodium carbonate (Na_2CO_3) proved the most effective, producing an activated carbon ($\text{Na}_2\text{CO}_3\text{-AC}$) with a specific surface area of $571 \text{ m}^2 \text{ g}^{-1}$ and the highest proportion of oxygenated surface groups (12.6 %). The relatively low microporosity (41.3 %) suggests that mesoporosity plays a crucial role in adsorption performance.

In terms of metal uptake efficiency, lead (Pb^{2+}) demonstrated the highest adsorption affinity, reaching a maximum uptake of 40 mg/g in synthetic water, followed by cadmium (Cd^{2+}) and copper (Cu^{2+}) at 13 mg g^{-1} and 12 mg g^{-1} , respectively. Column adsorption experiments revealed saturation times of 290 min for Pb, 16 min for Cd, and 80 min for Cu, with corresponding adsorption capacities of 26.8 mg/g , 4.1 mg g^{-1} , and 7.9 mg g^{-1} . The adsorption process appears to be primarily physical, given the limited presence of carboxyl functional groups, suggesting that post-modification strategies could further enhance adsorption efficiency.

When applied to real agrochemical wastewater, the adsorption capacity of $\text{Na}_2\text{CO}_3\text{-AC}$ decreased due to the complex composition of industrial effluents. The presence of competing metal ions such as Cr, Mn, Zn, and Cu significantly affected efficiency, with Cu uptake recorded at 2.531 mg g^{-1} in a low-pH copper oxychloride wastewater (WW1) and 1.132 mg g^{-1} in a general industrial wastewater with multiple contaminants (WW2). Compliance with wastewater discharge regulations requires increasing the adsorbent dose to 0.935 g (compared to 0.5 g in experiments) to meet legal limits in a 15-minute continuous operation cycle.

The work *Plastic waste to carbon adsorbent: activation with sodium carbonate and functionalization with citric acid* proposes the introduction of oxygenated surface groups via citric acid (CA) functionalization further enhances adsorption properties, particularly for heavy metal removal. The maximum Pb^{2+} uptake increased from $\sim 37 \text{ mg g}^{-1}$ (activated carbon) to $\sim 52 \text{ mg g}^{-1}$ after functionalization. However, this modification had minimal impact on acetaminophen adsorption, with a maximum uptake of $\sim 80 \text{ mg g}^{-1}$ remaining unchanged. The presence of carboxyl and carbonyl functional groups, confirmed through X-ray photoelectron

spectroscopy (XPS) and thermal programmed desorption (TPD), plays a key role in metal ion adsorption.

From an economic and environmental perspective, Na_2CO_3 activation reduces pollutant removal costs, making the adsorption process more economically viable. However, citric acid functionalization increases preparation costs, requiring an optimal concentration balance to maintain efficiency without excessive cost. LCA results indicate that while Na_2CO_3 activation slightly increases the environmental footprint compared to untreated char, citric acid modification significantly amplifies environmental impact due to higher chemical and energy consumption. Additionally, potential metal leaching from plastic-derived adsorbents presents a risk of secondary pollution, necessitating further evaluation before large-scale implementation.

The study *Transforming a mixture of real post-consumer plastic waste into activated carbon for biogas upgrading* demonstrates the feasibility of converting non-recyclable post-consumer plastic waste into activated carbon for CO_2 adsorption and biogas upgrading. The pyrolysis temperature and choice of chemical activation agent were found to be key factors influencing textural properties and adsorption performance.

Among the evaluated conditions, pyrolysis at 500 °C resulted in superior textural properties compared to 450 °C, leading to enhanced adsorption capacity. Chemical activation performance varied significantly, with potassium carbonate (K_2CO_3) achieving the highest CO_2 uptake (130.2 mg g⁻¹ at 273K) and micropore volume (0.307 cm³ g⁻¹), followed closely by potassium hydroxide (KOH) (125 mg g⁻¹ at 273 K), though KOH is more corrosive and environmentally hazardous. In contrast, sodium-based activators (Na_2CO_3 and NaOH) exhibited lower adsorption capacities, while zinc chloride (ZnCl_2) and ferric chloride (FeCl_3) resulted in poor textural development and CO_2 adsorption efficiency.

CO_2 uptake was strongly correlated with ultramicropore volume (<1 nm) and the presence of oxygenated functional groups. Dynamic adsorption tests confirmed that K_2CO_3 -activated carbon displayed superior CO_2 selectivity over CH_4 , making it a suitable candidate for biogas upgrading. The adsorption performance of K_2CO_3 -activated carbon was comparable to commercial zeolites, although with lower CH_4 purity and recovery. Furthermore, the material demonstrated stable adsorption capacity over five regeneration cycles, reinforcing its potential for industrial application.

The work *Promoting the circular economy: valorization of a residue from industrial char to activated carbon with potential environmental applications as adsorbents* presents that the chemical activation of industrial and agroforestry char residues has significant potential for developing highly microporous carbonaceous

materials, offering promising applications in environmental remediation, particularly for gas and liquid effluent treatment.

In terms of CO₂ capture, the adsorption capacity was primarily governed by the microporosity developed during KOH activation, with pore volumes predominantly consisting of micropores (~0.5 nm). The efficiency of CO₂ adsorption was also influenced by the presence of oxygen-containing surface functional groups, which played a critical role in enhancing uptake performance.

For the removal of heavy metals from aqueous solutions, the adsorption capacity was moderate due to the limited mesoporosity of the materials. Lead (Pb²⁺) exhibited the highest adsorption capacity, reaching saturation uptakes of approximately 20 mg g⁻¹.

In contrast, the removal of emerging organic contaminants, including acetaminophen, caffeine, and diclofenac, demonstrated significantly higher efficiencies. Saturation capacities ranged from 200 to 500 mg g⁻¹, positioning these materials as competitive alternatives for practical applications. The adsorption kinetics followed a pseudo-second-order model, indicating rapid adsorption rates suitable for real-world implementation.

Within the section titled *On the physical activation of biomass and urban waste chars for water treatment and CO₂ adsorption*, the porosity developed using physical activation with CO₂ was moderate, with surface areas ranging from 340 to 370 m² g⁻¹ and a significant contribution of microporosity, exceeding 70 %. Characterization using X-ray photoelectron spectroscopy (XPS) and chemisorption revealed the presence of carbonyl and quinone functional groups. These characteristics suggest that the material is highly efficient for CO₂ adsorption, making it a promising candidate for practical applications in CO₂ capture and storage, particularly in post-combustion effluents, owing to its high microporosity.

Nevertheless, physical activation with CO₂ did not produce formulations that were as competitive for water treatment as those obtained through chemical activation, especially when using aggressive chemicals such as alkalis. The maximum lead (Pb) uptake achieved was 25.5 mg g⁻¹, while the highest caffeine removal was 17.1 mg g⁻¹. Performance in fixed-bed column tests indicated that the regeneration process influenced the adsorption capacity during subsequent cycles; however, after an initial stabilization period post-regeneration, the material demonstrated stable performance.

Although these uptake values may be classified as low to moderate, depending on the nature of the polluted effluent, the physically activated materials may still be suitable, as the concentrations of emerging contaminants are often in the low parts-per-billion (ppb) range or lower, far from the saturation uptake levels of the

prepared adsorbents. The limitations associated with these materials could be significantly mitigated by the advantages of the physical activation process, such as the avoidance of aggressive and toxic chemicals, like alkalis, and the elimination of additional washing steps to remove chemical residues. Therefore, physical activation methods could serve as a viable alternative for developing a more sustainable and environmentally friendly activation process.

The study *Unraveling the lab-scaling up production of activated carbon from plastic-enriched waste* demonstrates the feasibility of chemical activation using sustainable agent, such as K_2CO_3 , which is considerably less corrosive compared to its traditional alkaline counterpart, KOH. The resulting materials exhibited an approximate microporosity of 63 %. The influence of the activation temperature showed that increasing the temperature from 700 to 800 °C enhanced the surface area. However, the rise in temperature negatively impacted the development of oxygenated functional groups, which were identified as carbonyl and quinonic groups.

For practical applications in CO_2 adsorption, both the presence of micropores and oxygenated groups were crucial, due to the electrostatic interaction between CO_2 and these groups, which promoted an enhanced uptake. Therefore, an intermediate temperature of 750 °C ($\sim 780 \text{ m}^2/\text{g}$ in the pilot plant kiln) was selected as a compromise between these factors. A char: K_2CO_3 ratio of 1:0.5 was chosen as the minimum value for defining the optimal performance of the adsorbent. Higher ratios did not significantly improve the microporosity or the oxygen content on the surface, resulting in a similar CO_2 uptake. Hence, the minimum K_2CO_3 proportion was selected from an economic standpoint.

The results comparing the laboratory and pilot plant furnaces highlighted a slight improvement at the larger scale. Interestingly, although K_2CO_3 did not melt within the working temperature range, the rotary agitation of the tubular kiln at the laboratory-pilot scale enhanced the surface area by an additional $\sim 50 \%$ compared to static preparation, reaching values of up to $1100 \text{ m}^2 \text{ g}^{-1}$. The optimal material was identified as a potential candidate for gas adsorption applications, such as CH_4 upgrading in CO_2 - CH_4 mixtures. The material displayed a selectivity value of around 6, which is the typical value reported in the literature for carbonaceous materials.

Besides particular conclusions for each section, the following *overall conclusions* are discussed.

This thesis has demonstrated the feasibility of the valorization of pyrolytic char produced from low quality residues into adsorbent materials.

Focusing on the different contaminants studied, it can be stated that heavy metals are best adsorbed by materials with mesoporous surface, due to the ionic size of

metals. The high presence of surface oxygenated groups is also important. It has been demonstrated that environmentally friendly chemicals such as Na_2CO_3 can substitute more harmful chemical such as KOH or NaOH for the activation process when the application is heavy metals removal. The best results for heavy metal adsorption were obtained using the material produced from rejected fraction of post-consumer plastic waste and activated with Na_2CO_3 , displaying an adsorption capacity of 40 mg g^{-1} for lead. This material presented the previously described characteristics of mesoporosity and presence of surface oxygenated groups. Adsorption capacity for lead of the same material but modified with citric acid was 52 mg g^{-1} , however, its usability has been questioned in this thesis due to a higher cost of the material per quantity of lead adsorbed, besides the increased environmental impact.

Considering the results of this thesis, the assumption that CO_2 is best adsorbed in materials with elevated microporosity and surface oxygenated groups was demonstrated. The best values for CO_2 adsorption capacity were obtained by the material produced from cellulose casings and activated with KOH, which produced a high volume of micropores due to the aggressive action of KOH. The percentage of surface oxygenated groups was also high. The material presented an adsorption capacity of CO_2 of 210.3 mg g^{-1} at 273 K and ambient pressure

In terms of contaminants of emerging concern, the most important factor is the development of high porosity with independence of porous size. The best adsorption results were obtained with the material olive stone activated with KOH, which corresponds with the value of highest porosity obtained among all the precursors and activation methods used, with a BET surface of $1186.8 \text{ m}^2 \text{ g}^{-1}$. Adsorption capacity of this material for the different contaminants of emerging concern tested ranged between $400\text{--}500 \text{ mg g}^{-1}$.

Comparing chemical and physical activation methods, physical activation method resulted in a lower porosity development, mostly of microporous type. Although the decrease in BET surface is noticeable, this did not affect the CO_2 adsorption in a great extent, obtaining close values to those obtained with KOH. This is probably due to the presence of microporosity. Therefore, CO_2 activation might be a good alternative to KOH for carbon dioxide adsorption. For heavy metals and CEC, physical activation did not reach a good performance.

Regarding the different waste precursors used, those with biomass origin tend to form materials with higher porosities. If the materials olive stone and SRF are compared, both in chemical and physical activation, the latter develops a lower BET surface. SRF contains plastic whose surface might be more difficult to degrade in order to develop the porosity. Analyzing the material rejection of post-consumer plastic waste activated with KOH, the porosity is also lower to biomass precursors

activated with KOH. The nature of the porosity tends to be microporous in biomass precursors.

For the industrial applicability, it is interesting to study the cost of the different materials, the reusability and possibility of leachates in the adsorption process. A techno-economic analysis was performed in chapter 3 for the material obtained from the rejected fraction of post-consumer plastic activated with Na_2CO_3 . The calculated cost was 13.8 € per kg of product produced, which is slightly higher when compared with market values. However, it must be said that costs were calculated using data gathered from experiments at small scale. Costs usually decrease at large-scale production.

In terms of reusability, the tested carbons had an excellent regeneration capability when used in gas effluents. In contrast, the adsorption capacity when used in aqueous streams decreased in the first cycle but remained constant in second and third cycle.

Regarding leachates in plastic-derived chars, the components that are lixiviated to a larger extent, such as Ca, P, Si, and Ti, do not display any problems for environmental applications in water due to the lack of toxicity. In contrast, the metals that might compromise the toxicity of the released effluent were detected at low concentrations, bearing in mind that the presented data to a solid–water (m/v) ratio of 1:10, an abnormally high dosage for the application.

Lastly, improvements in the set-up for industrial application, such as rotatory activation kilt, were tested, demonstrating that the use of such set up improves the textural properties of the material due to a better mixing of the precursor with the activation agent.

To conclude, it is necessary to discuss *the future work needed* to ensure the application of the developed materials in real environments.

Although the study confirms the feasibility of the developed materials for water and gas treatment, further research is required to optimize the balance between adsorption efficiency, cost-effectiveness, adsorption selectivity and environmental sustainability. Exploring alternative activation and functionalization methods with lower environmental impact and strategies to mitigate metal leaching will be crucial for large-scale adoption.

Further studies on adsorbent regeneration and reuse will be critical to ensure the sustainability of these materials, especially in aqueous treatment applications, where regeneration appears to be less efficient. The disposal of spent activated carbon, especially after use in adsorbing contaminants, can be problematic. Regenerating or recycling spent carbon adds complexity to the industry.

Additionally, optimizing the contact between the carbon precursor and the activating agent, as well as the post-activation washing process, represents another critical aspect that requires further research.

Maintaining consistent quality across batches of activated carbon can be challenging when the quality of the raw material or wastes vary. Lack of standardization in the industry can result in inconsistent performance in the end applications.

Appendix: Journals Metrics

Extracted from **Journal Citation Reports (JCR)**

Impact factor	Area	Rank	Quartile	Percentile	Year
Paper 1: Conversion of char from pyrolysis of plastic wastes into alternative activated carbons for heavy metal removal					
Journal: Environmental Research					
7.7	Environmental Sciences	36/358	Q1	90.1	2023
	Public, Environmental & Occupational Health	16/408	Q1	96.2	2023
Paper 2: Plastic Waste to Carbon Adsorbent: Activation with Sodium Carbonate and Functionalization with Citric Acid					
Journal: Applied Sciences					
2.5	Multidisciplinary Engineering	44/181	Q1	76.0	2023
	Multidisciplinary Chemistry	115/231	Q2	50.4	2023
Paper 3: Transforming a mixture of real post-consumer plastic waste into activated carbon for biogas upgrading					
Journal: Process Safety and Environmental Protection					
6.9	Chemical Engineering	22/170	Q1	87.4	2023
	Environmental Engineering	16/81	Q1	80.9	2023
Paper 4: Promoting the circular economy: Valorization of a residue from industrial char to activated carbon with potential environmental applications as adsorbents					
Journal: Journal of Environmental Management					
8	Environmental Sciences	35/358	Q1	90.4	2023

Impact factor	Area	Rank	Quartile	Percentile	Year
Paper 6: Unraveling the lab-scaling up production of activated carbon from plastic-enriched waste					
Journal: Journal of Cleaner Production					
9.8	Environmental Sciences	24/358	Q1	93.4	2023
	Environmental Engineering	9/81	Q1	89.5	2023
	Green & Sustainable Science & Technology	13/91	Q1	86.3	2023

