Silica micro- and nanoparticles reduce the toxicity of surfactant solutions

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Abstract

In this work, the toxicity of hydrophilic fumed silica micro- and nanoparticles of various sizes (7 nm, 12 nm, and 50 μm) was evaluated using the luminescent bacteria *Vibrio fischeri*. In addition, the toxicity of an anionic surfactant solution (ether carboxylic acid), a nonionic surfactant solution (alkyl polyglucoside), and a binary (1:1) mixture of these solutions all containing these silica particles was evaluated. Furthermore, this work discusses the adsorption of surfactants onto particle surfaces and evaluates the effects of silica particles on the surface tension and critical micellar concentration (CMC) of these anionic and nonionic surfactants. It was determined that silica particles can be considered as non-toxic and that silica particles reduce the toxicity of surfactant solutions. Nevertheless, the toxicity reduction depends on the ionic character of the surfactants. Differences can be explained by the different adsorption behavior of surfactants onto the particle surface, which is weaker for nonionic surfactants than for anionic surfactants. Regarding the effects on surface tension, it was found that silica particles increased the surface activity of anionic surfactants and considerably reduced their CMC, whereas in the case of nonionic surfactants, the effects were reversed.

Keywords

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Keywords

Silica nanoparticles; toxicity; nonionic surfactants; anionic surfactants; nanofluid.

1. Introduction

In recent years, nanoparticles (NPs) have attracted a large amount of scientific attention because of their potential applications in biomedicine, pharmacy, materials, catalysis, cleaning, electronics and pollutant removal [1-5]. Due to their widespread use and production, it is unavoidable that they will be released into the environment and sewage [6], where they can be toxic for biota or affect waste water treatment processes. In light of a growing concern about the environmental impact of new materials, the toxicity, hazards, fate, and environmental management of nanoparticles are being widely studied [6-11].

Silica micro- and nanoparticles occupy a prominent position in scientific research [12-13], where they are the basis for many applications due to their stability, exceptional physicochemical properties, low toxicity and ability to be functionalized with a range of molecules and polymers. Moreover, silica particles have a uniform size and shape and are resistant to alkali and acids [6, 14-16]. Silica nanoparticles are often used together with surfactants in nanofluids and foam stabilizers, as well as being paired for uses such as the immobilization of enzymes, oil recovery, or the removal of dyes [17-21].

The environmental impact of surfactants has been extensively studied since they can be recalcitrant, toxic to several organisms, or detrimental to autochthons or aerobic and anaerobic microorganisms in wastewater treatment plants [22-29]. However, toxicity interactions in mixtures of surfactants and nanoparticles remain underexplored. The predictability of joint effects is of great importance for a proper environmental risk assessment and is urgently required due to the increasing development of nanofluids, nanomaterials, and nanoproducts. Previously, Oleszczuk et al. [30] studied the toxicity of ZnO, TiO_2 and Ni nanoparticles with cetyl trimethylammonium bromide (CTAB), triton X-100 (TX100), and 4-dodecylbenzenesulfonic acid (SDBS) and concluded that the presence of

surfactants considerably reduced the toxicity of the nanoparticles tested. On the other hand, Barrena et al. [31] and Stampoulis et al. [32] reported on the increase in toxicity to plants of Au, Ag and Fe_3O_4 nanoparticles in the presence of surfactants.

This study reports on the joint toxicity of silica micro- and nanoparticles with an anionic surfactant (ether carboxylic acid), a nonionic surfactant (alkyl polyglucoside) and a mixture of the two, whose environmental impacts have been previously studied [23-25, 33-37]. Bacteria *Vibrio fischeri* were selected as test organisms since bacteria comprise the widest category of organisms in toxicity assessments. Bacteria *V. fischeri* have been said to have the most sensitive assay while testing a wider range of chemicals compared to other microorganism assays [38], and the comparability between tests based on them is excellent [39]. In addition, with the aim of increasing the understanding of cleaning efficiency and other aspects such as wettability and emulsifying capacity, the effect of micro- and nanoparticles on the surface tension and critical micellar concentration (CMC) of surfactants has been analyzed.

2. Materials and methods

2.1. Silica micro- and nanoparticles

Hydrophilic fumed silica nanoparticles (Aerosil 380 and Aerosil 200) and hydrophilic silica microparticles (Sipernat 50) were purchased from Evonik Industries AG (Essen, Germany). They have different mean diameters (D_m) and specific surface areas (S), covering a wide range of sizes and applications. Table 1 shows the values of D_m, S, and the tamped density (d) provided by the supplier. Zeta potentials (ZP) of the nanoparticles were measured in Milli-Q® water using a Zetasizer Nano (Malvern Instruments Ltd, Worcestershire, United Kingdom) (Table 1). Three measures were performed to obtain a mean ZP and its confidence interval (95%).

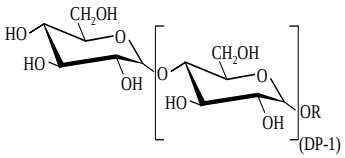
Table 1 Characteristic parameters of silica micro- and nanoparticles

Name	Abbreviation	D_m, nm	S, m^2/g	d, g/L	ZP, mV
Aerosil® 380	A380	7	380 ± 30	50	-36.0 ± 2.27
Aerosil® 200	A200	12	200 ± 25	50	-25.5 ± 1.89
Sipernat® 50	S50	50000	500	180	---

2.2. Surfactants

Two commercial surfactants and a binary mixture (1:1, mass basis) of them were tested: an anionic surfactant, ether carboxylic acid (EC), supplied by KAO Corporation (Tokyo, Japan), and a nonionic surfactant, alkyl polyglucoside (APG), manufactured by Henkel KgaA (Düsseldorf, Germany) and provided by Sigma-Aldrich (St. Louis, MO, USA). Table 2 summarizes their characteristics.

Table 2 Characteristics of the surfactants used

Surfactant	EC-$R_{12\text{-}14}E_3$	APG-$R_{8\text{-}14}DP_{1.3}$
Chemical Name	Laureth-4 Carboxylic Acid	Coco Glucoside
Commercial Name	AKYPO® RLM-25	Glucopon 650EC
Structure	$R_{12\text{-}14}$-$(CH_2$-$CH_2O)_3$-O-CH_2-COO^-	
CMC[a], g/L	29.08	33.2
Active matter [b], %	93.1	48.6

R: alkyl chain length, n-C_iH_{2i+1}-
E: degree of ethoxylation
DP: average number of glucose units per molecule
a: measured at 25ºC in Milli-Q® water
b: determined using infrared radiation [25]

2.2. Sample preparation

A 250-mg sample of silica particles was dispersed by sonication for 30 minutes (Sonorex RK 106 S, Bandelin, Berlin, Germany) in 1 L of Milli-Q® water containing 2% NaCl. Subsequently, surfactant was added to obtain the required surfactant concentration (1.0 to

$4 \cdot 10^3$ mg/L). The CMC and toxicity of solutions of surfactants and silica particles were determined as described in the following sections. Moreover, the Zeta potential of the nanoparticles was measured in a saline medium (2% NaCl) and in surfactant solutions, using a Zetasizer Nano (Malvern Instruments Ltd, Worcestershire, United Kingdom) (Fig. 1).

Silica nanoparticles A380 and A200 were analyzed by ultra-high resolution scanning transmission electron microscope (S/TEM) and high-angle annular dark-field imaging (HAADF) FEI TITAN G2 60-300. In addition, silica nanoparticles A380 were analyzed by a transmission electron microscopy (TEM) in saline medium (2% NaCl) and in surfactant solutions with bacteria *Vibrio fischeri* using a 200 kV microscope CM20 Philips. For this, a droplet of the suspension was polymerized in pure Embed 812, after being treated with glutaraldehyde overnight and osmium tetroxide for 2 hours. Blocks were cut (50-70 nm thickness) with a diamond blade DIATOME and applied onto 300 mesh Cu grills. Ultrafine cuts were contrasted with uranyl acetate and dried in a coal evaporator.

2.3. Critical micellar concentration

The critical micellar concentration (CMC) is defined as the concentration of surfactant above which micelles form and any additional surfactant added to the system will go into micelles. The CMC value was estimated from plots of surface tension as a function of surfactant concentration (1.0 to $4 \cdot 10^3$ mg/L) in a semi-log plot [40]. Surface tension has a rapid linear decrease followed by a slow decrease, and the break point in the plot shows the emergence of micelles. Surfactant solutions were prepared with the toxicity test conditions (i.e., 2% NaCl and 250 mg/L silica particles). Surface tension measurements were performed using the Wilhelmy Plate Method (BS EN 14370:2004) with a Krüss K11 tensiometer (Krüss GmbH, Hamburg, Germany) equipped with a 2-cm platinum plate. Five successive measurements were collected, and the standard deviation did not exceed ± 0.1 mN/m.

2.4. Toxicity tests with bacteria Vibrio fischeri

The toxicity test with the photobacterium *V. fischeri* (strain NRRL-B-11177) was administered using the LumiStox® 300 system according to UNE-EN ISO 11348-2:2009 guidelines (UNE-EN ISO 11348-2:2009). The bioluminescence of *V. fischeri* is inhibited by toxicants; this light inhibition can be quantified by a calibrated light meter and comparison with the light emitted by a blank sample without toxicant. Photobacteria were provided (dehydrated and frozen at -18ºC) by Dr. Bruno Lange GmbH & Co., (Düsseldorf, Germany). Bacteria were reactivated in a 8 g/L $C_6H_{12}O_6 \cdot H_2O$, 20 g/L NaCl, 2.035 g/L, $MgCl_2 \cdot 6H_2O$, 0.30 g/L KCl and 11.9 g/L solution. Nine surfactant concentrations with the same particle concentration (250 mg/L) and a control were inoculated with the reactivated bacteria. The pH of test solutions was adjusted to 7.0 ± 0.2, with either 1N HCl or 1M NaOH, before the assay was initiated. NaCl was added to set a final chloride concentration of 2% w/w in the samples. Samples were tested in duplicate in 3-ml vessels. The light emission at the start and after 15 min of contact with the toxicant was measured at a constant temperature (15ºC) using a LumiStox® 300 luminometer.

EC_{50} and EC_{20} (the concentrations of surfactant that inhibited 50% and 20% of the luminescence, respectively) were calculated following the procedure described by Ríos et al. [28].

Three replicates tests were performed to obtain a mean EC_{50} and its confidence interval (95%).

2.5 Differential Scanning Calorimetry (DSC) experiments

To corroborate that surfactants adsorb on the nanoparticles, some Differential Scanning Calorimetry (DSC) experiments of solutions of surfactants and silica particles were carried out. These experiments are a tool to help elucidate the adsorption.

DSC experiments, in the temperature range from -5 to 100 °C using a scanning rate of 1 °C/min, were performed with a DSC-1 instrument (Mettler Toledo). This equipment possesses a resolution of up to 0.04 μW. Samples were tightly sealed, and an empty pan was used as a reference. The amount of sample necessary to carry out the experiments was 30 μl. The absence of any changes in the signal at different scan rates indicates that the energetic transitions (related to adsorption) examined are under strict thermodynamic control as described by Chowdhry et al [41].

3. RESULTS AND DISCUSSION

3.1. Zeta potential of nanoparticles

The Zeta potential of the nanoparticles was determined under the conditions of the toxicity tests, i.e., 2% NaCl with anionic (EC) or nonionic (APG) surfactant, and was compared with their ZP in Milli-Q® water (Fig. 1) to analyze the stability of dispersions. As expected, the ZP is considerably less negative in a saline medium, as the ions modify the surface electric potential of the silica particles. In anionic surfactant solutions, the ZP reaches more negative values, indicating greater stability of the particles. On the other hand, in nonionic surfactant solutions, the ZP shows no such remarkable changes. Fig. 1 shows a comparison of the ZPs at different conditions. In all cases, the ZP of A200 particles was less negative than the ZP of A380 particles, showing the greater stability of the smaller nanoparticles. The ZP of S50 microparticles could not be measured due to their large size.

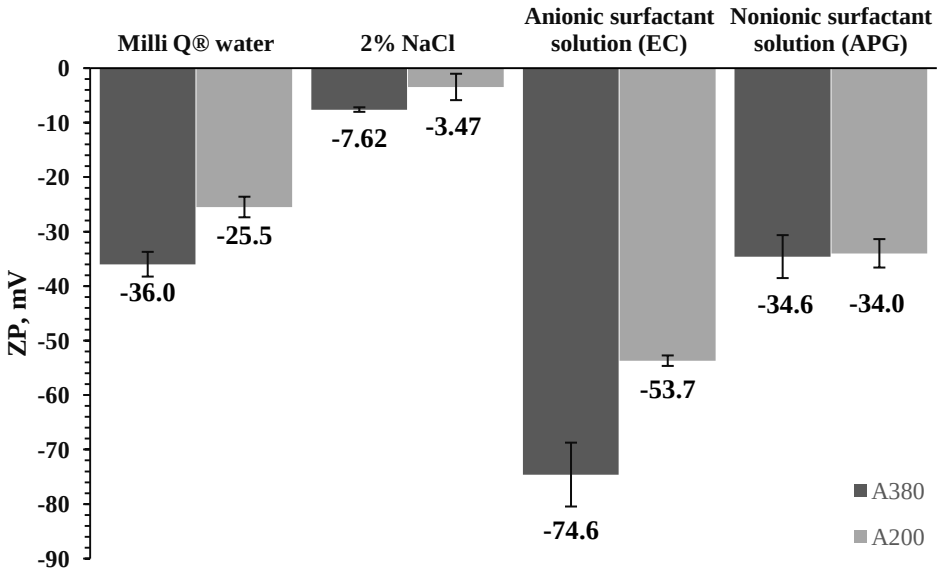


Fig. 1. Comparison of Zeta potentials of nanoparticles in different conditions

3.2 Surface tension and critical micellar concentration

The surface tensions of micro- and nanoparticle dispersions in Milli-Q® water at particle concentrations in the range of 5-2500 mg/L at a constant temperature (15ºC) were measured. In all cases, the surface tension did not change with concentration. The surface tension was approximately 72.2 ± 0.6 mN/m, very close to the surface tension of pure water. Hence, silica particles did not change the surface tension of water, probably due to their hydrophilic character; they may not have a preference for the air-water interface. These results agree with the values of surface tension measurements for Levasil® silica solutions found by Ma et al. [42].

The surface tensions for the surfactant solutions and the micro- and nanofluids were measured and the CMC was determined, using the conditions of the toxicity test (2% NaCl, 15ºC). CMC values and their variations are shown in Table 3. Two different results were obtained: micro- and nanofluids with the nonionic surfactant (APG) had an increased CMC with respect to the surfactant solution, whereas micro- and nanofluids with the anionic surfactant showed a

considerable reduction in their CMC. Comparison of the surface tension versus surfactant concentration is shown in Fig. S1 in the supplementary material. In addition, it was observed that the decreases in surface tension were the same for the three nanofluids using the same surfactant and different nanoparticles (Fig. S2 in supplementary materials), and their CMC values were similar or on the same order of magnitude.

The reduction of CMC and surface tension of the anionic surfactant is due to silica nanoparticles increasing the surface activity of anionic surfactants [42]. As described previously, the repulsive electrostatic forces between particles of the anionic surfactant favor the diffusion of surfactant toward the interface, which leads to a decrease in the surface tension [43]. According to Ma et al. [42], the presence of silica particles makes the Gibbs free energy of adsorption and micellization more negative, and therefore, they promote the adsorption and aggregation in micelles. In the case of the nonionic surfactant, adsorption and electrostatic forces are much weaker, and the opposite effect is seen. Changes in the Gibbs free energy of adsorption and micellization are negligible. Other authors [42, 44] also found a decrease in the efficiency of nonionic surfactants with silica particles.

Table 3 EC_{20} and EC_{50} of silica particles and surfactants (95% CI)

Sample	CMC[a], mg/L	CMC variation %	EC_{20}, mg/L	EC_{50}, mg/L	Tox. reduction %
A380	---	---	2104 ± 438	---	---
A200	---	----	1654 ± 398	---	----
S50	---	----	2434 ± 635	---	----
APG	63.42	----	4.38 ± 0.28	17.07 ± 0.87	----
EC	68.89	----	1.39 ± 0.06	3.35 ± 0.47	----
A380 + APG	87.91	41.45	6.22 ± 0.27	21.48 ± 1.97	25.84
A200 + APG	91.40	44.13	7.00 ± 0.56	24.53 ± 0.13	43.66

S50 + APG	91.36	44.05	5.71 ± 0.65	19.47 ± 1.76	14.04
A380 + EC	23.75	-65.53	4.08 ± 0.69	9.08 ± 1.23	171.13
A200 + EC	38.12	-44.66	3.26 ± 0.87	9.95 ± 0.86	197.12
S50 + EC	33.68	-51.11	2.64 ± 0.45	8.52 ± 1.50	154.50
APG + EC	74.66	---	1.12 ± 0.31	6.06 ± 0.85	---
A380 + APG + EC	65.23	-12.63	4.61 ± 0.74	11.37 ± 1.30	87.56
A200 + APG + EC	66.52	-10.90	4.53 ± 0.25	10.10 ± 1.25	66.73
S50 + APG + EC	67.37	-9.76	5.47 ± 0.31	11.13 ± 1.89	83.65

[a] 2% NaCl and 15ºC

3.3. Toxicity of silica particles

The inhibition of the bioluminescence of *V. fischeri* after 15 min of exposure in a range of particle concentrations from 20 mg/L to 2500 mg/L was determined. Silica nanoparticles can be considered as non-toxic, since the percentage of inhibition barely exceeds 10%. In addition, these percentages were achieved at very high particle concentrations (>1000 mg/L), which are unlikely to occur in the environment and wastewater. Other studies also categorized silica particles as non-toxic to other organisms and safe to the environment [5, 7, 45]. Values of the EC_{50} cannot be calculated because at higher concentrations of nanoparticles, the solutions become so dark that it interferes with the correct determination of the luminescence. Instead, values of EC_{20} were estimated and are shown in Table 3.

The biological action of silica nanoparticles in microorganisms is related to their membranotropic properties [11]. Some studies have reported that they can easily penetrate cells and interact with lipid membranes, stimulating the generation of reactive oxygen species (ROS), which are responsible for the peroxidation of biomolecules [45-48]. Therefore, this mechanism can be supposed as the main toxicological mode of action (MoA) of silica nanoparticles to *V. fischeri*.

205 There is currently controversy about the dependence of toxicity on silica particle size and
206 surface area [49]. In this study, we found that A200 (12 nm) were more toxic than A380 (7
207 nm) toxic. On the other hand, S50 microparticles (50 µm) showed the lowest toxic effects.
208 This fact agrees with the results from other studies in which nanoparticles under 100 nm
209 induced more effects in cells than larger particles [50]. However, it contrasts with the results
210 found by Adams et al. [51], who reported about similar antibacterial activity of silica particles
211 ranging from 14 nm to 60 µm. Adams et al. [51] also explained that nanoparticles tend to
212 aggregate, and the actual and effective sizes of particles are highly variable and differ from
213 their sizes in dry powders. The aggregation phenomenon was corroborated by means of a
214 HRTEM image of A380 and A200 silica nanoparticles (Fig. 2), and the size distributions
215 observed match with the mean diameter provided by the supplier (Table 1).

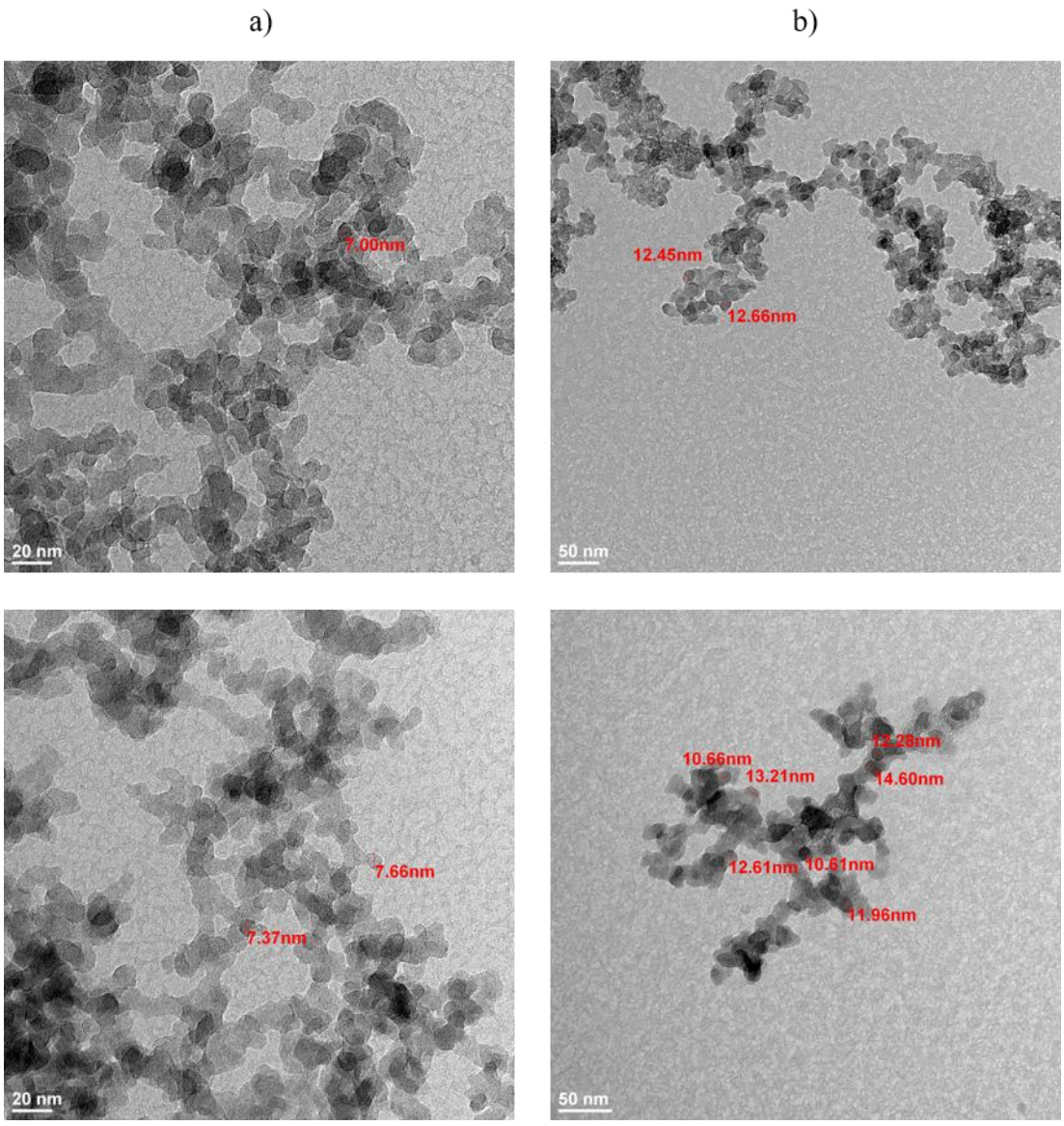
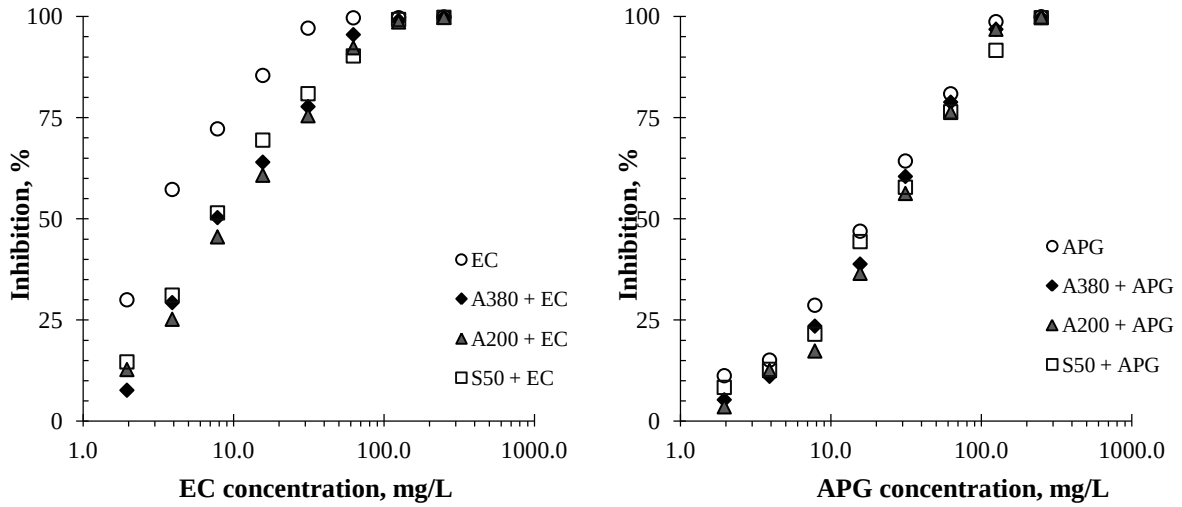


Fig. 2. HRTEM images. a) A380 b) A200

3.4. Toxicity of surfactants and silica particles

The luminescence inhibition of solutions of EC and APG in the presence of silica particles at a constant concentration (250 mg/L) has been studied. Fig. 3 shows the inhibition percentages at different surfactant concentrations, and Table 3 summarizes the calculated values of EC_{50} and EC_{20}.



223

224 **Fig. 3. Dose-response curves of EC and APG at a constant concentration of silica micro- and nanoparticles**
225 **to *V. fischeri*.**

226 Given the non-polar nature of APG, its MoA is likely non-polar narcosis Class 1 [52],
227 whereas given the anionic character of EC, it is expected to act as a polar narcotic Class 2
228 [53]. Differences between the MoA of these surfactants and the MoA of silica particles may
229 indicate that they act independently from each other (response addition), which is to say that
230 the organism's response to the surfactant is the same whether or not particles are present. Fig.
231 4 shows TEM images of *V. fischeri* with silica nanoparticles A380 at the EC_{50} concentration
232 determined for the nonionic surfactant APG (a) and the anionic surfactant EC (b) with A380.

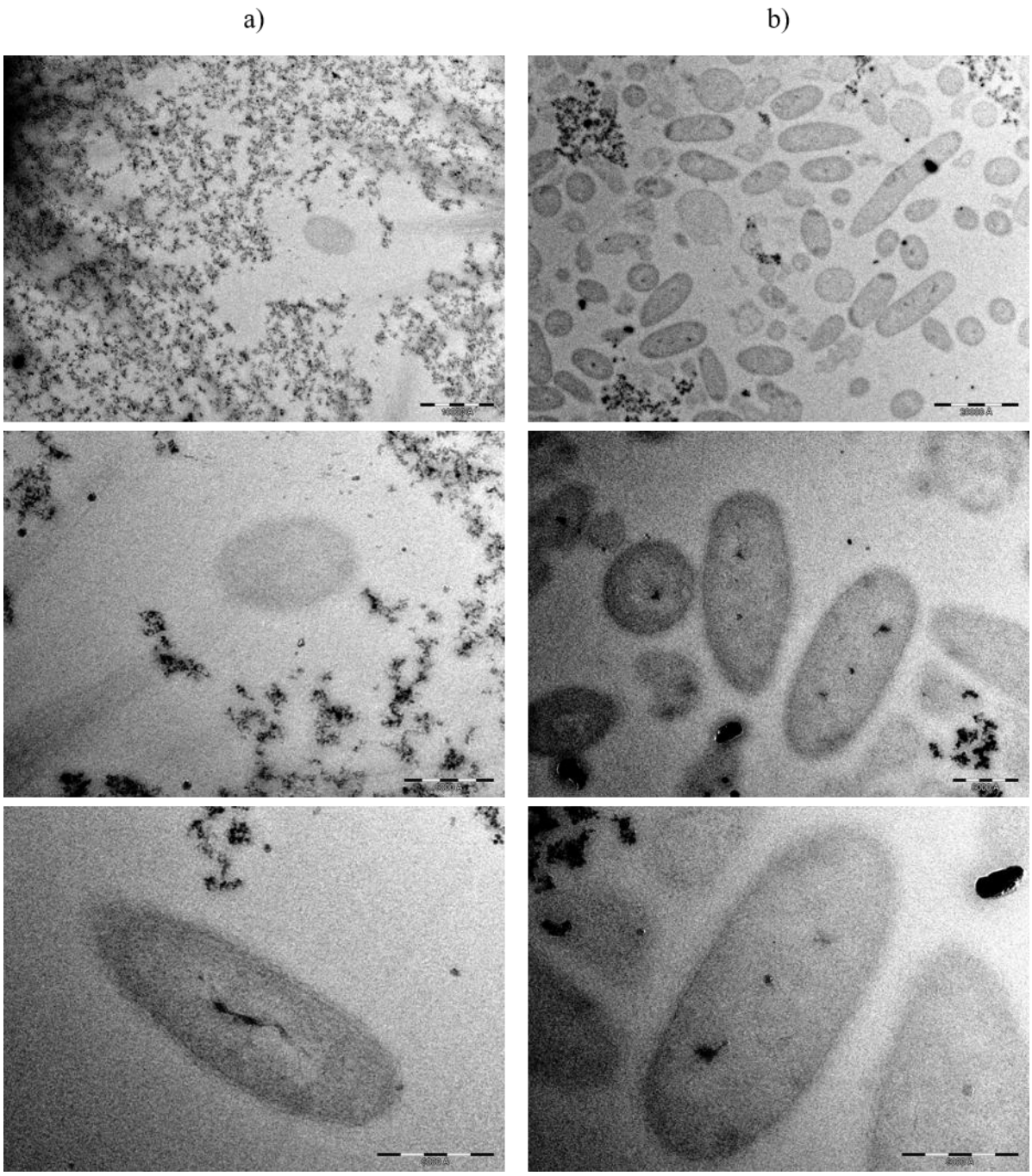


Fig. 4. TEM images of bacteria *V. fischeri* with silica nanoparticles A380. a) APG solution (21.48 mg/L), b) EC solution (9.08 mg/L).

For both surfactants, the percentages of inhibition were lower in solutions with silica particles than without them (Fig. 3). However, the differences were more pronounced in the case of the anionic surfactant (about 25% at low concentrations). In the case of APG, these differences are at most 10%. These deviations in the toxicity of surfactant micro- and nanofluids with

respect to the surfactant solutions can also be realized in the toxicity parameters EC_{50} and EC_{20} (Table 3, Fig. 5), which are above the values of the pure surfactant solutions. Considering the EC_{50}, we calculated the toxicity reduction and show those percentages in Table 3. This parameter makes the reduction of toxicity and the differences between the surfactants more evident. The most remarkable case is EC + A200, for which EC_{50} increased almost three times, and in all cases of anionic surfactant, the reduction of toxicity was higher than 150%. In the case of the nonionic surfactant, toxicity reduction percentages ranged from 14.04 to 43.66%.

Additionally, we tested a binary (1:1) mixture of the anionic and nonionic surfactants (EC + APG). Using the model of toxic units (TU) [28;54], where a TU is the sum of TU_i of the individual components (e.g., the ratio between the surfactant concentration in a mixture (C_i) and its toxicological acute endpoint (EC_{50i})), it can be stated that there is no synergistic or antagonistic effect and that the dose/concentration addition principle applies (TU=1 ± 0.2) [55]. In the case of micro- and nanofluids with a mixture of surfactants, a reduction in the toxicity was also observed. Nevertheless, it is possible to think that silica particles and surfactants act independently.

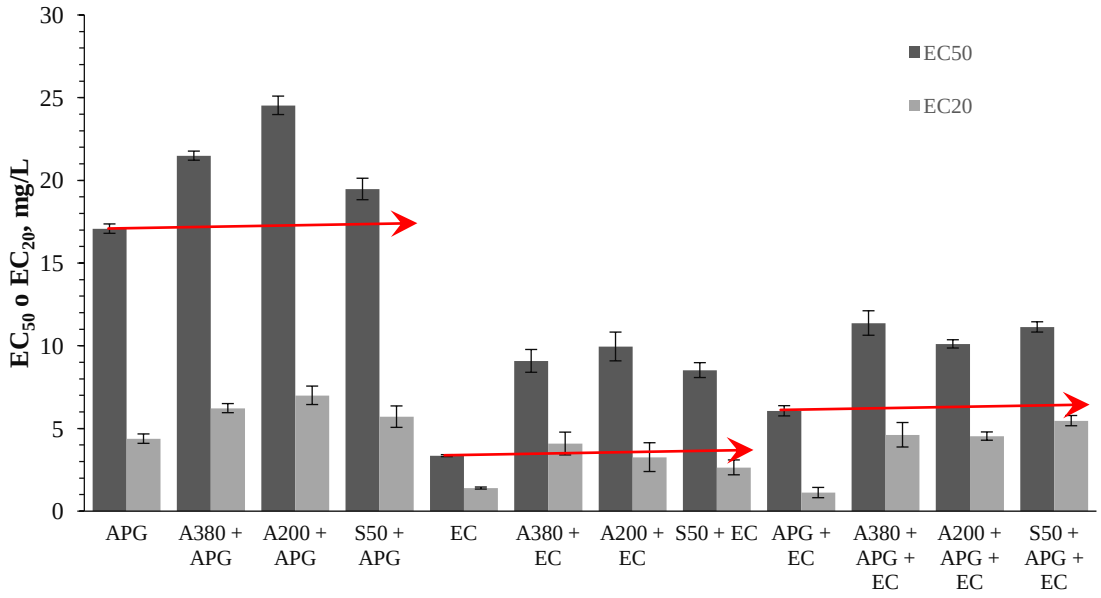


Fig. 5. EC_{50} and EC_{20} of solutions of EC and APG with silica particles.

When it comes to the differences in toxicity reduction depending on the particle size, A200 particles promoted the highest reduction for both surfactants, while S50 gave the lowest. However, particle size has no clear influence on the toxicity of surfactant micro- and nanofluids, as it was explained before due to the particle aggregation.

Toxicity reduction in surfactant micro- and nanofluids is promoted by adsorption of surfactant on silica hydrophilic particles, and the differences in toxicity reduction percentages between the anionic and nonionic surfactant can be attributed to their distinct ionic characters. Adsorption of surfactants on nanoparticles has been widely studied in recent years [41; 56-59]. From these studies, it can be interpreted that adsorption onto hydrophilic silica particle surfaces represents an aggregation process akin to micelle formation in the bulk solution, which depends on the surfactant character and structure (e.g., the relative size of the hydrophilic group and hydrocarbonated chain) [60]. Two adsorption models have been examined in the literature: bilayer formation and individual micelles decorating nanoparticles [61-62].

On the one hand, the anchoring of nonionic surfactant heads to the surface is due to weak interactions such as hydrogen bonding. When weak anchoring energies are present, micelle adsorption on the silica surface may be disfavored versus micelles in solution, implying little adsorption [58]. For example, Jurado et al. [18] investigated the interaction between silica micro- and nanoparticles and nonionic surfactants; they found that alkyl polyglucosides adsorbed slightly onto silica particles, and Lugo et al. [60] found low adsorption levels of another sugar surfactant (dodecyl-β-maltoside) onto silica surfaces. On the other hand, nanoparticles increase the surface activity of anionic surfactants and induce electrostatic repulsion between particles. Ahualli et al. [63] confirmed the adsorption of anionic surfactants

onto silica particles, creating a supercharged system. This is supported by the decrease in the ZP of EC and nanoparticles found in this study (Fig. 1).

DSC experiments on several aqueous systems containing both the surfactants, and the three types of micro- and nanoparticles were carried out in order to prove the adsorption process, which promoted a reduction on the toxicity. The results for the studied systems showed a single, endothermic peak, corresponding to the adsorption process and typical of a first order transition (see Figure S3 in supplementary materials).

Fig. 6 shows the luminescence inhibition percentages versus the surface tension of the surfactant and silica particle solutions. The inhibition percentages for the anionic surfactant with silica particles increase more sharply than for the nonionic surfactant when the surface tension decreases. Furthermore, it can be appreciated that the decrease in the surface tension due to the co-occurrence of silica particles and EC does not imply an increase in the percentages of inhibition, but rather the opposite. That is, greater effectiveness of the anionic surfactant does not entail a greater effect on *V. fischeri*.

Adsorption of a surfactant onto nanoparticles decreases the availability of the surfactant to partition into membranes, which reduces the toxicity. Stronger adsorption of anionic surfactants than nonionic surfactants onto silica particles makes them less available and promotes a greater surfactant toxicity reduction. Moreover, particles containing adsorbed surfactant can act as carriers of surfactant toward the interface, since spontaneous adsorption of particles at the interface decreases the energy of the system [42;6].

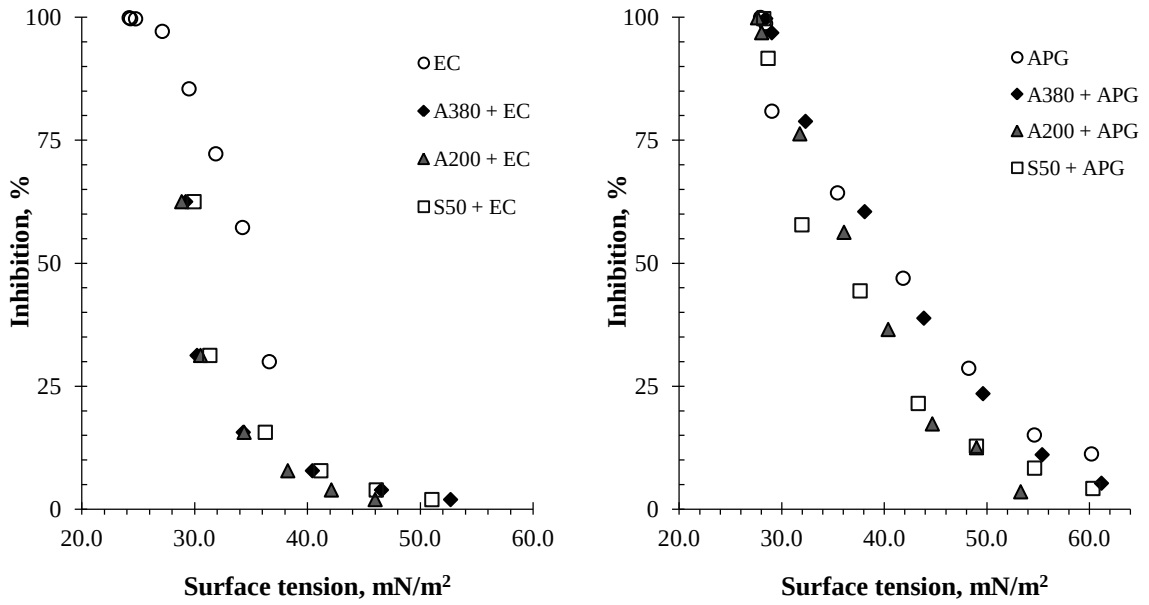


Fig. 6. Inhibition vs surface tension of solutions of EC and APG with silica particles.

4. Conclusions

In this study, it was found that hydrophilic fumed silica micro- and nanoparticles can be considered as non-toxic, showing percentages of inhibition that did not exceed 10% to bacteria *V. fischeri*. Moreover trends linking particle size and toxicity could be observed, which agree with data from the literature. In the case of mixtures of surfactant and silica particles, silica particles reduce the toxicity of both the anionic surfactant ether carboxylic acid (EC) and the nonionic surfactant alkyl polyglucoside (APG). However, the toxicity reduction was much higher in the case of the anionic surfactant than the nonionic surfactant. Differences can be explained by the adsorption of surfactant onto particle surfaces, which is weak in the case of nonionic surfactants and stronger in the case of anionic surfactants, causing a supercharged system. Adsorption of surfactants onto nanoparticles makes the surfactant unavailable to partition into membranes and cause toxicity. To corroborate our results, the surface tension and CMC of mixtures of surfactants and silica particles were measured. As a result, it was found that silica particles increase the surface activity of the

anionic surfactant (EC) and reduce its CMC considerably, whereas the particles decrease the efficiency of the nonionic surfactant (APG) and increase its CMC.

Acknowledgements

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