Environmental Impact Assessment of Nanofluids Containing Mixtures of Surfactants And Silica Nanoparticles

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Abstract

Due to the widespread use of nanoparticles in surfactant-based formulations, their release into the environment and wastewater is unavoidable, causing a toxic effect to biota and/or wastewater treatment processes. Because of concerns about the environmental impact of nanofluids, the study of the fate and environmental impact, hazards and toxicity of nanoparticles is beginning. However, the interactions between nanoparticles and surfactants as well as the biodegradability in mixtures have been little studied until now. In this work the environmental impact of nanofluids containing mixtures of surfactants and silica nanoparticles were evaluated. The systems studied were hydrophilic silica nanoparticles (size 7 and 12 nm), a non-ionic surfactant (alkyl polyglucoside), an anionic surfactant (ether carboxylic acid), and mixtures of them. The aerobic ultimate biodegradation and interfacial and adsorption properties of surfactants, nanoparticles and mixtures during the biodegradation process were also evaluated. Aerobic biodegradability was determined by measurements of dissolved organic carbon for solutions with variable concentrations of surfactants and nanoparticles. The ultimate biodegradation was studied below and above the CMC of the individual surfactants. Interfacial and adsorption properties of surfactants solutions containing nanoparticles are influenced by the addition of silica particles. It was determined that silica nanoparticles reduced the capability of non-ionic surfactants to decrease the surface tension. Thus, silica NP promoted a considerable increase of their CMC, whereas the effect was the opposite in case of anionic surfactants. The increasing concentration of surfactant and nanoparticles in the test medium causes a decrease in the maximum levels of mineralization reached for both types of surfactants. The presence of silica nanoparticles in the medium reduces the biodegradability of binary mixtures non-ionic-anionic- surfactants solutions, being this effect more intense for larger nanoparticles. These results could be taken into account to model the behavior of nanofluids in aquatic environments and to select appropriate nanofluids containing nanoparticles and surfactants with low environmental impact.

1. Introduction

Despite the large number of applications and the numerous advantages of surfactants in the industrial and economic fields, from an environmental point of view, they are considered as an important contaminant of the aquatic environment, also taking into account the high volumes of these substances that are spilled daily in this medium. Once used, the surfactants reach the treatment plants through urban and industrial wastewater and in certain cases are directly discharged into surface waters. During the treatment of wastewater, a high percentage of the surfactants present in the aquatic environment are eliminated by aerobic processes of biodegradation and adsorption in the particulate material, while the metabolites generated and the non-degraded surfactants are dispersed in the different environmental compartments. A growing problem is currently arising due to the mixing of waste, hospital and industrial water with significant surfactant load in wastewater treatment plants as well as surfactant mixtures of different nature. The concentrations of surfactants present in domestic wastewater can vary between 1–10 mg/L while they can reach levels of 300 mg/L in industrial wastewater (Siyal et al. 2020). Sewage

treatment plants can lower the concentration of surfactants up to 1–3 mg/L but the surfactants are still present in the active sludge leading to significant environmental impacts (Bautista-Toledo et al. 2014).

The study of the environmental behavior of the main classes of nonionic and anionic surfactants has received increasing interest in recent years from downstream users and regulators. Consequently, the emphasis is being placed on considering biodegradation as a basic and determining parameter to minimize the use and release of substances that may persist in the environment, generating a great proliferation of regulatory efforts and industrial agreements.

The EU Safer Detergents Regulation (Regulation (EC) No 648/2004, 2004) which required standardized tests of primary and ultimate biodegradation for industrial and domestic uses and applications of formulations with surfactants, was fundamental to establish a harmonized performance in the global industry of surfactants.

Additionally, the widespread adoption of the Globally Harmonized System (Globally Harmonized System of Classification and Labelling of Chemicals (GHS), 2017) of classification and labelling has increased the demand for surfactants with favorable safety and environmental profiles. As biodegradation is the main mechanism for removing organic compounds, the knowledge of biodegradability of surfactants in combination with other additives is necessary to understand environmental behavior of this mixtures before designing a detergent formula.

At that respect, the special properties of the particles (1 nm to 1 μ m) and the advantages that they offer in processes related to applications in catalysis, new materials or biomedicine, have led to their increasing use in consumer products such as detergents (Ma et al. 2008). Scientific interest in recent years has focused on silica nanoparticles (Slowing et al. 2010, Mamaeva et al. 2013), several detergent formulations and related formulations containing silica particles have been patented (Orlich et al. 2007). Actually nanoparticles are present in a large number of formulations and applications due to their physicochemical properties, low toxicity, stability and functionalization capacity with a range of polymers and molecules (Ríos et al. 2018a). Silica nanoparticles are frequently employed mixed with surfactants in oil recovery, nanofluids, immobilization of enzymes, removal of dyes, detergents or foam stabilizers (Maestro et al. 2014, Zhu et al. 2015, Patra et al. 2016, Plomaritis et al. 2019). Nanoparticles can contribute to the cleaning of surfaces both due to their abrasive effect and by improving the solubilisation.

In the same way as surfactants, particles of colloidal size can accumulate spontaneously in interfaces of the type liquid-gas or liquid-liquid acting as stabilizers of emulsions and foams (Eskandar et al. 2011). Simple algorithms have recently been used to estimate potential concentrations of NP from consumer products. However, the concentrations estimated by applying the abovementioned models are significantly lower than the results of many of the currently published studies (Tiede, 2009). A large variety of both organic (solid lipid nanoparticles) and inorganic materials (silica, clay, ferric oxide, titanium dioxide, alumina, carbon or latex) are used as stabilizers of oil emulsions in water or water in oil, when nanoparticles are used together with the

surfactants, synergistic effects can be observed in the production of emulsions and the appearance of stable foams, so it is of great interest to study these interaction effects from an environmental point of view. The colloidal particles play a role similar to the surfactant molecules if they are adsorbed in a fluid-fluid interface. Just as the affinity of a surfactant for the aqueous or fatty phase is quantified in terms of its hydrophilic-lipophilic balance (HLB), for solid particles this tendency is described by its wettability, given by its contact angle (Paunov et al. 2002). Recently, Safounane et al. have reported an improved emulsifying capacity when using mixtures silica- nanoparticles and ionic surfactants as emulsion stabilizers with opposite charge (Safouane et al. 2007).

Due to the widespread use of nanoparticles in formulations in recent years, their release into the environment and wastewater is unavoidable (Huang et al. 2017), causing a toxic effect to biota and/or wastewater treatment processes. Because the increasing concern about the environmental impact of latest materials, the study of the toxicity, hazards, fate and environmental impact of nanoparticles is beginning (Liu et al. 2014; Skorochood et al. 2016 Ríos et al. 2018b). The environmental impact of individual surfactants has been widely studied, as they can show toxicity to several aquatic organisms, recalcitrant or harmful to wastewater treatment plants (Lechuga et al. 2016; F. Ríos et al. 2017). However, the interactions between nanoparticles and surfactants as well as the biodegradability in mixtures of surfactants have not been sufficiently studied until now. A recent paper by Bimová et al. 2021 summarizes possible toxic effects of nanomaterials on environment and living organisms as a consequence of its application in different technologies, environmental sectors, and medicine. However this work does not include any reference on the mixtures nanoparticle-surfactant. In our humble point of view, this reinforces the lack of knowledge on this particular field.

The predictability of joint effects of solutions containing surfactant and nanoparticles is of great interest for an adequate assessment of environmental risk due to the growing development of nanoproducts, nanomaterials and nanofluids.

The growing concern in recent years to design non-polluting detergents has led to the development and use of more environmentally friendly surfactants such as the ether carboxylic derivative surfactants and alkyl polyglucosides analyzed in this study. Surfactant ether carboxylic acid are used in cleaning and cosmetic products which are going to be in contact with the skin. These surfactants have the property of improving the foaming capacity of the surfactant formulations, decreasing the level of irritation (Jurado et al. 2011) when they are compared with other anionic surfactants. Alkyl polyglucosides have great advantages compared to other classes of surfactants. Their natural origin is the cause of their good physical and environmental properties. Moreover, alkyl polyglucosides present good compatibility and foam production, excellent cleaning efficiency, wettability and ocular and dermatological safety, and have been proved to be readily biodegradable in aerobic conditions (Jurado et al. 2002; Zgoła-Grześkowiak et al. 2008). All this makes them potential components in a variety of domestic and industrial applications (Pantelic and Cuckovic, 2014; Tasic-Kostov et al. 2014).

The OECD 301 series of readily biodegradable tests are considered a standard for screening purposes. (OECD, 1992). Ready biodegradability tests are conservative in nature and stringent enough to assume rapid and complete biodegradation of compounds in aquatic environments (OECD, 1992).

Biodegradability tests can produce variable results attributable to changes in inoculum, inoculum origin, and ratio, resulting in false negatives. (Lundgren et al. 2013). In this sense, "positive" results can be considered sufficient evidence of biodegradability and can generally substitute for negative results.

. Due to the high production volumes and the massive and dispersed use of surfactant-based formulations, this work has focused on biodegradation of anionic and nonionic surfactants and their relative risk profiles compared to mixtures of surfactants and surfactants-nanoparticles.

In this work, it has been studied the aerobic biodegradability of nanofluids, solutions containing silica nanoparticles in combination with an anionic surfactant (ether carboxylic acid), a non-ionic surfactant (alkyl polyglucoside), whose individual environmental impacts have been previously assessed (Jurado et al. 2013; Ríos et al. 2017), and mixtures of them. In addition, with the purpose of gain insight into the environmental behavior and other aspects related to interfacial phenomena and cleaning efficiency, the effect of nanoparticles on the surface, interfacial tension and Critical Micellar Concentration (CMC) of surfactants and mixtures have been measured.

2. Materials And Methods

2.1. Silica nanoparticles

Two types of hydrophilic silica nanoparticles (Aerosil 380 and Aerosil 200, Evonik Industries AG (Essen, Germany)), were used. Table 1 shows the physico-chemical properties of nanoparticles used in this study: mean diameter (D_m), specific surface area (S), tapped density (d) and pH. Nanoparticles have been observed in TEM using an ultra-high resolution scanning transmission electron microscope (S/TEM) and high-angle annular dark-field imaging (HAADF) FEI TITAN G2 60–300. The images show amorphous structures for both nanoparticles which tend to be spherical in shape (Fig. 1), but showing values of sphericity of 0.851 and 0.943, for both of Aerosil 380 and Aerosil 200, respectively. TEM analyses were performed, to corroborate this statement.

Table 1
Physico-chemical properties of nanoparticles

Nanoparticle	Abbr.	D_m , nm	S, m ² /g	d, g/L	pH value
Aerosil® 380	A380	7	380 ± 30	50	6.24–6.72
Aerosil® 200	A200	12	200 ± 25	50	6.14–6.54

2.2 Surfactants

A non-ionic surfactant alkyl polyglucoside (APG) supplied by Sigma-Aldrich (St. Louis, USA) and an anionic surfactant ether carboxylic acid (EC) provided by KAO Corporation (Tokyo, Japan) were studied. The surfactants were either commercial products. Table 2 summarizes their main characteristics. A binary mixture of these surfactant was also studied at the proportion 1:1 (w/w).

Table 2. Details of surfactants used in the tests

Surfactant	EC-R ₁₂₋₁₄ E ₃	APG-R ₈₋₁₄ DP _{1.3}
Chemical Name	Laureth-4 Carboxylic Acid	Coco Glucoside
Trade Name	AKYPO® RLM-25	Glucopon 650
Strcuture	$R_{12-14}-(CH_2-CH_2O)_3-O-CH_2-COO^-$	
Active matter ^a , %	93.1	48.6

^a: Determined using infrared radiation (Ríos et al. 2016)

R: Length of the alkyl chain, n-C_iH_{2i+1}-

E: Ethoxylation degree

DP: Mean number of glucose unit per surfactant molecule

2.3. Sample preparation

A magnetic stirrer was used to wet the silica particles by the aqueous media, then the dispersion and de-agglomeration process was done by ultrasonication for 30 minutes (Sonorex RK 106 S, Bandelin, Berlin, Germany) in 1 L of ultrapure water, successively the surfactant was aggregated to obtain the suitable concentration. Ultrasonic cavitation helps to dispreads particles, since it generates high shear that breaks particle agglomerates. Interfacial tension, superficial tension and biodegradability of surfactants solution with silica nanoparticles were assessment as is described in the next sections.

2.4. Surface and interfacial tension

Surface and interfacial tension were determined for nanoparticles and surfactants. Also, during the biodegradability test, surface and interfacial tension were determined over time. Surface tension was measured at 25 °C using the Wilhelmy Plate Method with a Krüss KSV tensiometer equipped with a 2-cm platinum plate (Krüss GmbH, Hamburg, Germany). The platinum plate was cleaned by heating to a reddish orange colour with a burner prior to use. The standard deviation was calculated by carrying out successive measurements, resulting in values less than 0.1 mN/m. Interfacial tension (IFT) between

dodecane and aqueous solutions were determined at 25°C by a pendant drop tensiometer (KSV CAM 200, KSV Instruments Ltd, Finland). Measurements were performed in triplicate.

The critical micellar concentration CMC was calculated by drawing the surface tension vs the surfactant concentration (0 to $5 \cdot 10^3$ mg/L). The break point in the plot shows the formation of micelles. Results of CMC for anionic and non-ionic surfactant are shown in Table 3.

2.5. Biodegradation and adsorption tests

Ultimate ready biodegradability tests followed the OECD 301E test guideline (OECD 1992). Ready biodegradability was determined for solutions containing individual and mixtures of surfactants. Reference assays was used as a positive control with a readily biodegradable surfactant (linear alkylbenzene sulfonate) to check the activity of the microbial population existing in the test medium. The biodegradation tests are based on the removal of organic compounds measured as dissolved organic carbon (DOC) (OECD, 2001). This test is quite rigorous, due to the relatively high concentration of surfactant, the only carbon source, and the low proportion of inoculum and the test compound. All experiments were performed at 25°C. In the biodegradation test the surfactant solutions with nanoparticles are the unique carbon source for the microorganisms. The surfactant and the nanoparticle solution are prepared in a mineral medium, which is inoculated and incubated under aerobic conditions in darkness for 28 days. Test medium previously aerated for 30 min with carbon dioxide-free air, and prepared according to the guideline, consisted of glass-distilled water and mineral salts. Duplicate test systems were run for each test solution, along with positive control, and blank samples. The solution (for which the biodegradability is to be determined) is inoculated with 0.5 mL of fresh activated sludge inoculum obtained from a municipal wastewater treatment plant that operates with active sludge (Granada, Spain, 37°09'54.1"N–3°37'31.8"W) selected because it deals predominantly with non-industrial, municipal wastewater. The microbial activity of the supernatant was determined to be 10^5 to 10^6 CFU/mL. Supernatant of microbial sludge was added to the test medium.

The biodegradation process is determined by means of the residual-surfactant concentration over time by dissolved organic carbon (DOC) measurements determined in samples filtered through a 0.45 µm Millipore membrane. In the reference test, the initial concentration of surfactant was 5 mg/L in all cases, and the average biodegradability reached at the end of the test was 98.34% thus fulfilling the criteria set by the OECD of 90% after 5 days for the soft standard and allowing thus the validity of the assay.

Test surfactants concentration ranged from 25 to 50 mg/L in order to ensure at least 40 mg ThOD/L. Test temperature was maintained at $25^\circ\text{C} \pm 1^\circ\text{C}$ (some minor deviations of less than 1°C). All test vessels were stirred constantly using magnetic stir bars at 125 sweep/min. All glassware was cleaned using a solution of ammonium persulfate in H_2SO_4 (98%).

Adsorption experiments were carried out at the same conditions of biodegradation tests in the absence of microorganisms.

3. Results And Discussion

3.1 Surface and interfacial tension

Surface and interfacial tension of nanoparticles dispersions in Milli-Q® water at the range 0–1.000 mg/L at 25°C were determined. For both nanoparticles dispersions the surface and interfacial tension did not changed with the concentration, and values were around 44.6 ± 0.4 mN/m for interfacial tension and 71.3 ± 0.6 mN/m for surface tension, close to those between dodecane and pure water (Table 3). Therefore, the silica particles are not surface active, they do not have preference for the water-air/dodecane interface due to their hydrophilic character. These results are consistent with the surface tension data obtained by Ma et al. (Ma et al. 2008) and Vatanparast et al. (2018) (Vatanparast, 2018) for Levasil® silica solutions.

Table 3
Surface and interfacial tensions of solutions tests

	Nanoparticle (mg/L)	Surfactant (mg/L)	Surface tension, (mN/m)	Interfacial tension, (mN/m)	CMC, (mg/L)
A380					
	0	–	72.28	43.41	–
	250	–	70.35	43.51	–
	1000	–	71.38	44.04	–
A200					
	0	–	72.28	43.41	–
	250	–	72.01	42.97	–
	1000	–	71.32	43.48	–
APG-R₈₋₁₄DP_{1.3}					29.08
	–	25	65.20	31.06	
	–	50	44.89	24.88	
EC-R₁₂₋₁₄E₃					33.24
	–	25	34.31	35.99	
	–	50	35.11	30.24	
EC-R₁₂₋₁₄E₃+APG-R₈₋₁₄DP_{1.3}					44.76
	–	25	52.46	32.13	
	–	50	42.05	27.47	
EC-R₁₂₋₁₄E₃+A200					
	250	50	33.8	31.71	28.40
	1000	50	28.3	23.85	27.92
EC-R₁₂₋₁₄E₃+A380					
	250	50	34.39	30.05	26.71
	1000	50	29.96	23.37	25.48

	Nanoparticle (mg/L)	Surfactant (mg/L)	Surface tension, (mN/m)	Interfacial tension, (mN/m)	CMC, (mg/L)
APG-R₈- 14DP_{1.3}+A200					
	250	50	49.93	26.87	32.74
	1000	50	49.95	27.08	31.63
APG-R₈- 14DP_{1.3}+A380					
	250	50	48.29	27.63	31.82
	1000	50	49.86	28.03	31.24
EC-R₁₂₋₁₄E₃+APG-R₈- 14DP_{1.3}+A200					
	250	50	30.4	35.5	38.42
	1000	50	35.1	36.2	42.15
EC-R₁₂₋₁₄E₃+APG-R₈- 14DP_{1.3}+A380					
	250	50	31.3	48.5	45.27
	1000	50	29.0	47.6	46.32

Anionic and non-ionic surfactants decrease the surface tension of air–water interfaces and the interfacial tension of liquid-liquid interfaces. Taking into account results shown in Table 3, the inclusion of negatively charged hydrophilic silica nanoparticles (diameters 7–12 nm) in surfactants solutions modifies their interfacial properties. Due to the assumed no surface-active character of the silica nanoparticles, the changes of interfacial properties from those of the single surfactant system is attributed to nanoparticles-surfactant interactions (Vatanparast, 2018). In case of the anionic surfactants, silica nanoparticles increase the surface activity and therefore the efficiency of the EC surfactants due to the repulsive coulomb interactions between the surfactants and nanoparticles which promote the surfactant adsorption at air–water interfaces. Similar results were found by Ma et al. (Ma et al. 2008) in systems with SDS involving nanoparticles of diameters 13 nm. For solutions involving nanoparticles and non-ionic surfactants effectively decrease the efficiency and increases the interfacial tensions, the nanoparticle effects are similar compared to those involving air–water interfaces.

The surface and interfacial tension for the solutions of surfactant containing nanoparticles was measured and the CMC was determined at 25°C. Solutions containing nanoparticles and non-ionic surfactant (APG) increased the CMC respect to pure surfactant solution, whereas solutions nanoparticles-
Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js ar results were obtained by Rios et al. (Ríos et al.

2018a) for systems anionic-non-ionic surfactant and silica nanoparticles. The modification on surface and interfacial tension were the same using the same surfactant and different nanoparticles and values of CMC were similar or in the same order of magnitude (Fig. 2). Decrease of CMC with anionic surfactant is due to repulsive electrostatic forces between particles with anionic surfactant that favors the diffusion of surfactant molecules toward interface (Zargartalebi et al. 2015). Silica particles makes the Gibbs free energy of adsorption and micellization more negative (Ma et al. 2008), promoting the adsorption and aggregation in micelles. The decrease in CMC is greater in the case of anionic surfactant solutions containing smaller nanoparticles. In case of non-ionic surfactant, the effect is the opposite because adsorption and electrostatic forces are much weaker, in this case micellization and effects in Gibbs free energy are negligible.

3.2. Biodegradability of surfactants and silica nanoparticles

The aerobic biodegradation of ether carboxylic acid and alkyl polyglucoside solutions in combination with hydrophilic fumed silica nanoparticles at 250 mg/L was studied. Initial surfactant concentration in biodegradability test was below and above CMC, 25 and 50 mg/L. Surfactant adsorption onto materials can influence considerably in the environmental impact of surfactants, some authors have studied this phenomena (Belanger et al. 2006; van Compernelle et al. 2006). Adsorption tests were carried out for experiments with anionic and nonionic surfactants and mixtures of the surfactants with nanoparticles A200 and A380. During the tests, the presence of surfactant was determined by DOC measurements. Also, the surface and interfacial tension were analyzed during the whole adsorption experiment (Fig. 3). Abiotic tests were carried out in a dilution of HgCl_2 to confirm the adsorption, and it was found that the residual concentration values of surfactant remain around 99% during the period of biodegradation. The surface and interfacial tension is approximately constant, which confirms there is no adsorption of the surfactants on the nanoparticles. This fact is observed independently of both the ionic character of the surfactant and the nanoparticles size. Thus, in the adsorption tests presented in this work, the results indicate that the contribution of the abiotic process in the degradation of the surfactant can be neglected even in the presence of nanoparticles. When there are solutions with nanoparticles and surfactants the surface and interfacial tension is lower for the larger nanoparticles. If several adsorption experiments are compared according to the surfactant character, it is observed that the interfacial and surface tension is lower for the anionic surfactant even in the presence of nanoparticles, evidencing less adsorption of anionic surfactants on nanoparticles comparing with non-ionic surfactants. That fact could be explained by electrostatic repulsion between the anionic surfactant and the hydrophilic silica nanoparticles which are negatively charged.

Figure 4 shows the time course of the biodegradability over the degradation period of solutions of APG and EC at initial surfactant concentration of 25 mg/L. The tests were carried out with surfactant solutions without nanoparticles (surfactant solutions 25–50 mg/L) and solutions of surfactant containing nanoparticles in concentrations of 250 mg/L. The final results showed that the effects produced by the presence of nanoparticles are highly dependent on the initial surfactant concentration in the test medium. Generally, results show that the presence of nanoparticles reduces primary and final biodegradability.

This reduction in the biodegradability of the anionic surfactant due to the presence of nanoparticles is 7.06% when the concentration of nanoparticles increases from 0 to 250 mg/L and 10.67 % for non-ionic surfactants. Regardless of the presence of nanoparticles in the solutions, the anionic surfactant is more biodegradable than the non-ionic surfactant. Table 4 shows that EC and APG are readily biodegraded. A surfactant can be considered as biodegradable if when performing one of the tests indexed in Annex III of Regulation (EC) No. 648/2004 (EC Regulation, 2008) a minimum level of 60% of ultimate biodegradation is overcome at 28 days. The surfactants EC and APG fulfils this requirement, yielding 91.8% and 80.64% of DOC removal respectively for initial concentrations of 25 mg/L and 80.15% and 60.49% for initial concentrations of 50 mg/L.

Surface and interfacial tension was also determined during the biodegradation process for solutions containing nanoparticles. As the biodegradation process goes by, the increase of surface and interfacial tension confirms the disappearance of the surfactant from the medium, what agreed with the degradation curves obtained (Fig. 4). In case of the nonionic surfactant (APG), the increase of the superficial and interfacial tension during the biodegradation test is smoother than for the anionic surfactant, a fact that may be related to the degradation metabolites of the APG having a certain interfacial activity. APG follows a central scission biodegradation pathway in which a ω -oxidation and a central scission lead to dicarboxylic acids (Jurado et al. 2011), to which an interfacial activity is associated (Lee and Hildemann, 2013). Independently of the presence of nanoparticles in the biodegradation tests, it is observed that the anionic surfactant has a higher surface and interfacial activity compared to the nonionic surfactant. This fact is directly related to the low adsorption of the anionic surfactant observed during the nanoparticles adsorption tests and with the higher biodegradability of EC compared to APG. The higher hydration capacity of the polar head of anionic surfactant makes adsorption more difficult than for nonionic. For APG, the adsorption of surfactants onto nanoparticles drove the nanoparticles towards the interfaces due to the increased hydrophobicity (Ravera et al. 2006). On the other hand, APG form suspensions and only a small part of the surfactant may be available for bacteria and be susceptible to biodegrade (Zgoła-Grześkowiak et al. 2008), confirming its lower biodegradation with respect to EC.

When comparing the influence of nanoparticles size on the biodegradability it is observed that the larger particles cause higher biodegradability independently of the character of the surfactant (Fig. 4). Both surfactants could decrease the nanoparticle aggregate diameter and increase their effective concentrations. To corroborate this fact some parameters characteristic of the biodegradation profiles (Jurado et al. 2007) were calculated: latency time (t_L), half-life time ($t_{1/2}$), mean biodegradation rate (V_M), percentage of primary biodegradation reached at 50 h of assay (B) and mineralization (Min). Table 4 summarizes the values of characteristic parameters of the biodegradation profiles obtained. Equations 1 and 2 shows the dependence on biodegradation (B) and mean biodegradation rate with nanoparticles concentration for APG and nanoparticles A200.

$$V_m = 0.159 \cdot e^{0.0015[A200]}$$

1

$$B = 22.22.e^{-0.001}[A200]$$

2

Table 4. Characteristic parameters of the biodegradation profiles

	t_L (h)	$t_{1/2}$ (h)	V_M (%/h) (a)	B (%)	Min (%) (b)
APG-R ₈₋₁₄ , 25 mg/L	15.12	117.36	0.17	25.60	80.64
EC-R ₁₂₋₁₄ , 25 mg/L	16.32	52.32	0.83	46.50	91.8
APG-R ₈₋₁₄ , 25 mg/L. A200 250 mg/L	15.96	122.52	0.29	17.54	76.66
APG-R ₈₋₁₄ , 25 mg/L. A380 250 mg/L	21.60	177.24	0.23	25.04	65.53
EC-R ₁₂₋₁₄ , 25 mg/L. A200 250 mg/L	78.24	206.64	0.28	2.55	87.02
EC-R ₁₂₋₁₄ , 25 mg/L. A380 250 mg/L	21.18	46.64	0.57	57.12	77.38
1. Calculated for a 50 % biodegradability 2. Data for the ultimate biodegradation profiles					

The nanoparticles affected the acclimation time of the microorganisms, t_L ; this value varied between 15.96 hours for the assay APG-A200, and 78.24 hours for the assay of EC-A200. The latency time and half-life time, notably augmented for the nanofluids containing nanoparticles A200. The presence of nanoparticles in the biodegradability test did not altered the form of the resulting curve, excepting for the anionic surfactant EC and the nanoparticles A200, the shape of the curve was exponential and the biodegradation process became slower (B equal 2.55 %) and a long lag phase was observed, although the final mineralization reached was the highest of the tests carried out with nanoparticles (Min equal 87.02 %). So, it is possible to establish a dependence of biodegradability on silica particle size. ZP of particles A200 was less negative than ZP to particles A380, revealing the greater stability of the smallest nanoparticles. On the other hand, TEM image of A380 silica nanoparticles used in this study can corroborate the aggregation phenomenon that can have a direct effect on results on minor biodegradation.

The influence of the initial concentration of surfactant on biodegradability has been demonstrated (Fig. 5). In general, the surfactants biodegrade more easily at lower initial concentrations in the presence and absence of nanoparticles, this is the case for the two families of surfactants studied. The minimum level of 60% of ultimate biodegradation at 28 days is not reached for anionic and non-ionic surfactants when initial concentration of surfactant is 50 mg/L in the presence of nanoparticles regardless of their size.

This phenomenon is reflected in the characteristic parameters calculated for the biodegradation profiles, such as V_M , t_L , $t_{1/2}$, and B . So that the average velocity of biodegradation V_M , and biodegradability B , are greater for lower initial concentrations and the latency time t_L , half-life time $t_{1/2}$ are greater.

For nanofluids containing A200 the reduction of biodegradability, which is attributed to the increase in the concentration of surfactants, is more pronounced for the non-ionic surfactant.

3.3. Biodegradability of mixtures surfactant-nanoparticles

The biodegradability for anionic/non-ionic surfactant mixtures were evaluated in order to understand the interactions and synergism between different kinds of surfactants. Surfactants are often used as co-surfactants in many formulations, and therefore the ecotoxicological and interfacial interactions in the binary mixtures 1:1 weight of ether carboxylic derivative surfactants and alkyl polyglucosides were investigated. Mixtures of surfactants in the detergent, household care and industrial formulations are generally between non-ionic/non-ionic, cationic/cationic, anionic/anionic and amphoteric/amphoteric surfactants. However, it has been demonstrated that the synergistic effects between them increase with the difference of the charges (Werts and Grady, 2011), meaning that synergism between non-ionic/non-ionic or anionic/anionic is less than between non-ionic/anionic surfactants (Kume et al. 2008).

The biodegradation of APG-EC binary mixtures is lower than solutions with single surfactants. The explanation of this negative synergistic effect is found in the reduction of the electrostatic repulsion between the head groups of the anionic surfactants by inclusion of nonionic head groups, resulting in a worse aggregate stability and thus an increase in CMC when there are binary mixtures of anionic-non-ionic surfactants. This fact occurs both in presence and absence of nanoparticles (Fig. 6).

Data for binary mixtures indicate that the least biodegradability appears when mixture formed by the surfactant APG-EC and larger nanoparticles was made up. These results may allow to formulate surfactant mixtures for commercial purposes with augmented biodegradability, especially if surfactants EC and APG are incorporated.

4. Conclusions

In this work it has been investigated if silica nanoparticles have the potential to introduce enhancement in biodegradability of surfactants and other surfactant properties particularly its interfacial and adsorption behaviors. Binary mixtures of non-ionic anionic surfactants have also been investigated. The non-ionic and anionic surfactants studied decrease the surface tensions of air–water interfaces. The inclusion of hydrophilic silica nanoparticles that are negatively charged, reduced the efficiency of non-ionic surfactants and increased considerably their CMC, but in case of anionic surfactants the effect was the

Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js nanoparticles in the test medium resulted in a

decrease in the relative maximum mineralization for both types of surfactants. These results imply that the surfactants assayed at low concentrations may be considered safe for the environment formulated as nanofluids with and without nanoparticles at the initial surfactant concentration of 25 mg/L. Binary mixture measurements indicate that the least biodegradability mixture was formed by the surfactant APG-EC and larger nanoparticles. These results may allow to formulate surfactant mixtures for commercial purposes with augmented biodegradability, especially if surfactants EC and APG are incorporated.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

The datasets generated and/or analysed during the current study are not publicly available due the dataset on which this paper is based is too large to be retained or publicly archived with available resources, but are available from the corresponding author on reasonable request.

Competing interests

Not applicable

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Authors' contributions

Lechuga M: Conceptualization, Investigation, Methodology, Writing- Original draft preparation.

Fernández-Serrano M: Conceptualization, Data curation, Writing- Original draft preparation.

Rios F: Visualization, Investigation.

Fernández-Arteaga A: Writing - Review & Editing, Supervision.

Jiménez-Pobles P: Methodology, Writing- Reviewing and Editing.

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Authors' information (optional)

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Figures

Figure 1

TEM images of nanoparticles a) A380 and b) A200

Figure 2

Surface tension of nanofluids versus surfactant concentration

Figure 3

Surface and interfacial tension of nanofluids during the adsorption test. Initial surfactant concentration 25 mg/L

Figure 4

Time course of the biodegradability of APG and EC. Initial surfactant concentration 25 mg/L

Figure 5

Influence of surfactant concentration on biodegradability profiles

Figure 6

Biodegradability profiles for binary mixtures of surfactants and nanoparticles

Supplementary Files

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