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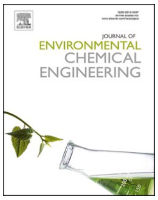

Pilot-scale assessment of modified activated carbon for minimizing disinfection by-products in freshwater

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ABSTRACT

Water purification is essential to ensuring access to drinking water and safeguarding the health of both livestock animals and humans. One of the most common methods to purify water in drinking water treatment plants (DWTPs) is chlorination and chlorine dioxide. However, these processes can produce undesirable and potentially harmful by-products, such as chlorite (ClO_2^-) and chlorate (ClO_3^-). While granulated activated carbon (GAC) is classically and effectively employed to eliminate many hazardous contaminants, it exhibits inadequate efficiency in the removal of ClO_2^- and ClO_3^-. In an attempt to improve the current methods, a GAC has been here modified with an alkylquaternary ammonium-based surfactant, the 1-hexadecylpyridinium chloride monohydrate (CPC). Upon the selection of the best reaction conditions in terms of surfactant functionalization, reaction time and the prevention of pellets breakage, the synthesis of the modified carbon (CPC@GAC) was successfully scaled up to kilograms. Then, a pilot scale experiment was performed in a DWTP filling a 0.21 m^3-column bed with the CPC@GAC material. When using real water flows (with corresponding to empy bed contact times-EBTC of 3.9, 5.2, 7.8 and 15.5 min), the time to reach 50 % of saturation ($t_{50\ \%}$) was 6.0, 22.9, 22.0 and 54.8 days, respectively. These values surpass those obtained with non-modified GAC, thereby demonstrating the practical applicability of this modified adsorbed in water disinfection treatments.

1. Introduction

Drinking water is essential for human life. Water covers 70 % of our planet, and it is easy to fall into the misconception that it will remain an abundant resource indefinitely. However, inadequate sanitation led to 2.4 billion people worldwide exposed to diseases, such as cholera and typhoid fever, and other water-borne illnesses [1]. Thus, drinking water purification is crucial to life, as directly impacts both public health and environmental well-being. The most prevalent method employed in water purification is water disinfection, which primarily focuses on oxidizing organic matter and neutralizing harmful bacteria, viruses, and other pathogens [2,3]. Chlorination and the use of chlorine dioxide are two of the most widely used and effective strategies for disinfecting water in drinking water treatment plants (DWTPs) [4]. They are highly effective oxidizers, capable of eliminating 99.99 % of bacteria and viruses with minimal doses (6–70 $mg \cdot min^{-1} \cdot L^{-1}$) [5]. Nonetheless, disinfection processes can also produce undesirable and potentially harmful by-products, including chlorite (ClO_2^-) and chlorate (ClO_3^-), as a result of the disproportionation of the disinfecting agents [4,6]. Despite the low toxicity of these oxyanions (*i.e.,* oral lethal dose 50 (LD_{50}) of ClO_3^- is 50 $mg \cdot kg^{-1}$ in humans), recent studies relate their presence in potable water with chronic illnesses (*i.e.,* hormonal disorders or abnormal high concentration of methemoglobin) [7,8]. Considering the information above mentioned, the European Council has recently established a maximum allowable concentration of 0.25 $mg \cdot L^{-1}$ for both ClO_2^- and ClO_3^- in water intended for human consumption [9]. Therefore, it is crucial to develop solutions to reduce the level of these oxyanions in drinking water.

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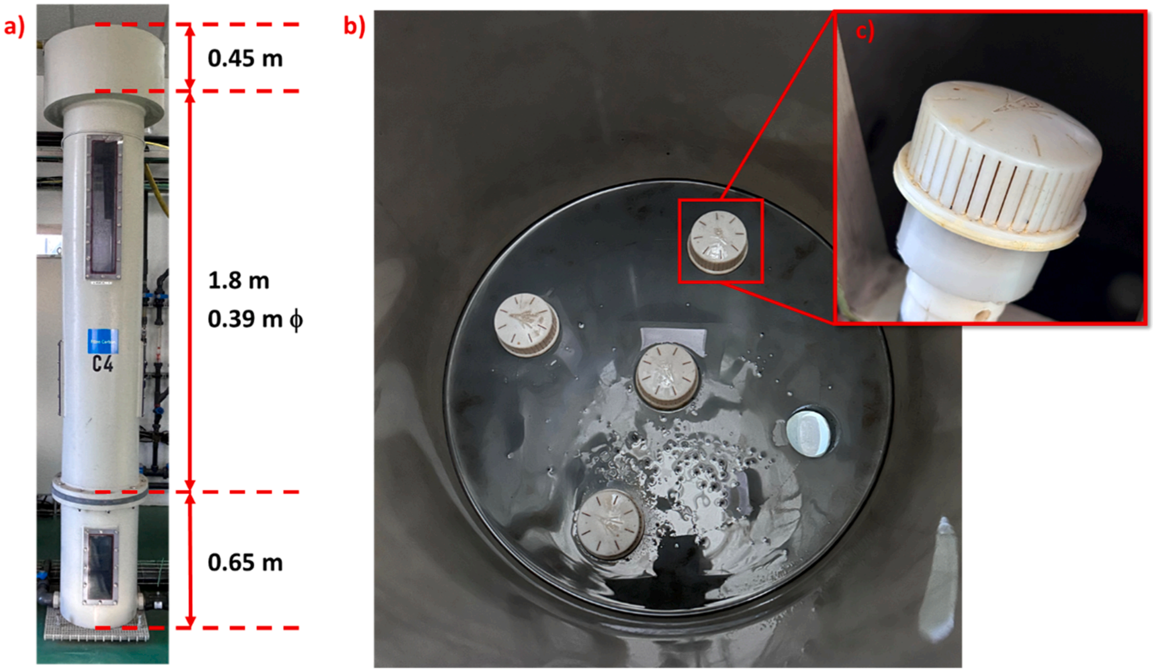


Fig. 1. Pilot scale column used in a DWTP of Canal de Isabel II S.A., M.P. (Madrid, Spain), a) adsorption column system, b) button section equipped with drain nozzles, and c) drain nozzles.

Although the best way to reduce the presence of ClO_2^- and ClO_3^- is to prevent their formation during drinking water purification, there is no established method to eliminate these potentially harmful oxyanions once formed. In this regard, several post-chlorination technologies have been suggested for eliminating them, including ion exchange, membranes, reductant species, bioreactors, and heterogeneous catalysis [10-15]. However, their widespread use is limited due to challenges related to complex implementation and maintenance, high costs, and/or inadequate durability, which highlights the need to explore alternative solutions.

Beyond the aforementioned strategies, adsorption is considered the most effective technique for efficiently removing trace contaminants from water sources, thanks to its low cost and high effectiveness. As the demand for better water quality grows, there is an increasing need for more advanced adsorbents with enhanced properties to meet stricter water quality regulations. Adsorbent materials (*i.e.,* activated carbon) in various forms have been utilized for centuries in water treatment and as detoxifying pharmaceutical agents in medical applications [16]. A review of the currently employed methods reveals that granulated activated carbon (GAC) filters are extensively used to remove class I compounds (organic compounds responsible for taste, odor and color issues). Besides, GAC material shows a high affinity to remove ClO_2^-, but an inadequate effectiveness for ClO_3^- [17-19]. Granulated iron hydroxide, activated alumina, and zeolite are other popular adsorbents [20-22]. Particularly, GAC is considered a proper adsorbent for water treatment due to its advantageous properties: low-cost effectiveness and availability (the adsorbent accounting for 70 % of the operational cost); ease procurement and transportation to treatment plants; chemical and mechanical stability; favorable textural properties (*i.e.*, high surface area); important adsorption capacity and efficiency; fast kinetics and potential for regeneration and reuse [23]. Considering that activated carbon beds are vastly implemented in DWTPs, the modification of the GAC (currently used in the upgrading of wastewater treatment plants) appears as a promising option. Recently, we have reported the modification of two GACs with five different quaternary ammonium-based surfactants [24]. A GAC modified with 1-hexadecylpyridinium chloride monohydrate (CPC) was selected as the most efficient adsorbent demonstrating its potential under continuous flow conditions and recyclability (4-cycles of 160 h-each, eliminating 100 and 50 % of ClO_2^- and ClO_3^-, respectively). To bridge the lab-scale to industrial-scale, here we report the synthesis of a GAC modified with CPC surfactant (named as CPC@GAC) at kilogram scale, and its implementation in a pilot plant scale of a real DWTP. Initially, the reaction conditions for the preparation of CPC@GAC were studied by modifying the molar ratio of GAC and CPC. Then, the synthesis was scaled up to the kg-scale, and the as-prepared CPC@GAC was used to fill a column of a DWT pilot plant with 145 L capacity. Then, the ClO_2^- and ClO_3^- removal capacity was evaluated under continuous water flow using the same operational parameters typically used in DWTPs.

2. Materials and methods

All reactants and solvents were commercially obtained and used without further modification. Commercial granulated charcoal activated carbon (GAC) was purchased from Scharlau; and industrial GAC, AquaSorb 2000 (12 × 40 mesh), was supplied by Jacobi Carbons España S.L. 1-Hexadecylpyridinium chloride monohydrate (CPC, 96–101 %) was purchased from Fisher Scientific S.L. Sodium chlorite ($NaClO_2$, 80 %) and sodium chlorate ($NaClO_3$) were purchased from VWR International, S.L. Sodium carbonate (Na_2CO_3) solution (72 mM in water for Metrosep A Supp 7) was purchased from Sigma Aldrich. Deionized water was acquired from Serviquimia S.L. The pilot scale experiments were developed at the DWTP of Colmenar Viejo with water samples supplied by Canal Isabel II S.A., M.P. (Spain).

2.1. *Optimization of the surfactant-modified activated carbon*

Activated carbon is the traditional material used in water treatment processes, with 42.3 % of its total production dedicated to this application [25]. In pursuit of enhancing the performance of currently used materials in DWTPs, the functionalization of commercial GAC was performed based on a method previously reported by some of us [24]. Briefly, a commercially available GAC was suspended in a CPC cationic surfactant aqueous solution for 5 h. Finally, the mixture was filtered to obtain the CPC@GAC material. The design of the best synthetic strategy was optimized considering several parameters (reagents concentration, stirring and time), and quantifying the cationic surfactant functionalization degree and the reaction yield (Supporting Information-SI, Section S1). The quantification of the surfactant functionalization was performed by elemental analysis (EA) and thermogravimetric analysis (TGA).

In the optimized synthesis, 17 mmol (5.79 g) of CPC were dissolved in 100 mL of deionized water under stirring (400 rpm) for 15 min. Then, 2.13 mol (25.5 g) of commercial GAC (molar ratio CPC:GAC:H_2O 1:125:327) were added to the previously prepared solution at room temperature, and the resulting mixture was left to evolve for 5 h. The CPC-modified activated carbon (CPC@GAC) was collected by filtration under vacuum and washed with 300 mL of Milli-Q water in order to eliminate the excess of surfactant used during the impregnation. The modified CPC@GAC material was dried at 100 °C overnight. A total of 0.38 ± 0.01 mmol CPC·g^{-1} GAC was obtained, corresponding to a 59.2 % reaction yield (based on GAC·H_2O and estimated with EA). The optimized procedure was repeated using the industrial GAC, achieving 0.29 ± 0.02 mmol CPC·g^{-1} GAC (reaction yield of 45.9 %, based on GAC·H_2O and estimated with EA).

2.2. *Scale-up synthesis*

The scale-up synthesis was performed in a pilot-scale 300 L polyethylene terephthalate (PET) vessel. 11 kg (0.031 kmol) of CPC were dissolved in 180 L of distilled water under stirring for 10–15 min. Then, under static conditions (without stirring) 46 kg (3.83 kmol) of industrial GAC (molar ratio CPC:GAC:H_2O 1:125:327) were added to the previously prepared solution at room temperature, and the reaction was left to evolve for 5 h. The CPC@GAC was collected by filtration and washed with 200–225 L of deionized water in order to eliminate the excess of CPC used during the impregnation. The quantity of CPC in industrial activated carbon during the scale-up material was 0.28 ± 0.05 mmol CPC·g^{-1} GAC (reaction yield of 42 % based on CGA·H_2O and estimated with EA data). Space time yield (STY) of 736 kg·m^{-3}·day^{-1} were calculated considering the total reactor volume. The material was further characterized by TGA and N_2 sorption measurements.

2.3. *Column set-up and pilot plant study*

The purification pilot scale study was carried out using the facilities of the DWTP of Colmenar Viejo of Canal de Isabel II S.A., M.P (Madrid, Spain). A pilot scale column, with an effective volume of 0.21 m^3, was utilized for the elimination of ClO_2^- and ClO_3^-. The column dimensions were an inner diameter of 0.39 m and total height of 2.90 m, formed by a headspace of 0.45 m, an effective total length of 1.8 m and a bottom section of 0.65 m. The bottom section was equipped with drain nozzles, facilitating the separation and retention of the CPC@GAC or GAC pellets (Figs. 1 and S11). The pelletized material was charged inside the column and prior to the adsorption test, the column was cleaned with 200 L of deionized water for 19 h under static conditions, and then, 200 L during 30 min under flow conditions in order to eliminate the excess of CPC. The presence of leached CPC was discarded by UV–vis analysis (limit of detection = 0.0017 mM). Although The column was filled with 80 kg of CPC@GAC or GAC (used as control), occupying a total bed height of 1.2 m, corresponding to a volume of 0.145 m^3 (145 L). As normally found in DWTPs, the water inlet was positioned at the upper section of the column, while the effluent was continuously discharged from the bottom of the column through an overflow mechanism. The column was fed with real drinking water previously doped with ClO_2^- and ClO_3^- (concentrations ranging from 0.18 to 0.25 mg·L^{-1}). Different flow rates (9.3, 18.5 and 27.8 L·min^{-1}) were evaluated using CPC@GAC, working during 7.3, 31, 41.45 and 93 days, respectively. These values correspond to a total of 194, 1241, 1104 and 1245 m^3 of water flew through the column, respectively. It is important to highlight that no recirculation of water was used and the pilot scale system was designed to achieve real plant operating conditions with empty bed contact times (EBTC) in the range of 3.9, 5.2, 7.8, and 15.5 min, as typically employed in real conditions [26,27]. At certain intervals of time (3 samples *per* day during 93.1 days), an aliquot of 10 mL was collected after passing through the column, filtered in nylon (0.22 µm), and analyzed by IC. The pH value was monitored (ranging from 6.75 to 6.90) but not controlled along all the process.

2.4. *Physicochemical characterization and water analysis*

TGA were performed on a SDT Q-600 thermobalance (TA Instruments, New Castle, USA) under air flow (100 mL·min^{-1}) from room temperature to 700 °C with heating profile of 5 °C·min^{-1}. EA were performed in a Flash 2000 analyzer (Thermo Scientific). N_2 sorption isotherms were collected at 77 K using a Micromeritics TriStar II PLUS surface area and porosity analyzer. Previously, the materials were outgassed at 200 °C for GAC and 100 °C for all the CPC@GAC samples, under primary vacuum for 16 h. The surface area was determined by the Brunauer-Emmett-Teller (BET) equation in the relative pressures $p/p_o < 0.03$. Pore size distribution and pore volume were estimated by the Horvath-Kawazoe (HK) method using a sphere geometry model (p/p_o = 0–0.98). Besides, the external surface, microporosity area and volume were calculated by the *t*-plot method (p/p_o = 0.3–0.6).

2.5. *Ionic Chromatography (IC)*

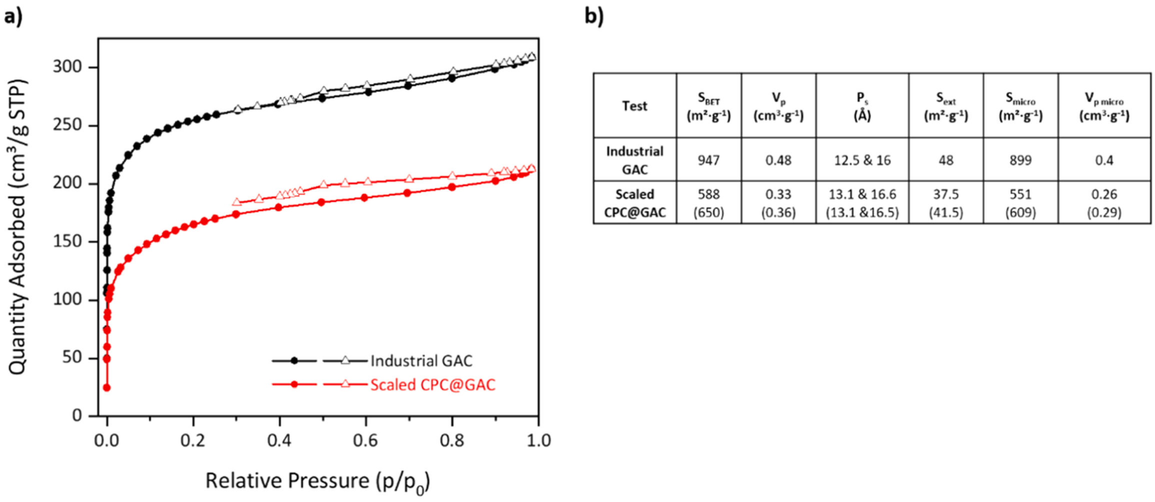
The anions content in water was analyzed using a 930 Compact IC Flex (Metrohm Hispania Spain), equipped with a 919 IC autosampler plus, and STREAM sequential suppressor. Samples were retained in a Metrosep A Supp 7 column (5 µm, 250 nm x 4 mm, Metrohm Hispania, Spain). The column was also equipped with a Metrosep A Supp 5 Guard pre-column (5 µm, 5 mm × 4 mm, Metrohm Hispania, Spain) and a Metrosep A Supp 16 S-Guard post-column (4.6 µm, 5 mm × 4 mm, Metrohm Hispania, Spain). Analyses were performed using a flow rate of 0.7 mL·min^{-1}, at 45 ºC and with an injection volume of 100 µL. The retention times for F^-, ClO_2^-, Cl^-, NO_2^-, Br^-, ClO_3^-, NO_3^-, and SO_4^{2-} were 6.94, 9.51, 11.07, 13.52, 16,52, 17.96, 19.74, and 30.58 min, respectively.

3. Results and discussion

3.1. *Optimizing surfactant impregnation*

The design of the best synthetic strategy was optimized considering three main parameters: molar ratio GAC:CPC, the reaction time and the impact of stirring during the reaction. Here, we discuss in brief their influence: ***i)*** GAC and CPC concentration (Test 1–3; see Table S1): the most concentrated reaction (molar ratio GAC:CPC:H_2O = 125:1:326.8 *vs.* 125:1:793.7 or 125:1:5555.5) led to the higher level of functionalization (*ca.* 0.54 ± 0.02 mmol CPC·g^{-1}); ***ii)*** reaction time (Test 4–5) had no significant impact on the functionalization of activated carbon, resulting in an identical surfactant loading when using different reaction times (5 *vs.* 18 h); and ***iii)*** reaction stirring (Test 3 & 5): there was a rise on CPC content (30 %) under stirring when compared with static conditions. Therefore, the most effective synthesis strategy was selected based on the surfactant incorporation, given that it represents the most costly reactant (58,·2.97 and 0.54 €·kg^{-1} for CPC, GAC and deionized water; April 2025 prices) [28-30]. Note here that the amount of cationic surfactant in the CPC@GAC material was determined by elemental analysis (EA) and thermogravimetric analysis (TGA, see Section S1).

The obtained CPC@GAC composites were fully characterized. The successful functionalization was demonstrated through N_2 sorption isotherms measured at 77 K. Once functionalized with the CPC surfactant, the porosity of the obtained materials was significantly reduced (from 1400 m^2·g^{-1} for the GAC to a range of 568–780 m^2·g^{-1} for the different composites; Figure S2 and Table S2). Despite the surface reduction, the solids maintain an important accessible porosity. In this regard, the CPC molecules might be located in the inner porosity and/or



Test	S_{BET} $(m^2 \cdot g^{-1})$	V_p $(cm^3 \cdot g^{-1})$	P_s (Å)	S_{ext} $(m^2 \cdot g^{-1})$	S_{micro} $(m^2 \cdot g^{-1})$	$V_{p\ micro}$ $(cm^3 \cdot g^{-1})$
Industrial GAC	947	0.48	12.5 & 16	48	899	0.4
Scaled CPC@GAC	588 (650)	0.33 (0.36)	13.1 & 16.6 (13.1 &16.5)	37.5 (41.5)	551 (609)	0.26 (0.29)

Fig. 2. a) N_2 adsorption-desorption isotherms at 77 K of pristine industrial GAC (black) and scaled CPC@GAC (red), and their b) textural properties (BET surface-S_{BET}, pore volume-V_p, pore size-P_s, external surface-S_{ext}, microporous surface-S_{micro}, microporous pore volume-$V_{p\ micro}$). In parenthesis values calculated by subtracting the surfactant weigh. Empty symbols correspond to the desorption branch, respectively.

on the outer surface of GAC particles. Thus, corrected surface areas were calculated by subtracting the surfactant weight, demonstrating that the porosity of the commercial GAC is not recovered. Although it is hard to venture into, we may conclude that the surfactant association modifies the accessible porosity, probably through two different manners: by hampering the diffusion and/or by functionalizing the inner porosity of the GAC (Table S2). TGA strengthens this assumption that exhibited two weight losses at 195 and 275 °C, corresponding to the decomposition of the surfactant located on the external surface of the particles and, the subsequent loss associated to the CPC inserted within the porosity (probably in a stronger interaction; Figure S1). Considering all the above, the material synthetized using conditions of Test nº 5 (molar ratio GAC:CPC of 125:1, static conditions, 5 h; Table S1) was selected. Through this strategy a 0.38 ± 0.01 mmol CPC·g^{-1} GAC was attained, corresponding to a 59.2 % reaction yield (based on CPC·H_2O and estimated with EA data). Finally, by using static functionalization conditions, pellets breakage was successfully avoided, thereby improving the processability of the material.

Following the optimization of the reaction conditions, the same procedure was applied using an industrial-grade activated carbon (industrial GAC), as it is a cost-effective material. Importantly, the industrial GAC utilized in this research is currently used in DWTPs, and was supplied by the water management company Canal de Isabel II S.A., M. P. (Spain). When industrial GAC was utilized, the amount of associated surfactant reached 0.29 ± 0.02 mmol CPA·g^{-1} GAC, being lower than the functionalization achieved in the non-industrial GAC material (0.54 ± 0.02 mmol CPC·g^{-1}). This could be explained by the lower textural properties of this industrially obtained adsorbent when compared with the commercial one (947 *vs.* 1400 $m^2 \cdot g^{-1}$, respectively). In this line, upon the modification, the resulting industrial CPC@GAC material suffered a similar reduction of the surface than the commercial one (around 50 %), exhibiting an important accessible porosity (480 $m^2 \cdot g^{-1}$; Figure S4 and Table S3). Besides, the isotherm sorption correction and TGA demonstrated the aforementioned location of the surfactant (both on the external surface and within the porosity).

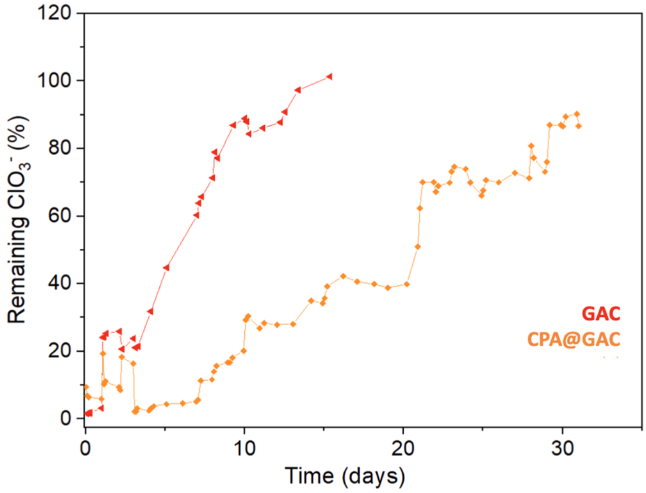


Fig. 3. Continuous flow removal of ClO_3^- using 80 kg of GAC (triangles, red) or CPC@GAC (rhombus, orange), a water flow of 27.8 L·min^{-1} and a flux of 13.9 $m^3 \cdot h^{-1} \cdot m^{-2}$, which corresponds to an EBTC of 5.2 min. The Y-axis was estimated by remaining concentration in out-flow compared to concentration in-flow.

3.2. Scale up material

In the transition from laboratory-scale synthesis to industrial application, one of the primary factors to consider is the production cost. Considering the current prices of the compounds used in the preparation of CPC@GAC (58,·2.97 and 0.54 €·kg^{-1} for CPC, GAC and deionized water, respectively), the optimal reaction process was stablished based on the amount of CPC incorporated to the composite. Furthermore, the utilized process is defined as an environmentally sustainable and green approach, involving the use of entirely non-harmful solvents and requiring no energy consumption. The optimal impregnation conditions were scaled up using a 300 L PET vessel (see details in Section 2), leading to a batch of CPC@GAC up to *ca.* 46 kg (*per* single reaction, 42 % in the reaction yield), with a STY of 736 kg·m^{-3}·day^{-1} (calculated considering the total volume of the reactor). Importantly, STY exceeding 500 kg·m^{-3}·day^{-1} are regarded as indicative of high productions rates at low cost [31], demonstrating that this reaction can be considered an efficient and economically viable process. The resulting material was characterized, reaching a similar associated surfactant than that obtained in the low-scale reaction (reached 0.28 mmol CPC·g^{-1}), with an accessible porosity of 590 $m^2 \cdot g^{-1}$ (Fig. 2). Considering all these encouraging results (impressive STY, remaining accessible porosity, and high surfactant incorporation), we proceeded to evaluate its potential for the adsorption of ClO_2^- and ClO_3^- in a real DWTP.

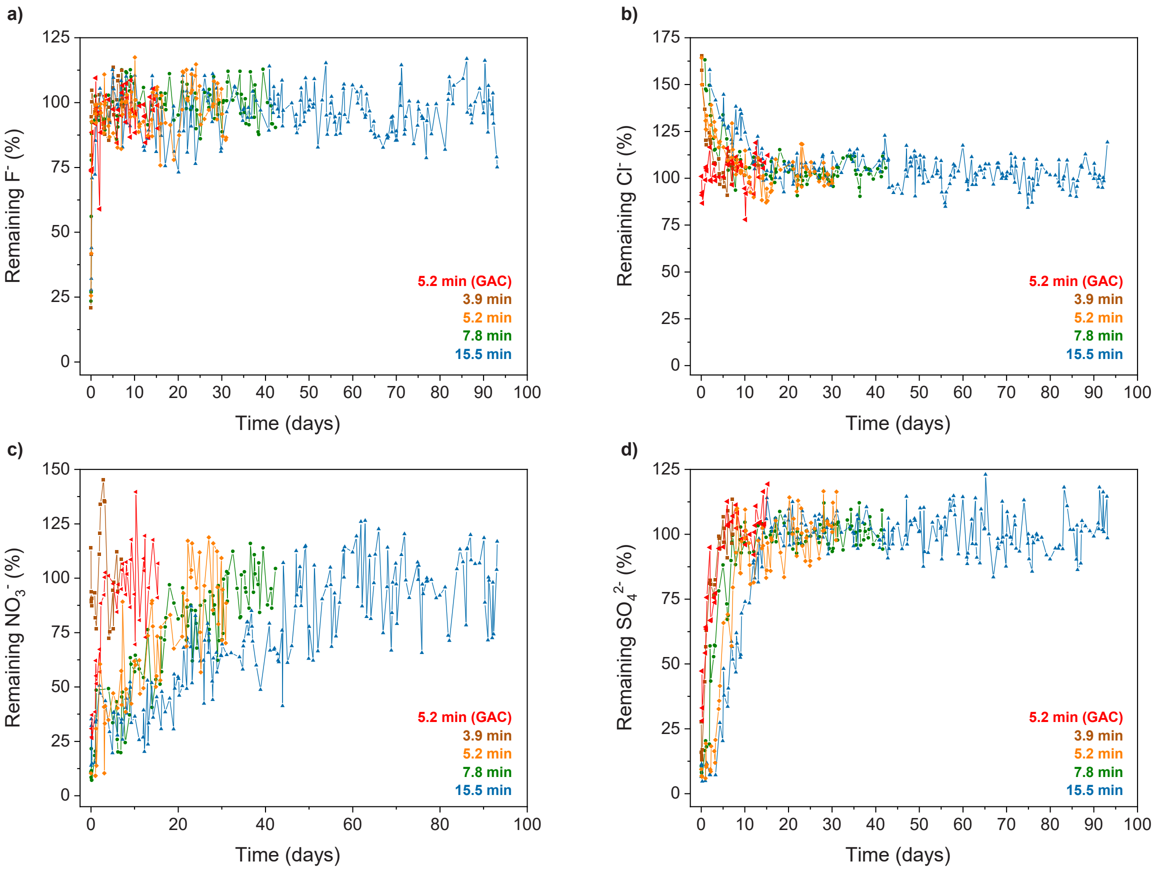


Fig. 4. Continuous flow removal of a) F$^-$, b) Cl$^-$, c) NO_3^-, and d) SO_4^{2-} using GAC (red, turned triangles) at EBTC of 5.2 min, and CPC@GAC at different EBTC: 3.9 (squares, brown), 5.2 (rhombus, orange), 7.8 min (circles, green) and 15.5 min (triangles, blue). The Y-axis was estimated by remaining concentration in our-flow compared to concentration in-flow.

3.3. Real continuous flow testing at a pilot plant

Leveraging the previously reported efficient performance of the CPC@GAC material for the ClO_2^- and ClO_3^- adsorption under continuous flow conditions [24], a pilot-scale continuous flow study was here conducted, working in an operational DWTP. Following the currently used conditions, the water flow used during these experiments (9.3–27.8 L·min^{-1} with an EBTC in the range of 5.2–15.5 min) is within the range of the typically used one in DWTPs (*i.e.*, 5–15 min) [26]. It is worth noting that the selected GAC is already employed in DWTPs, which facilitates the successful implementation of the modified CPC@GAC. Furthermore, the inlet water was previously doped with ClO_2^- and ClO_3^- (with concentrations ranging from 0.18 to 0.25 mg·L^{-1}), according to the maximum permissible oxyanions' concentration of 0.25 mg·L^{-1}, as limited by the new EU directive [9].

CPA@GAC demonstrated to have an excellent oxyanions removal capacity at the studied conditions, even working at low EBTC (5.3 min). The breakthrough curve revealed that the CPC@GAC column was able to successfully adsorb up to 81.8 % of ClO_3^- from drinking water during 10 days (Figs. 3 & S6). Under these conditions, the time to reach 50 % of saturation ($t_{50\,\%}$) was 22.9 days. These impressive values largely exceed those obtained with the non-functionalized GAC, which was able to adsorb 9.1 % of ClO_3^- after only 10 days, with a $t_{50\,\%}$ of 4.0 days. Regarding ClO_2^-, 100 % was eliminated in all tested conditions. This is probably due to the reduction from ClO_2^- to Cl$^-$ by oxidation of other soluble species (such as acetate) [32-34] in interaction with GAC, as previously reported [4]. This synergistic and dualistic functionality of CPC@GAC - as both a catalyst and an adsorbent - also contributes to the effective reduction of organic matter intended for human consumption. This is particularly relevant in meeting regulatory standards, which require the total organic carbon (TOC) $\leq$ 0.5 mg of organic matter *per*·L^{-1} and oxidizability indicator and 5 mg of oxygen *per* L^{-1} [9]. Specifically, TOC and oxidizability parameters significantly decrease in contact with CPC@GAC (*e.g.,* TOC: from ~2.8–0.7 mg·L^{-1} and oxidixability: from ~2.5–0.3 mg·L^{-1} after only 1 day). At this point, it should be noted that the adsorbent regeneration was previously demonstrated by anionic exchange using a NaCl aqueous solution (12.6 M) [35]. The results demonstrated that after 4 cycles of adsorption/desorption, CPC@GAC was able to eliminate 100 and 50 % of ClO_2^- and ClO_3^-.

Following with a low EBTC (5.3 min) analysis, when the concentration of other anions found in drinking water (F$^-$, Cl$^-$, NO_3^-, and SO_4^{2-}) is considered, NO_3^- and SO_4^{2-} were retained in the column, while Cl$^-$, and F$^-$ did not interact with the CPC@GAC material (Fig. 4). Notably, their concentrations in the effluent always remained below the drinking water limit for human consumption [36]. Again, the adsorption of NO_3^- and SO_4^{2-} was improved when using the CPC functionalized activated carbon ($t_{50\,\%}$ for $NO_3^- = 11.1$ *vs.* 0.2 and $t_{50\,\%}$ for $SO_4^{2-} = 5.0$ *vs.* 0.2 days, for GAC and CPC@GAC, respectively). These results are in agreement with previous studies reported for the efficient elimination of NO_3^- and SO_4^{2-} by GAC or surfactant modified GAC [37-40]. Finally, the potential leaching of CPC during oxyanions adsorption was analyzed by UV–vis. The results confirmed the absence of free CPC in all water samples (limit of detection = 0.0017 mM), exhibiting the potential of CPC@GAC for safe use in water treatment.

Transient, gradual or abrupt changes in source water quality that may compromise treatment effectiveness can be triggered by various factors, including climate-related meteorological events, as well as accidental or intentional contamination [41]. Therefore, the design principles that underpin the majority of treatment systems in DWTPs predate climate adaptation considerations. One basic adaptation

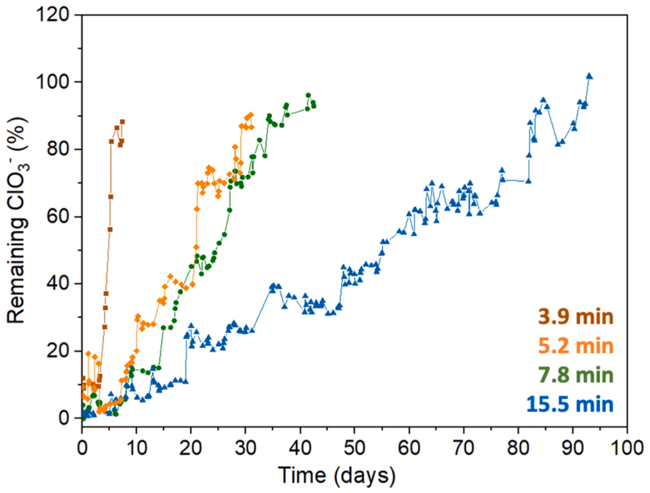


Fig. 5. Continuous flow removal of ClO_3^- using CPC@GAC at different EBTC: 3.9 min (squares, brown), 5.2 min (rhombus, orange), 7.8 min (circles, green) and 15.5 min (triangles, blue). The Y-axis was estimated by remaining concentration in our-flow compared to concentration in-flow.

mechanism is the possibility to modify the water flow. Thus, the oxyanions adsorption capacity of the CPC@GAC scaled column working at different water flows was tested, using EBTCs below and above of the standard flow rate (EBTC = 5.3 min). When using EBTC of 3.9, 7.8 and 15.5 min, the breakthrough curve demonstrated that the CPC@GAC column was able to successfully adsorb up to 100 % of ClO_2^- and 90 % of ClO_3^- from drinking water during 0.2, 8.2 and 21.9 days, respectively (Figs. 5 & S7), which corresponds to 5, 281 and 217 m^3 of water, respectively. The $t_{50\ \%}$ changed accordingly, reaching 6.0, 22.0 and 54.8 days when using EBTC values of 3.9, 7.8 and 15.5 min, corresponding to 160, 586 and 734 m^3 of water, respectively. Collectively, these findings demonstrate the potential of the easily modified CPC@GAC material for the efficient removal of ClO_2^- and ClO_3^- under operational conditions currently used in real DWTPs.

4. Conclusions

The removal of ClO_2^- and ClO_3^- from drinking water represents a critical challenge for insuring compliance with the stringent regulatory limits established by the European Union. Considering that GAC is one of the primary adsorbents utilized in DWTPs, this study demonstrates a straightforward functionalization of industrial GAC with the cationic surfactant CPC at kilogram scale, achieving excellent space-time-yield (STY) and processability, and demonstrating both technical economic viability The capacity of the modified CPC@GAC material to eliminate oxyanions (ClO_2^- and ClO_3^-) under realistic continuous flow conditions underscores its relevance and adaptability for integration into existing DWTP installations. Future work can be anticipated in applying this interesting treatment in real DWTP filters, based on a cost analysis and leaching evaluation. From a broader perspective, this work advances the field by bridging the gap between lab-scale innovation and full-scale operational deployment, contributing to the development of more sustainable and effective technologies for safeguarding public health.

CRediT authorship contribution statement

Eduardo Arozamena: Writing – review & editing, Writing – original draft, Investigation. **Margarita Amado:** Writing – review & editing, Writing – original draft, Investigation. **Antonio Lastra:** Writing – review & editing, Writing – original draft, Investigation. **Lydia Saez:** Writing – review & editing, Writing – original draft, Investigation. **Sánchez-Cano Gabriel:** Writing – review & editing, Writing – original draft, Investigation. **Patricia Horcajada:** Writing – review & editing, Writing – original draft, Investigation. **Sara Rojas:** Writing – review & editing, Writing – original draft, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2025.119506.

Data availability

Data will be made available on request.

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