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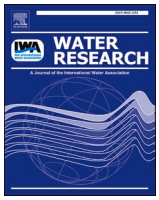

Complete biodegradability assessment of polyoxyethylene glycerol ester non-ionic surfactant: Aerobic, anaerobic, combined biodegradation and inhibitory effects

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ABSTRACT

Aerobic and anaerobic biodegradability have become one of the most relevant characteristics for all contaminants. This is especially important in case of surfactants, which are discharged in wastewater treatment plants or directly into the aquatic bodies. The aim of this study is the integral assessment of the biodegradability of the non-ionic surfactant polyoxyethylene glycerol ester PGE-OE_{17}. The aerobic and anaerobic biodegradation of PGE-OE_{17} was evaluated at different initial surfactant concentrations, and the evolution of the toxicity of the surfactant and its by-products was followed during the aerobic and anaerobic processes using bacteria *Vibrio fischeri*. PGE-OE_{17} was not completely biodegradable neither aerobically nor anaerobically, and the increase in the initial surfactant concentration had a negative effect in the biodegradation. Toxicity of the surfactant solutions and degradation by-products had a first increase followed by a gradual decrease during both tests, revealing that toxic substances released can harm the microorganisms and therefore hinder the biodegradation. Additionally, combined aerobic-anaerobic biodegradation tests were performed, consisting in a first aerobic treatment of different duration and initial concentration, followed by a complete anaerobic treatment. Results showed that a balance between aerobic and anaerobic biodegradation duration can maximize the biodegradation rates in comparison with only aerobic or anaerobic tests.

1. Introduction

In recent decades, the consumption of surfactants has significantly increased year by year and is projected to increase at a CAGR (Compound Annual Growth Rate) of 2.5 until 2028 (Mordor Intelligence, 2023). Their wide versatility and properties make them ideal for a multitude of industrial or domestic applications. Among these applications, the use as washing agents in industrial and domestic detergent solutions, as emulsifiers or solubilizers, is the most important. After their use, the surfactants arrive together with the wastewater at the wastewater treatment plants (WWTPs) or are even discharged directly into rivers, lakes, seas and oceans.

Concentrations of surfactants in the environment can vary widely depending on the source and type of surfactant involved as well as by the geographic region, use practices, chemical disposal, environmental regulations, and other variables (Mackay and Fraser, 2000; Wu et al., 2023). Concentrations of surfactants in wastewater can range from low levels, in less industrial and less populated areas, to more significant concentrations, in areas where there are industrial or municipal discharges. Surfactants are often detected in surface water and groundwater due to these sources of contamination (Faccenda et al., 2022; Kumar et al., 2022).

The presence of surfactants causes environmental problems in aquatic and operational ecosystems in WWTPs, due to the interference with oxygen transfer, toxicity to aquatic organisms and biodegradation difficulties, especially under anaerobic conditions. Consequently, their potential impacts on biological wastewater treatment process and on the environment have raised increasing public concern (Khalil and Liu, 2021; Lechuga et al., 2016; Ríos et al., 2016, 2017c, 2023; Zhang et al., 2021; Zhou et al., 2021). Concentrations of non-ionic and anionic surfactants in untreated wastewater were found until 17,000 mg/L (Camacho-Muñoz et al., 2014; Collivignarelli et al., 2019). Some authors determined that anionic surfactants can still be detected in treated wastewater with concentrations up to 872 μg/L, while in case of non-ionic surfactants, 0.24–3.0 μg/L of alcohol ethoxylates were detected in the effluents from sewage treatment plants (Dyer et al.,

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2006; Huang et al., 2021; Motteran et al., 2017).

Traditionally, the most used surfactants have been linear alkylbenzene sulfonate (LAS) and sodium lauryl ether sulfate (SLES) as anionic surfactants, and ethoxylated fatty alcohols as nonionic surfactants, but due to the growing environmental concern they are being progressively replaced by surfactants from renewable sources and with better environmental profiles such as alkylpolygucosides or polyoxyethylene glycerol esters (Santos et al., 2015; Vicaria et al., 2022). Polyoxyethylene glycerol esters (PEGs), also known as glycol esters, are compounds that result from the reaction of glycerin with ethylene oxide. These compounds are used in various industrial applications, including cleaning formulations, due to their surfactant and emulsifying properties. Their excellent compatibility with the rest of the formulation components, their very low water content, and their stability in the final formulation make them attractive for use in concentrated detergents, pods laundry detergents, multipurpose cleaning products, and personal care products among others (Amato and Vingola, 2021; Bao and Yin, 2022; Batchelor, 2023; Shearouse and Hibbard, 2019). For instance, (Trujillo-Cayado et al., (2018) studied the use of polyoxyethylene glycerol esters to obtain ecological emulsions and Jurado-Alameda et al. (2011) patented their use in highly wetting surfactants formulations.

Traditionally, biodegradability of surfactants has been addressed in the first place under aerobic conditions, as it is one of the most used treatments in wastewater processing (Khuntia et al., 2021). Although numerous studies on the aerobic biodegradation of most common surfactants are available, latest reviews and publications only cover the most traditional surfactants such as LAS, fatty alcohol sulphates, cocaamidopropyl betaine, alkylpolyglucosides, fatty alcohol ethoxylates or alkylphenol ethoxylates (Jurado et al., 2011, 2013; Ríos et al., 2017b; Khalil and Liu, 2021), and complete studies addressing new surfactants are scarce.

In addition, much of the primary degradation of organic wastewater takes place under anaerobic conditions, either directly treatment of wastewater, as post-treatment of sewage sludge or as the main purification process when it occurs in open pipes, drains, and anaerobic zones widely prevalent in the environment. Therefore, it is essential to include anaerobic biodegradation assessment as an obligatory indicator of complete biodegradability (Marinho et al., 2022). Some studies warn that surfactants, and their breakdown products, are persistent and accumulate in the environment due to high surface adsorption capacity in combination with lower rate of biodegradation under typical anaerobic conditions (Khalil and Liu, 2021; Khuntia et al., 2021; Motteran et al., 2022). Unfortunately, anaerobic studies are very limited to the most widely used families of surfactants, such as LAS or ethoxylated fatty alcohols (Motteran et al., 2014; Khalil and Liu, 2021), and have been ignored for most of the surfactants. The anaerobic biodegradation of surfactants is of vital importance due to its role in compliance with European regulations that promote the anaerobic digestion of wastewater, organic solid waste and sludge. This process is relevant to the production of biogas and the reduction of the energy dependence based on petroleum or fossil gas, contributing to a more sustainable and respectful approach to the environment (European Commission, 2022). Interest in anaerobic processes has experienced significant growth, driven by the need to find more efficient and green solutions for waste treatment and power generation (Bumharter et al., 2023). In this context, the study of the anaerobic biodegradation becomes essential to understand how surfactants decompose in the absence of oxygen and how its presence can negatively affect aquatic and terrestrial ecosystems. In depth knowledge about anaerobic biodegradation of surfactants will not only allow us to comply with the environmental standards required by European legislation, but will also provide us with tools to optimize resource management and move towards a more efficient circular economy.

Furthermore, for a proper biodegradability assessment, the biodegradation course should be monitored. A recent review (Arora et al., 2023) indicates that the inhibitory effects of the by-products and metabolites produced during the aerobic and anaerobic surfactant degradation remains unknown and poses a challenge that needs to be addressed. Their adsorption on the microbial sludge hinders biodegradation rates by obstructing the exchange of gases and nutrients between the microorganisms and the medium (Mantzavinos et al., 2001), and can have higher toxics effects than the initial surfactants (Johnson et al., 2021).

In the case of the new generations of surfactants, such as PEGs, the studies related to aerobic and anaerobic biodegradation are very scarce and do not reflect all the circumstances in which surfactants can undergo biodegradation processes or act as toxic agents for the biota of aquatic systems and sewage sludge. Ríos et al. (2017c) studied the toxicity of PEGs and their mixtures with other surfactants, obtaining that PEGs can have a toxic effect on algae, *Daphnia magna* and bacteria, which is an indicative of potential detriment to the biodegradation processes.

This work includes a novel complete biodegradation study for a polyoxyethylene glycerol ester, under aerobic and anaerobic conditions. First, individually with different initial concentrations of surfactant to evaluate the effect of the concentration and its influence on the final biodegradation that can be achieved. And secondly, we study a combined process consisting of an aerobic treatment followed by a subsequent anaerobic treatment of the non-biodegraded surfactant and the intermediate by-products generated during the primary aerobic treatment. The biodegradability of surfactants is usually explored or aerobically or anaerobically, but not in a combined treatment, such as it could be the flow of not completely aerobic biodegradable surfactants, which pass to the anaerobic treatment along with the sludge (Palmer and Hatley, 2018), and in which the not aerobically biodegradable by-products can be degraded by the anaerobic microorganisms (Biktasheva et al., 2022). Consequently, this combined treatment allows the identification of the best conditions to maximize the total biodegradation and/or the methane production. In addition, this study addresses some of the aspects less studied for most of the surfactants, like the potential bacterial inhibition of the biodegradation liquors and their evolution during the aerobic and anaerobic processes.

2. Materials and methods

2.1. Surfactant and reagents

In the present work, we tested the aerobic and anaerobic biodegradability of a polyoxyethylene glycerol ester non-ionic surfactant ($PGE\text{-}OE_{17}$) supplied by Kao Corporation (Tokyo, Japan). $PGE\text{-}OE_{17}$ is a non-ionic surfactant of vegetable origin (cocoa oil) and commonly used in the formulation of laundry detergents and household products. The relative low foaming power, high active content, good stability, low eyes and skin irritation potential and high compatibility with other surfactants and enzymes, make it a good alternative to traditional non-ionic surfactants to be used in laundry pods, concentrated detergents, hand dishwasher, cosmetics, and personal care products. It can also be used as emulsifier or as fragrances solubilizer. Table 1 shows its properties and molecular structure, in which $x + y + z = 17$ as an average number of ethylene oxide molecules.

Rest of reagents were of analytical grade and provided by Merk KGaA (Darmstadt, Germany). Solutions were prepared in ultrapure MilliQ® water (resistivity 18.2 MΩ·cm at 25 °C).

2.2. Active matter analysis

The active matter of the surfactant was determined using infrared radiation (Model AD-4714A, A&D, Tokyo, Japan). The humidity in the sample was recorded every 30 s for 90 min, as a difference from the initial weight and using 105 °C as the drying temperature. The active matter is determined by subtracting the determined humidity from 100 %.

Table 1
Characteristic parameters and molecular strcture of PGE-OE_{17}.

Parameter	Value	Molecular structure
INCI	Glycereth-17 cocoate	$CH_2\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_x\text{-}R$
CAS	68201–46–7	|
HLB	15	$CH\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_y\text{-}R$
Active Matter, %	99.0	|
Carbon content, %	41.72[a]	$CH_2\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_z\text{-}R$
CMC, mg/L	13.30 ± 0.42	
		$(x + y + z) = 17$
		R = H or R'CO (cocoate chain)

INCI: international nomenclature of cosmetics ingredients.
CAS: Chemical Abstracts Service.
HLB: Hydrophilic-Lipophilic Balance.
CMC: Critical Micelle Concentration in MilliQ® water, 25 °C.
[a]Determined by Elemental Analysis.

2.3. Critical micelle concentration (CMC)

The critical micelle concentration (CMC) is the minimum surfactant concentration above which micelles are spontaneously formed in a solution. To calculate the CMC, the surfactant surface tension was measured for different concentrations (in the range of 0.1 to $1{\cdot}10^4$ mg/L). Plotting surface tension as a function of surfactant concentration on a semi-logarithmic scale results in a rapid linear decrease followed by a gradual decrease. The formation of micelles is established at the breaking point. The Wilhelmy Plate Method was used to measure surface tension using a tensiometer model K11 (Krüss GmbH, Hamburg, Germany) fitted with a 2-cm platinum plate as detailed by Rincón-Romero et al. (2023).

Before each measurement, the plate was carefully cleaned and dried using a Bunsen burner. The standard deviation for the surface tension measurement did not exceed 0.1 mN/m during the six subsequent observations. The jacketed cell is maintained with a thermostatic water bath at 25 ± 0.5 °C. CMC determination was performed in triplicate to obtain a mean CMC and its confidence interval (95 %).

2.4. Aerobic biodegradation test

For the aerobic biodegradation, the modified OECD 301E screening test (OECD 301, 1992) was performed. The surfactant PGE-OE_{17} is easily soluble and non-volatile and therefore suitable to be tested by this technique. This test consists of using a known concentration of surfactant as the sole source of organic carbon (25–100 mg DOC/L), in 1.2 L of mineral culture medium, and inoculating with 0.5 mL of secondary effluent from a WWTP operating with activated sludge and predominantly receiving domestic wastewater, (Plus code: 597G+W2). The inoculum was previously aerated during 7 days in mineral medium without any supply of carbon to reduce the free carbon content. The mineral medium was prepared adding in 1L: 85 mg KH_2PO_4, 217 mg K_2HPO_4, 334 mg $Na_2HPO_4{\cdot}2H_2O$, 5 mg NH_4Cl, 27.50 mg $CaCl_2$, 22.50 mg $MgSO_4{\cdot}7H_20$ and 0.25 mg $FeCl_3.6H_20$. The pH was adjusted to 7.4 ± 0.2, with either 1 M NaOH or 1 N HCl, before the test was initiated. To keep this culture medium aerated in the dark at 22 ± 1 °C, an orbital shaker was used. To monitor the ultimate biodegradation, samples were taken at regular intervals for 28 days, and the dissolved organic carbon (DOC) was analyzed. A blank without surfactant was run in parallel to subtract the DOC changes due to the endogenous activity of the bacteria. To calculate the mineralization (*%Min*), i.e. the degree of ultimate biodegradation, the concentration of DOC, corrected with the blank value, is expressed as a percentage of the initial concentration (Eq. (1)).

$$\%Min = \left[1 - \frac{(C_i)_t - (C_{bl})_t}{(C_i)_0 - (C_{bl})_0}\right] \cdot 100 \quad (1)$$

where:

$(C_i)_0$: initial DOC in the inoculated medium containing the test substance (mg DOC/L).

$(C_i)_t$: DOC in the inoculated medium containing the test substance at time t (mg DOC/L).

$(C_{bl})_0$: initial DOC in a blank inoculated mineral medium (mg DOC/L).

$(Cbl)_t$: DOC in a blank inoculated mineral medium at time t (mg DOC/L).

Experiments were conducted in duplicate for each concentration. To check the procedure and inoculum, sodium benzoate is used as standard. 40 mg DOC/L of sodium benzoate was set up in parallel as part of a normal test run, which achieved a biodegradation of 70 % within 14 days. To verify the absence of abiotic biodegradation or adsorption, a sterile control without inoculum containing $HgCl_2$ was conducted. In this test, the values of DOC remained constant throughout the entire biodegradation period.

2.5. Anaerobic biodegradation test

The anaerobic biodegradation was assessed following the ISO 11734:1995 guideline (European Commission, 1995) as described by Ríos et al., (2016), (2017c). In this test, the production of biogas in samples containing the surfactant is measured and compared with a control (blank) without surfactant. The surfactant, PGE-OE_{17}, was tested in duplicate at different initial concentrations (0, 25, 75 and 100 mg DOC/L). The production of carbon dioxide and methane was measured using the system Oxitop® Control (WTW, Welheim, Germany). This system features 510 mL glass reactors with a magnetic stirrer. The reactors are sealed with a cap containing an electronic pressure gage, which allows continuous monitoring of pressure increase in the reactors headspace. Under the test conditions, a large part of the CO_2 produced will be present in the liquid phase in the form of dissolved CO_2, carbonic acid, carbonate, or hydrogen carbonate. The carbon (inorganic (IC) plus methane) resulting from the anaerobic biodegradation of the test substance is quantified from the net gas production and net formation of IC in the liquid phase minus the blank control values. The anaerobic inoculum was collected from the wastewater treatment plant in Granada, Spain, which mainly receives domestic wastewater (Plus Code: 597G+W2), and was incubated in anoxic conditions and without any supply of carbon for 7 days at 35 ± 1 °C to minimize nonspecific gas production. Table 2 shows the characteristic parameters of the sludge, determined according to the Standard Methods for the examination of water and wastewater (APHA-AWWA-WPCF, 1992). Immediately before their use in the anaerobic test, the sludge was centrifuged and washed 4 times with a mineral salt solution to reduce the inorganic carbon (IC) to a value less than 10 mg/L.

The mineral salt solution was prepared adding in 1 L of deoxygenated water: 0.27 g KH_2PO_4, 1.12 g $Na_2HPO_4{\cdot}12H_2O$, 0.53 g NH_4Cl, 0.075 g $CaCl_2{\cdot}2H_2O$, 0.10 g $MgCl_2{\cdot}6H_2O$, 0.02 g $FeCl_2{\cdot}4H_2O$, 0.001 g resazurin, 0.1 g $Na_2S{\cdot}9H_2O$ and 10 mL of solution of trace elements (50 mg/L $MnCl_2{\cdot}4H_2O$, 5 mg/L H_3BO_3, 5 mg/L $ZnCl_2$, 3 mg/L $CuCl_2$, 1 mg/L $Na_2MoO_4{\cdot}2H_2O$, 100 mg/L $CoCl_2{\cdot}6H_2O$, 10 mg/L $NiCl_2{\cdot}6H_2O$, and 5

Table 2
Characteristic parameters of the anaerobic sludge.

Parameter	Value
pH	7.45
Total solids, g/L	26.4
Volatile acidity, ppm CH_3COOH	261
Alkalinity, ppm $CaCO_3$	2457
Rate Volatile acidity/Alkalinity	0.11

mg/L Na_2SeO_3). In the reactors, 330 mL of the surfactant solution and 20 mL of anaerobic sludge were added to obtain a solid concentration of 1.5 g/L and a final volume of 350 mL. Surfactants solutions were adjusted to pH 7.0 ± 0.2 and incubated in darkness at 35 ± 1 °C during 60 days. Net biogas pressure (Δp) was automatically registered and transduced to mass net carbon produced as gas in the headspace (m_h) using the gas law equation Eq. (2):

$$m_h = \frac{1200 \cdot 0.1 \cdot (\Delta P \cdot V_h)}{R \cdot T} \quad (2)$$

where ΔP is the difference between the initial and final pressures in the test reactor minus the corresponding value in the blank, and V_h is the headspace volume in the container (0.16 L).

To calculate the extent of biodegradation (D_h), the Eq. (3) is used, where m_v is the mass of the test substance carbon.

$$D_h(\%) = \frac{m_h}{m_v} \cdot 100 \quad (3)$$

At the end of the test the inorganic carbon dissolved was analysed (m_i). This measurement allows calculating the total mass of gasified carbon (m_t), by adding m_h plus m_i.

The percentage of final mineralization (D_t) is calculated using the Eq. (4).

$$D_t(\%) = \frac{m_t}{m_v} \cdot 100 \quad (4)$$

where m_v is the mass of the test substance carbon.

The sodium benzoate was used as reference to validate the test (ultimate anaerobic biodegradation > 60 %). And to verify the absence of abiotic degradation, a sterility test was conducted without an inoculum using $HgCl_2$ (10 mg/L), that inhibits microbial activity.

2.6. Inhibition test with bacteria Vibrio fischeri

For the measurement of toxicity, bioluminescent bacterium *Vibrio fischeri* was used as test organism. Bacteria *V. fischeri* are inhibited by toxicants, this light inhibition can be quantified by a calibrated light meter and compared with the light emitted by a blank without toxicant. The photobacteria (strain NRRL-B-11177) and the system LumiStox® 300 was provided by Hach-Lange S.L.U., (Barcelona, Spain) and used following the guideline UNE-EN-ISO 11348–2:2009 (UNE-EN-ISO 11348–2, 2009). Light inhibition of samples taken at different biodegradation times from the aerobic and anaerobic tests and a control were performed in triplicated and compared with the light emitted by a blank without toxic sample. The light emission after 15 min and 30 min of contact was measured at a temperature of 15 °C using the luminometer. Percentages of the inhibition caused by the samples were calculated as described in previous works (Ríos et al., 2018, 2017c):

The luminescence intensity was corrected considering its natural decrease in the absence of the toxic sample, factor f_k:

$$f_k = \frac{I_{t(0)}}{I_{0(0)}} \quad (5)$$

where $I_{0(0)}$ and $I_{t(0)}$ are the readings of luminous intensity in the well containing concentration 0 at time 0 and after 15 min or 30 min.

The inhibition percentage (inhibitory effect) was calculated by the Eqs. (6) and (7).

$$H_t\ (\%) = \frac{(I_{0t(c)} - I_{t(c)})}{I_{0t(c)}} \cdot 100 \quad (6)$$

$$I_{0t(c)} = f_k \cdot I_{0(c)} \quad (7)$$

where f_k is the average correction factor of the control samples, $I_{0(c)}$ and $I_{t(c)}$ are readings of light intensity in the well containing concentration c at time 0 and after 15 min and 30 min. As control performance criterion, the factor f_k must be in the range 0.8–1.2. The validity of the test was also checked using potassium dichromate as reference.

2.7. Analytical measurements

Dissolved organic carbon (DOC) was measured using the Shimadzu VCSH/CSH TOC analyzer equipped with an auto-sampler (Shimadzu Co., Kyoto, Japan). Samples were filtered through a 0.45-μm polyvinylidene fluoride filter (Merck Millipore Co., Darmstadt, Germany) before DOC analysis. In the TOC-analyzer, DOC is calculated as total carbon (TC) minus inorganic carbon (IC). TC of the sample is first catalytically oxidized to form carbon dioxide. A carrier gas, containing the carbon dioxide, flows to a dehumidifier and pass through a halogen scrubber before it reaches the cell of a non-dispersive infrared NDIR gas analyzer, where the carbon dioxide is detected. IC is measured by acidifying the sample with HCl to obtain a pH less than 3, when all the carbonates produce carbon dioxide. The carbon dioxide and dissolved carbon dioxide are volatilized by bubbling synthetic air through the sample and detected by the NDIR. A standard platinum TOC catalyst was used to measure samples containing DOC over 5 mg/L and a high sensitivity platinum TOC catalyst was used for samples with DOC content below 5 mg/L. Both catalysts were provided by Shimadzu Co. (Tokyo, Japan). The TOC-analyzer was calibrated using standards prepared from potassium hydrogen phthalate, sodium hydrogen carbonate, and sodium carbonate.

3. Results and discussion

3.1. Aerobic biodegradability

We studied the ultimate biodegradation of PGE-OE_{17} at different initial surfactant concentrations (S_0) (25, 50, 75, and 100 mg DOC/L) to analyze the effect of the toxicant on the adaptation capacity of the microorganisms and on the biodegradation profiles of the surfactant. The range of concentrations studied included the recommended one in the OECD 301E guideline (10–40 mg DOC/L). Fig. 1 shows the biodegradation profiles for the studied concentrations during the 28 days of the tests.

For the comparison and quantification of the surfactant biodegradation at different initial concentrations, the following biodegradation parameters have been calculated from the biodegradation curves (Jurado et al., 2011; Ríos et al., 2017b) (Table 3): final mineralization (*%Min*) as the ultimate biodegradation after 28days; latency time (t_L) which is time needed for the non-adapted microorganisms to acclimatize themselves to the new substrate; and mean biodegradation rates (VM_{25} and VM_{50}) which are the mean velocity of biodegradation until 25 or 50 % biodegradation of the surfactant is achieved.

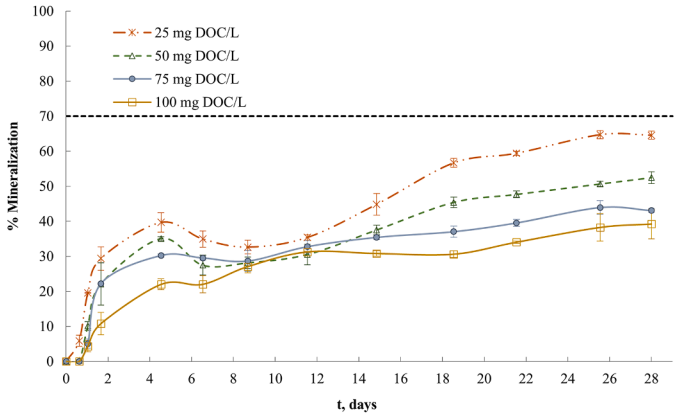

Fig. 1. Aerobic biodegradation profile of PGE-OE_{17} at initial concentration (25–100 mg DOC/L). line: threshold of 70 %. (I, standard deviation).

Table 3
Biodegradation parameters for aerobic biodegradation of PEG-OE_{17} at initial concentrations (25–100 mg DOC/L).

S_0, mg DOC/L	*% Min*	t_L, days	VM_{25},%/day	VM_{50},%/day
25	64.58	0.50	20.00	3.05
50	52.48	0.65	11.74	1.02
75	43.09	0.70	11.36	–
100	39.23	0.70	3.21	–

Final mineralization in all cases was below the threshold of 70 % indicated by the OECD 301E guideline to classify the substance as readily biodegradable, even for the lowest concentration on 25 mg DOC/L. This can be explained because the modified OECD 301E screening test is one of the strictest biodegradation methods due to the low concentration of microorganisms, which shows up the difficulties on the biodegradation of some surfactants (OECD 301, 1992). Results show that final mineralization (*% Min*) was directly related with the initial concentration of the surfactants and ranged from 39.23 % for the highest concentration (100 mg DOC/L) to 64.58 % for the lowest concentration (25 mg DOC/L). This is related with the toxic effects of the surfactant to the microorganisms responsible of the biodegradation and it can be also appreciated in the latency times (t_L), which are higher for the higher initial concentrations. Nevertheless, it is worth noting that they are not excessively long (0.5–0.7 days). Mohan et al. (2006) also reported the inhibitory effects of Triton X-100 on the aerobic biodegradation, and also a direct effect of the initial concentration in the t_L. To compare the biodegradation rate at the beginning of the test, VM_{25} was calculated. As expected, the highest value was obtained with an initial concentration of 25 mg DOC/L, being 6 times higher than VM_{25} with 100 mg DOC/L. Intermediate concentrations had intermediate values of VM_{25}. VM_{50} was only calculated to 25 and 50 mg DOC/L, as the higher concentration did not reach 50 % biodegradation, but the trend observed was similar (higher concentration, lower rate). These results align with the results of the study conducted by Najim et al. (2022) where, using non-adapted mixed bacterial cells, found that the higher the concentration of sodium dodecyl sulfate (SDS) was, the lower the biodegradation rates were. This also agrees with the results found in other studies with different surfactants (Jurado et al., 2011, 2012; Mohan et al., 2006) in which the percentages of biodegradation of fatty-alcohol ethoxylates, Triton X-100, alkylpolyglucosides and ether carboxylic derivatives surfactants were higher when the initial surfactant concentrations were lower. The opposite trend was observed by Ríos et al. (2017a) on the aerobic biodegradation of amine-oxide based surfactants, likely because these nitrogen-containing surfactants provide part of the nitrogen needed by the microorganism metabolism. In the case of PGE-OE_{17}, it only provides C, H and O, likely not limiting for the living and growth of the microorganisms, moreover, it is a toxic surfactant to some bacteria (Ríos et al., 2017b).

For the biodegradation test with the initial concentration of 100 mg DOC/L, liquor samples were taken at 2, 6, 12, 20 and 28 days to determine the inhibition activity to bacteria *V. fischeri*, this allows to check the evolution of the toxicity caused by the remaining surfactant and its possible intermediate by-products, generated during the biodegradation, although they were not identified due to the difficulty to isolate them in the complex biodegradation matrices. Evolution of the inhibition during the biodegradation test is shown in Fig. 2 and inhibition data are shown in Table 4. Values are indicated for a contact time of 15 and 30 min between the sample and bacteria. Additionally, for each biodegradation test with different initial concentrations (25, 50 and 75 mg DOC/L) the inhibition was determined at the beginning and at the end of the test (Table 4).

Ríos et al., reported the toxicity of PGE-OE_{17} to bacteria *V. fischeri* and determined the dose-response curves (Ríos et al., 2017c). For an initial concentration of 100 mg DOC/L (approximately 41.72 mg surfactant/L), they reported an inhibition of around 45 % with a contact

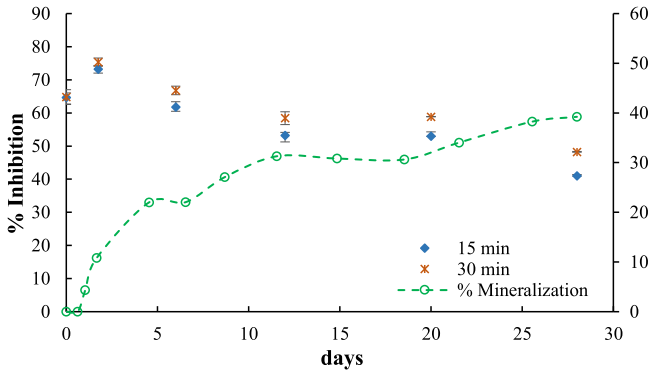

Fig. 2. Evolution of inhibition effects of biodegradation samples from biodegradation test (100 mg DOC/L) to bacteria *V. fischeri* (contact time, 15 and 30 min) and aerobic biodegradation profile. (I, standard deviation).

time of 15 min, which is a little lower than the initial inhibition of luminescence observed for the sample at time 0 of the biodegradation test. The same happened for the initial inhibition percentage of the other biodegradation tests, 25, 50 and 75 mg DOC/L when compared with the results of the mentioned study (Ríos et al., 2017c) Discrepancies can be explained by the difference in the mineral medium of the biodegradation test and the reproducibility of the results, but in any case, they are in the same order of magnitude. At the start of the biodegradation test for the 100 mg DOC/L tests, inhibition of luminescence was 62.57 % and 64.87 % for a 15 min and 30 min of contact times respectively. After 2 days, inhibition increased to 67.72 % and 71.34 % (15 and 30 min), showing that the intermediate by-products generated at the beginning of the biodegradation could have a higher inhibitory effect to the microorganisms than the starting surfactant. Over the course of the test, the inhibition slowly decreased until 41.04 % and 48.24 % (15 min and 30 min) after 28 days biodegradation, which could be an indicative that with the degradation of the surfactant and the possible intermediate products, the inhibitory effects of the liquor decreases.

Comparing the biodegradation and inhibition profiles during the biodegradation test, it can be observed that after the increase of the inhibition (between 2 and 6 days) the biodegradation rates (the slope of the biodegradation curve) had a slowdown or decline. This could explain the difficulties of the microorganisms to degrade the surfactant and the low values of final mineralization (*% Min*) achieved, likely because the surfactant and the possible intermediate by-products could interfere with the proper metabolism of the bacteria.

Additionally, looking at the inhibition percentages to the biodegradation tests of 25, 50 and 75 mg DOC/L at the beginning and end of the test (Table 4), it could be stated that inhibitory effects of the biodegradation liquor also decrease as consequence of the biodegradation of the surfactant. Moreover, the higher the initial concentration is the higher the inhibition is. Table 4 also shows the percentage of the inhibition reduction between day 0 and 28 for each biodegradation test. When comparing the initial inhbition of 25 mg DOC/L with the final inhibition of 50 mg DOC/L experiments, a reduction in the inhibition of the solution can be appreciated, as for a *%Min* of ~50% of the 50 mg DOC/L, the inhibition % is lower than the initial inhibition % of the 25 mg DOC/L surfactant solution. This is also the case when comparing the 50 and the 100 mg DOC/L initial and final inhibitions, respectively, as with a %Min of only ~40% for the final solution of the 100 mg DOC/L test, the inhibition % is lower than the initial inhibition % of the 50 mg DOC/L.

3.2. Anaerobic biodegradability

The anaerobic biodegradability of PGE-OE_{17} at different initial surfactant concentration (S_0) (25, 50, 75, and 100 mg DOC/L) was also studied. The substance concentration recommended by the ISO 11734:1995 guideline (European Commission, 1995) (100 mg DOC/L)

Table 4
Percentage of inhibition of biodegradation samples to bacteria *V. fischeri*, and inhibition reduction percentages.

	Luminescence inhbition, % (SD) 0-days		2-days		6-days		12-days		20-days		28-days		% Inhibition reduction (28-days)	
S_o, mg DOC/L	15 min	30 min	15 min	30 min	15 min	30 min	15 min	30 min	15 min	30 min	15 min	30 min	15 min	30 min
25	40.41 (1.74)	42.56 (0.99)	–	–	–	–	–	–	–	–	29.38 (3.68)	33.6 (3.54)	27.3	21.0
50	47.66 (1.50)	50.87 (1.42)	–	–	–	–	–	–	–	–	34.50 (0.97)	40.6 (0.73)	27.6	20.2
75	56.47 (2.11)	57.47 (1.18)	–	–	–	–	–	–	–	–	33.60 (0.76)	39.6 (0.41)	40.5	31.2
100	64.65 (1.38)	64.87 (2.13)	73.22 (0.93)	75.40 (1.18)	61.80 (1.58)	66.80 (1.29)	53.23 (0.93)	58.44 (1.94)	52.97 (1.31)	58.86 (0.06)	41.04 (0.35)	48.24 (0.11)	36.5	25.6

is included in the interval of the initial concentrations studied. Fig. 3 shows the biodegradation profiles based on the headspace gas (D_h) and Table 5 shows the biodegradation parameters such as latency time (t_L), percentage of final anaerobic biodegradation based on the headspace gas (D_{hf}), percentage of final mineralization (D_t) and mean biodegradation rate to reach 15 % and 25 % of the anaerobic biodegradation (VM_{15} and VM_{25}) (Ríos et al., 2016; Ríos et al., 2017b).

Latency time values (t_L) show that lag phase is practically negligible and there is not a significant adaptation problem of the anaerobic microorganisms. Only in the case of the lowest initial concentration (25 mg DOC/L), t_L was a bit higher (0.67 days), but it is not significatively relevant considering the total duration of the test.

In all cases, anaerobic biodegradation increased rapidly during the first week of the test reaching biodegradation percentages higher than 20 %, but, after approximately 2 weeks, the biodegradation rate diminished considerably for the initial surfactant concentrations of 25 and 50 mg DOC/L and almost stopped for the 75 and 100 mg DOC/L tests. The highest mean biodegradation rates, VM_{15} and VM_{25}, occurred at the lowest initial surfactant concentration, and VM_{25} decreased with the increase of the initial concentration, revealing the negative effect of the surfactant on the biodegradation course. The final mineralization (D_t) of PGE-OE$_{17}$ ranged from 38.82 % for the lowest initial surfactant concentration to 25.56 % for the highest concentration, or what is the same, the lowest the initial concentration was the higher the final mineralization achieved was. According to the guideline OECD 311 (OECD 311, 2006), the complete anaerobic biodegradation can be assumed to occur if 75 % of the theoretical gas production is reached. Therefore, PGE-OE$_{17}$ cannot be considered completely biodegradable under anaerobic conditions. This can be explained by the possible inhibition effects of the surfactant to the anaerobic microorganisms, which implies a decrease in the methanogens activity (Zheng et al., 2023). He et al. (2019); Khalil and Liu. (2021); Zhang et al. (2021) reported how

Table 5
Biodegradation parameters for anaerobic biodegradation of PEG-OE$_{17}$ at initial concentrations (25–100 mg DOC/L).

S_o, mg DOC/L	t_L, days	VM_{15}, %/day	VM_{25}, %/day	D_{hf},%	D_t,%	I_h,%
25	0.67	5.04	2.68	34.10	38.82	19.81
50	0.16	3.21	2.27	29.89	33.71	34.73
75	0.19	3.33	1.85	23.20	28.76	57.78
100	0.17	3.03	1.47	24.72	25.56	57.46

the activity of anaerobic microorganisms can be negatively affected by surfactants.

To quantify the inhibition effects of the surfactant on the endogenous biogas production, percentages of inhibition (I_h) can be calculated by Eq. (8) (Ríos et al., 2016):

$$I_h = \left(1 - \frac{m_{hf}}{m_b}\right) \cdot 100 \quad (8)$$

Where m_{hf} is the final biogas production and m_b is the endogenous biogas production of the blank. Inhibition percentages (I_h) values are shown in Table 5, where it can be appreciated that there was an inhibition higher than 50 % for the tests with an initial surfactant concentration of 75 and 100 mg DOC/L, whereas for the 25 and 50 mg DOC/L the inhibitions were lower, 19.81 % and 34.73 % respectively. Hence, it can be corroborated that there are inhibitory effects of the PGE-OE$_{17}$ to the anaerobic microorganisms and that they are dependent on the surfactant concentration.

In addition, to understand the inhibitory effects of the biodegradation liquors during the progress of the tests, samples of the anaerobic biodegradation reactor, with the initial concentration of surfactant of

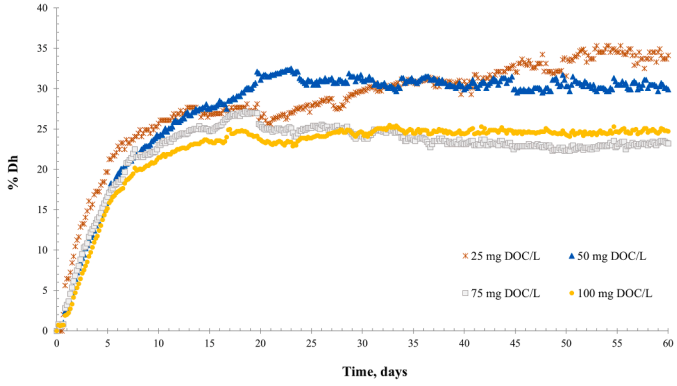

Fig. 3. Anaerobic biodegradation profiles of PGE-OE$_{17}$ at initial concentration (25–100 mg DOC/L).

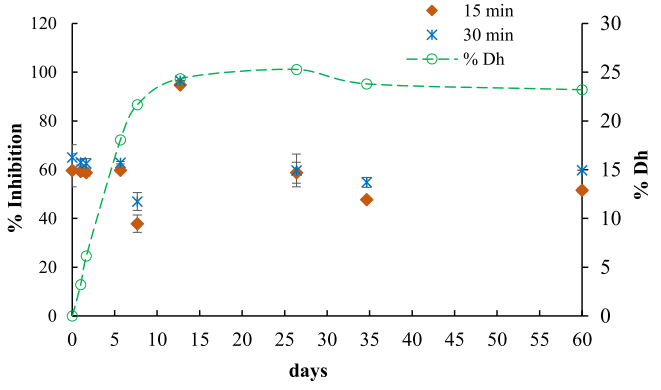

Fig. 4. Evolution of inhibition effects of anaerobic biodegradation samples from biodegradation test (75 mg DOC/L) to bacteria *V. fischeri* (contact time, 15 and 30 min) and anaerobic biodegradation profile (D_h). (I, standard deviation).

75 mg DOC/L, were taken at several biodegradation times to test the potential toxicity with bacteria *V. fischeri*. Fig. 4 shows the evolution of the inhibition effect on the luminescence of bacteria over the time of anaerobic biodegradation.

It is worth noting that after the first week in which the inhibition of the samples did not decrease there was a decrease at day 8 followed by a significant increase at day 12. The biodegradation profile (D_h) was overlapped in the Fig. 4, and it can be observed how the increase of the inhibition matches with the stoppage of the anaerobic biodegradation, likely because the by-products generated can be toxic to the anaerobic microorganisms causing their death or inhibiting their proper growth stopping or slowing down the anaerobic biodegradation. Intermediates and by-products in sewage sludge anaerobic digestion such as sulfates ammonia, volatile fatty acids or sulfides/sulfates have been also reported as inhibitory compounds of the methanogenic processes (Yuan and Zhu, 2016).

3.3. Combined aerobic-anaerobic biodegradation

For the complete assessment of the biodegradability of the surfactant PGE-OE$_{17}$, a combined aerobic and anaerobic biodegradation test was conducted. This consisted in a first aerobic treatment followed by an anaerobic biodegradation treatment.

On the one hand, after the 28 days of the aerobic biodegradation tests with different initial surfactant concentrations (25, 50, 75 and 100 mg DOC/L), the remaining biodegradation liquors were treated under anaerobic conditions for 60 days. Fig. 5 shows the percentage of biodegradation achieved by the aerobic test and the percentage of the anaerobic biodegradation of the remaining surfactant and the intermediate by-products.

Results show that after the aerobic biodegradation test, in which the percentage of biodegradation is higher for the lower initial surfactant concentrations, the anaerobic biodegradation cannot complete the total biodegradation of the surfactant. The contribution of the anaerobic biodegradation was higher for the test with the initial concentration of 50 mg DOC/L (8.02 %), being lower in case of 25 and 75 mg DOC/L, and practically negligible for the highest concentration. This means that the remaining surfactant or the intermediate by-products of the aerobic biodegradation are not anaerobically biodegradable. Even for the lowest initial concentration, total biodegradation did not reach the 70 %. As it was found with the previous results, biodegradation products could have inhibitory effects to the aerobic and anaerobic microorganisms, this also happens in regular wastewater treatment in which by-products and intermediates are often found to be the leading cause of anaerobic process upset (Yuan and Zhu, 2016). Looking at the results, it can be stated that the lowest the aerobic biodegradation is, the higher inhibition of the anaerobic biodegradation can be. In other words, when the concentration of DOC is higher after the aerobic biodegradation test, the subsequent anaerobic biodegradation is prevented. However, the post anaerobic biodegradation can contribute to the degradation of some intermediate by-products which were non-biodegradable aerobically.

A second set of experiments involved the aerobic and anaerobic biodegradation PGE-OE$_{17}$ with different times of the first aerobic treatment (0, 2, 7, 12, 19 and 28 days) followed by 60 days of anaerobic treatment. The initial surfactant concentration of the aerobic test was 100 mg DOC/L. Fig. 6 shows the percentage of biodegradation achieved by the aerobic test, the percentage of the anaerobic biodegradation of the remaining surfactant and by-products, and the total time of the combined tests.

The sample subjected only to the anaerobic biodegradation (60 days) reached the lowest biodegradation (25.56 %), whereas when the samples are coming from a first aerobic treatment, the anaerobic biodegradation can help to reach higher percentages of total biodegradation. Reasonably, at lower times of aerobic biodegradation (and lower aerobic biodegradation) the contribution of the anaerobic biodegradation is higher since there is more carbon available for the methanogenesis. This results, could also imply that the aerobic treatment (even with a low treatment time) could partially reduce the amount of toxic compounds for the anaerobic microorganisms, increasing the anaerobic biodegradation.

In all cases of a combined treatment, the anaerobic process complemented the aerobic one reaching total biodegradation percentages between 39.5 and 50.5 %. Therefore, the anaerobic treatment is a good complementary treatment for the mineralization of the surfactant, which, additionally, allows to obtain methane that can be used as energy source, and could shorten the time needed for the aerobic treatment. Novak et al. (2011) also studied combinations of aerobic and anaerobic treatments for the sludge waste reduction and nitrogen removal with enhanced yields.

In summary, the highest percentages of total biodegradation were achieved with a complete aerobic biodegradation (28 days) and the subsequent anaerobic treatment (60 days) for the lowest surfactant concentrations (Fig. 5), since part of the intermediate by-products of the first treatment are degraded anaerobically. It is worthy to note, that the initial concentration of the surfactant has a relevant effect, and for high surfactant concentrations (100 mg DOC/L), anaerobic biodegradation does not contribute much, because the high concentration of surfactant has a negative impact on the anerobic microorganisms. Comparing the results of the combined biodegradation tests for the same initial concentration (100 mg DOC/L) at different times of the aerobic treatment, the optimum was found with the combination of 17 days of aerobic test and the complete anaerobic biodegradation test, while the highest methane potential was obtained with an aerobic treatment of 7 days followed by an anaerobic treatment.

Even though total biodegradation percentages are not higher than

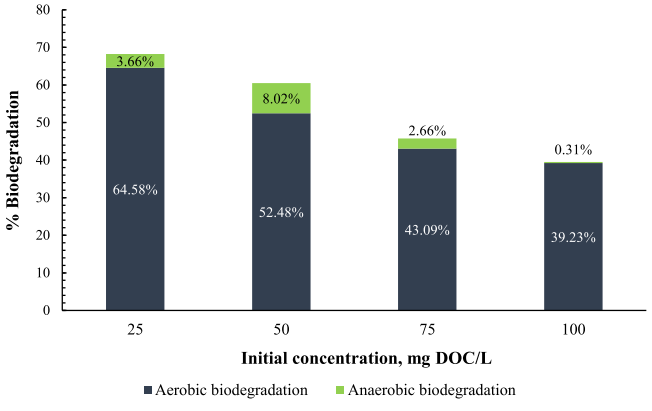

Fig. 5. Combined aerobic and anaerobic biodegradation of PGE-OE$_{17}$ at different initial surfactant concentrations.

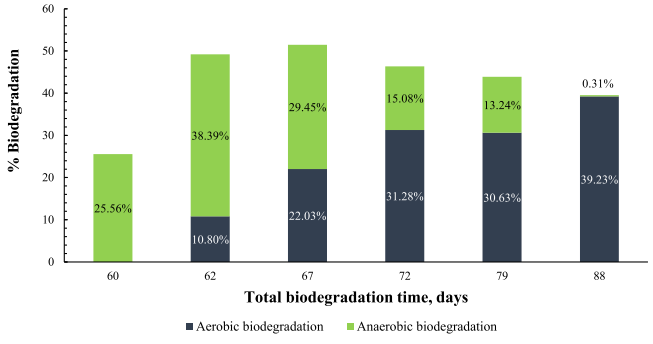

Fig. 6. Combined aerobic and anaerobic biodegradation of PGE-OE$_{17}$ at different treatment times of the aerobic test (0, 2, 7, 12, 19 and 28 days). Duration of the anaerobic test 60 days. Initial surfactant concentration 100 mg DOC/L.

70 %, anaerobic biodegradation treatment could be optimized by changes in some parameters as time, temperature, surfactant and concentration, or the preadaptation of the anerobic microorganisms to the surfactant. This would favor the methanogenic processes and the biogas production as alternative to fossil energies.

4. Conclusions

In this study we found that the surfactant PGE-OE_{17} was not completely aerobically biodegradable following the method OECD 301E (OECD 301, 1992) (%Min < 70 %), and the higher the initial surfactant concentration was, the lower the final mineralization obtained. This can be explained by the inhibition effects of the surfactant on aerobic bacteria. Inhibition of the biodegradation liquor to bacteria *V. fischeri* was followed during the biodegradation test, and an increase in the inhibition at the beginning of the test was observed. The surfactant PGE-OE_{17} was also not completely anaerobically biodegradable according to the ISO 11734:1995 (European Commission, 1995), and the increase of initial surfactant concentration has a negative effect on the final biodegradation rate achieved. PGE-OE_{17} inhibited the endogenous biogas production of the anaerobic bacteria, and it was found that after two weeks of the test some intermediate by-products with higher inhibition potential could have been formed, and, likely, responsible for slowing or stopping the anerobic biodegradation. The isolation and identification of the possible by-products generated during aerobic and anaerobic biodegradation is a challenge that will be addressed in further works. Additionally, the combined test (aerobic + anaerobic) showed that the anaerobic biodegradation of PGE-OE_{17} can be enhance by a partial initial aerobic biodegradation, increasing both total biodegradation (vs total aerobic or total anaerobic) and biomethane potential.

CRediT authorship contribution statement

Francisco Ríos: Conceptualization, Methodology, Formal analysis, Validation, Investigation, Data curation, Supervision, Funding acquisition, Project administration, Visualization, Writing – original draft, Writing – review & editing. **Francisco Caparrós-Salvador:** Conceptualization, Formal analysis, Validation, Writing – review & editing. **Manuela Lechuga:** Writing – review & editing, Validation, Visualization. **Mercedes Fernández-Serrano:** Writing – review & editing, Validation, Visualization.

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.

Data availability

Data will be made available on request.

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