

## Effect of linear alkylbenzene sulfonate (LAS) on the coagulation of ZnO nanoparticles in aqueous matrix

Dáfnis Barsanulfa Guimarães, Francisco Javier Cuba Teran\*,  
Renata Medici Frayne Cuba

Federal University of Goiás (UFG), Goiania 74605-220, Brazil, emails: paco@ufg.br (F.J. Cuba Teran),  
dafnisguimaraes@gmail.com (D.B. Guimarães), renatafrayne@ufg.br (R.M. Frayne Cuba)

Received 17 September 2021; Accepted 30 December 2021

---

### ABSTRACT

The widespread use of anionic surfactant linear alkyl sulfonate (LAS) and zinc oxide nanoparticles (nano-ZnO) makes it possible for both compounds to coexist in aquatic environments. Along with the effect of LAS on chemical coagulation, this study shows the importance of LAS on aggregation, sedimentation, zero charge point (ZCP) and removal of nano-ZnO in the coagulation process using tannin and FeCl<sub>3</sub> as primary coagulants. The results showed that at concentrations above 100 mg L<sup>-1</sup>, LAS negatively influenced the aggregation and sedimentation of nano-ZnO. On the other hand, surfactant did not significantly interfere with the ZCP of nano-ZnO, with both coagulants, showing better results when submitted to the pH coagulation process near the obtained ZCP. Increasing the LAS concentration significantly influenced the efficiency of the coagulation process, showing that at concentrations of 300 mg L<sup>-1</sup>, the removal efficiency dropped below 5% at different pH values. In summary, this study may contribute demonstrating that the presence of LAS can alter the behavior of nano-ZnO and significantly reduce the efficiency of the coagulation process.

*Keywords:* Linear sulfonate alkylbenzene; Zinc oxide nanoparticles; Aggregation; Chemical coagulation

---

### 1. Introduction

The growing demand for water resources has raised serious concerns due to the effect of unknown contaminants in the long term, as thousands of artificial chemicals are currently used and there are different ways in which these contaminants can enter aquatic and terrestrial environments [1–3].

Many of these pollutants, such as linear alkyl sulfonate (LAS) surfactant and emerging zinc oxide nanoparticles (nano-ZnO), enter the environment, disperse and persist to a greater extent than predicted, leading to the high possibility of the coexistence of these two compounds in the water environment [3–6].

LAS is an anionic surfactant of great production due to its industrial, domestic and commercial employment.

It is the active ingredient of most detergents due to its performance of functions such as emulsification, detergency, and wetting [1,7,8].

Nano-ZnO, because it is a versatile material, has several morphologies and meets the most varied applications, such as photodegradation, electronic and optoelectronic industries, manufacture of rubbers, glasses, plastics, zinc source for food industries, anti-bactericidal, cosmetics, and wide application in solar filter production, due to its excellent UV absorption and reflective properties [9–12].

Chalew et al. [13] reported that although removed by conventional and advanced treatment, NPs such as silver, titanium dioxide (TiO<sub>2</sub>) and zinc oxide (ZnO) were detected in post-treatment water, exposing the need to consider these NPs as emerging contaminants of drinking water to determine appropriate processes to be applied for their removal.

---

\* Corresponding author.

The systematic emission of residual LAS in the natural environment, due to its high world production and use in various applications, occurs through direct or indirect discharges of urban and industrial wastewater, and its concentration varies in surface waters, sediments and dry mass of treated sludge [14,15].

According to the European Union Technical Guidance Document (TGD), concentrations above  $0.27 \text{ mg L}^{-1}$  LAS are considered relevant for environmental risk assessment because they cause toxic effects to aquatic and terrestrial ecosystems, so they need to be monitored [8].

Resolution No. 357 of the National Council for the Environment in Brazil [16], which determines guidelines for the classification of water bodies and establishes the conditions and patterns of effluent release, establishes that the maximum limit for the concentration of tensoactive substances that react to methylene blue is  $0.5 \text{ mg L}^{-1}$  LAS in freshwater and  $0.2 \text{ mg L}^{-1}$  LAS for saline and brine water.

From another perspective, Consolidation Ordinance No. 5 of the Ministry of Health of Brazil [17] establishes the maximum permissible value of  $0.5 \text{ mg L}^{-1}$  surfactant (such as LAS), for water potability.

On the other hand, nano-ZnO does not have specific regulations, and it is still necessary to manage the risk of these nanomaterials and their concentrations, given the tendency to increase the potential for the release of these nanoparticles to the environment, given their variety of applications and widespread consumption [10,18–20].

In the aquatic environment, the aggregation of nanoparticles results from the interaction between the surface of the nanoparticles and the components of the water and is strongly influenced by several factors, such as salinity, solution, surface chemistry, concentration of suspended particles and pH, especially where the nanoparticles approach their zero-load point pH (ZCP) [21].

Thus, the coexistence of nanoparticles, once released into the aquatic environment, with other preexisting contaminants is inevitable, and their interaction alters their properties (particle size, surface load, structure), presenting systemic effects on their toxicity [22,23].

In 2018, Khan, studying the coagulation of ZnO particles, reported that not only do nano-ZnO coexist with other components but also interact with them in different ways in the same system, and surfactants are more likely to coexist with nano-ZnO [23]. Zhou et al. [24] studied the removal of microplastics using polyaluminum chloride (PAC) and  $\text{FeCl}_3$  coagulation in 2021, obtaining better results in alkaline conditions. You et al. [25] studied the application of PAC and cationic polyacrylamide for the removal of nano-ZnO particles in 2021 with efficiencies of 98.5% and 99.17% in pure-water and kaolin environments, respectively.

Godinez and Darnault [26] sustained that surfactants can adsorb nanoparticles and affect solubility and transport in porous media, altering their electrostatic, hydrophobic and sterile behavior, as well as affecting their interaction forces. Li et al. [6,27] demonstrated that several functional groups of surfactants are adsorbed on the surface of nano-ZnO, increasing colloidal stability and the release of  $\text{Zn}^{2+}$  ions in water bodies. The modification of the properties of NPs, when in dissolution, affects the process of chemical coagulation.

As chemical coagulation is a largely used technique for improving suspended solids sedimentation and phosphorous removal, the widespread presence of surfactant compounds in water and wastewater can lead to detrimental effects related to surface physicochemical interactions and steric resistance [28].

Exploring the effects of surfactant LAS on nano-ZnO and their physical-chemical properties, as well as performing an evaluation during the coagulation process, can lead to a greater understanding of the coexistence of these two contaminants in the aquatic environment.

Some studies have been conducted focused on the removal of nanoparticles (NPs) [4,6,10] from aqueous matrices, however few have been directed to assess their coagulation in the presence of surfactants [29]. Thus, the objective of this work was to study the influence of the anionic surfactant LAS (C12), known commercially as sodium dodecyl benzene sulfonate, on the aggregation and sedimentation and on the efficiency of the chemical coagulation process of ZnO nanoparticles. In particular, the effect of LAS on the sorption capacity and stability of nano-ZnO in various pH ranges was analyzed, as well as the interference of LAS in the removal of NPs by chemical coagulation.

Our results will permit us to extend the investigation directed toward the definition of threshold values of LAS concentration to prevent its deleterious effect, and they will also encourage the implementation of techniques for the removal of ionic or nonionic surfactants from water and wastewater.

## 2. Materials and methods

### 2.1. Experimental approach

The experiments were conducted to obtain the results of the effect of LAS on the coagulation of nano-ZnO by means of the experimental setup described in Fig. 1. Briefly, stock suspensions with different concentrations of ZnO were prepared and tested to obtain coagulation data and to conduct tests to obtain ZCP. Different LAS, tannin and  $\text{FeCl}_3$  concentrations were applied to obtain consistent results.

### 2.2. Chemical reagents

99% pure zinc oxide nanoparticles (neon) and sodium dodecyl benzene sulfonate (SDBS) (neon) were purchased from local suppliers.

To correct the pH and in the coagulation-flocculation process, hydrochloric acid (neon), sodium hydroxide (neon) and sodium bicarbonate (neon) were used. Two types of coagulants (inorganic and organic) were used in the comparative order, hexahydrate iron chloride (III) and tannin (Tanfloc SG).

### 2.3. Preparation of stock suspensions

Initially, 0.5 g of ZnO nanoparticles was dispersed in 1 L of ultrapure water and then submitted for 30 min to an ultrasonic bath (Q335D, 40 kHz, Quimis, Brazil) with the purpose of deagglomerating and dispersing the

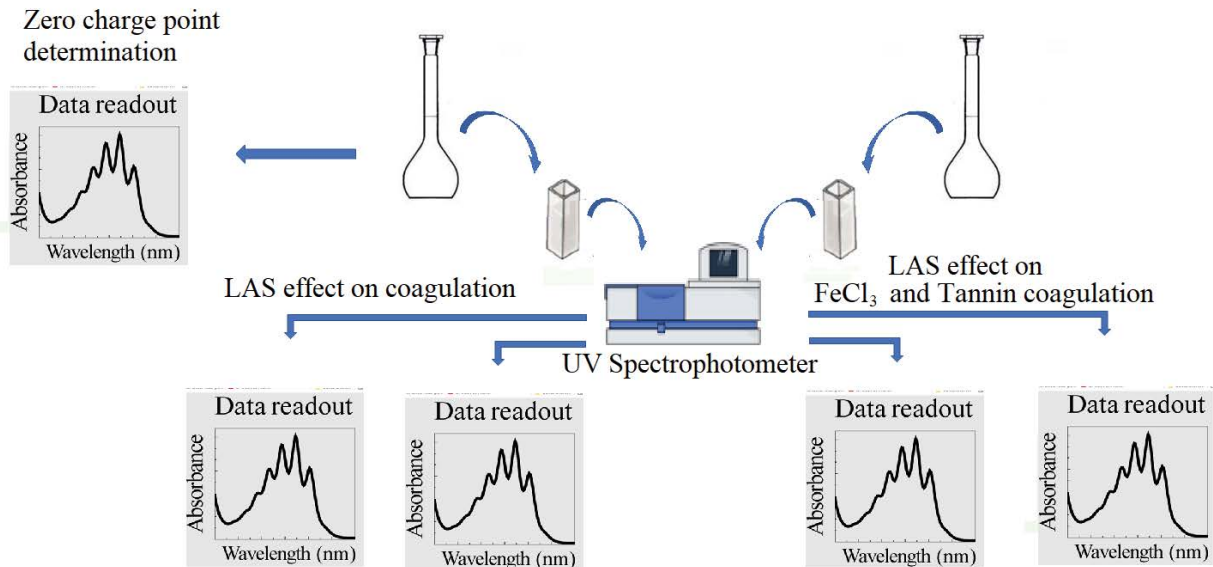


Fig. 1. Experimental setup for data obtention and analysis.

nanoparticles, facilitating sample homogenization. The  $1.0 \text{ g L}^{-1}$  stock solution of LAS, and coagulants,  $0.1 \text{ M}$  ( $\text{FeCl}_3$ ) and  $0.1 \text{ M}$  tannin (tanfloc SG) were prepared by dissolution in ultrapure water. All stock solutions were kept under refrigeration up to  $6^\circ\text{C}$  in a dark bottle before being diluted to their required concentration in the experimental phase.

#### 2.4. Effect of surfactant concentration on the aggregation and sedimentation of nanoparticles

The experiments consisted of diluting the stock suspensions of nano-ZnO to two different concentrations,  $50$  and  $100 \text{ mg L}^{-1}$  and subjecting them to surfactant concentrations from  $0$  to  $300 \text{ mg L}^{-1}$ , concentrations already found in the natural water matrix and in municipal and industrial wastewater treatment plants [30–33].

The sedimentation process of ZnO aggregates was monitored through optical absorption by means of an UV-Vis spectrophotometer (DR 5000, Hach) using a  $10 \text{ mm}$  quartz cubette in a  $378 \text{ nm}$  wavelength, which according to Zhou and Keller [34] corresponds to the best peak absorption of zinc oxide in the spectrum.

The results of each suspension were recorded for  $24 \text{ h}$ , and the first  $4 \text{ h}$  were measured hourly. The sedimentation of the ZnO aggregate was expressed by means of the  $C/C_0$  relation, where  $C_0$  is the initial absorbance and  $C$  is the absorbance recorded at different time intervals during the experimental period. All determinations were made in triplicate.

Allen et al. [35] and Allen et al. [36] modeled solid sedimentation using first-order decay equations when studying sediment behavior in urban drainage systems (2014) and flooded areas (2015). They concluded that the use of the first-order decay constant  $k$  is an effective parameter for studying in detail the behavior of solid sedimentation. In cases where at the end of the study period, the decay was close to zero, Eq. (1) was used, whereas when

a residual concentration of ZnO remained in the liquid medium, Eq. (2) [37,38] was used.

$$C = C_0 e^{-k \cdot t} \quad (1)$$

$$C = C_r + (C_0 - C_r) \cdot e^{-k \cdot t} \quad (2)$$

#### 2.5. Measurement of the zero charge point of zinc oxide nanoparticles

As nanoparticles in the aqueous phase can be stabilized by electrostatic forces, pH control was applied to influence the surface load and, therefore, the formation of aggregates or clusters. Thus, the effect of LAS concentrations on nano-ZnO was analyzed in the ZCP. The methodology used was based on the 11-point method, and all values were measured in triplicate [39].

The experiment consisted of suspending the concentrations of nano-ZnO in aqueous solutions with varying concentrations of LAS ( $0$ – $300 \text{ mg L}^{-1}$ ) and subjecting them to different initial pH values (range  $2.0$ – $12.0$ ) adjusted with  $\text{HCl}$  ( $0.1 \text{ M}$ ) and  $\text{NaOH}$  ( $0.1 \text{ M}$ ) solutions and maintained under agitation during the period from  $24 \text{ h}$  to  $140 \text{ rpm}$ .

With the variation of the pH of these solutions, it can be verified that at a certain pH of the initial solution, the variation between the pH of the initial suspension and the final pH (pH deviation) is zero. This is the indicative pH of the ZCP. Thus, the ZCP of each solution was obtained by calculating the mean between the points at which this deviation tended to zero.

#### 2.6. Chemical coagulation of zinc oxide nanoparticles

The last stage of the work was characterized by the coagulation test by means of a jar tester (Policontrol, Floc

control II model) under conditions of rapid mixing, slow mixing and sedimentation [27,40].

Briefly, two concentrations of nano-ZnO (50 and 100 mg L<sup>-1</sup>) to compare the performance of these concentrations in the coagulation process. For each jar, LAS concentrations varied from 0 to 300 mg L<sup>-1</sup>. In all, there were 72 samples for the coagulation assay under different concentrations of nanoparticles, different pH values (4.0, 7.0 and 10.0), different concentrations of surfactant and the use of organic and inorganic coagulants.

The optimal dosages for both coagulants, FeCl<sub>3</sub> and tannin, were determined to be in the range between 0 and 10 mg L<sup>-1</sup>, and the pH of the solutions was adjusted using HCl (0.1 M) and NaOH (0.1 M).

After preparation of the samples, before starting the coagulation process, 3 mL aliquots were collected, and the initial absorbance of the NPs in the spectrophotometer was determined using a wavelength of 378 nm, as described previously.

The jar tests were divided into three phases: (1) rapid mixing to start coagulation for 2 min at 200 rpm, (2) slow mixing to promote the encounter of destabilized particles for 20 min at 40 rpm and (3) sedimentation for 30 min [27,40].

After sedimentation, aliquots of 3 mL were collected for the purpose of reading the final absorbance of the NPs.

### 3. Results

#### 3.1. Effect of surfactant on aggregation and sedimentation of zinc oxide nanoparticles

The influence of different LAS concentrations under two distinct concentrations of nano-ZnO was observed with a spectrophotometer for 24 h and is shown in Fig. 2. As shown in Fig. 2A and B, the samples that did not have the presence of the surfactant presented a reduction of more than 50% of the ZnO aggregates at the first hour of the assay. This rapid agglomeration coincides with results

in previous studies that indicated that it is common for nanoparticles when hydrated to cluster and form flakes that sediment at a higher speed, since they move quickly and randomly due to the effect of Brownian movement [6,29,32]. Thus, particles with the same molecular geometry form aggregates with higher volumes, showing a significant effect on their sedimentation rates [40,41].

However, when the surfactant was added to the sample, it was already possible to note that the sedimentation rate of the nanoparticles decreased as the LAS concentration increased. The results were even more significant at concentrations of 100 mg L<sup>-1</sup> of the surfactant when compared to the samples absent from it. Fig. 2A and B clearly show the late sedimentation behavior of these nanoparticles in the presence of 300 mg L<sup>-1</sup> of LAS, and at the end of the 24 h, more than 15% of the nano-ZnO was in suspension. Anionic surfactants, due to the presence of ionic groups, have a greater possibility of stabilizing a suspension containing nanoparticles; once adsorbed in the nanoparticles, they can alter their electrostatic, steric and hydrophobic interactions, dispersing and stabilizing them [6,21,40,42].

Additionally, in Fig. 2 it can be observed that in samples containing 100 mg L<sup>-1</sup> of ZnO nanoparticles, the sedimentation rate in relation to time was higher than that of the 50 mg L<sup>-1</sup> of the nanoparticles, which is explained by the fact that the increase in the concentration of NPs consequently increases the ionic forces, facilitating their aggregation and consequently their sedimentation due to the tendency of aggregation through the electrostatic, steric and van der Waals forces [21,26,43].

The experiment presented in Fig. 2B, due to the addition of 300 mg L<sup>-1</sup> of LAS, the system showed a different behavior, since the increase in the concentration of nanoparticles correlated with an increase in surfactant increased LAS absorption in NPs, increased the stability of the suspension and prevented the sedimentation process. Charge reversion can explain this behavior, which is consistent with the results of a study in which Li (2017) states that

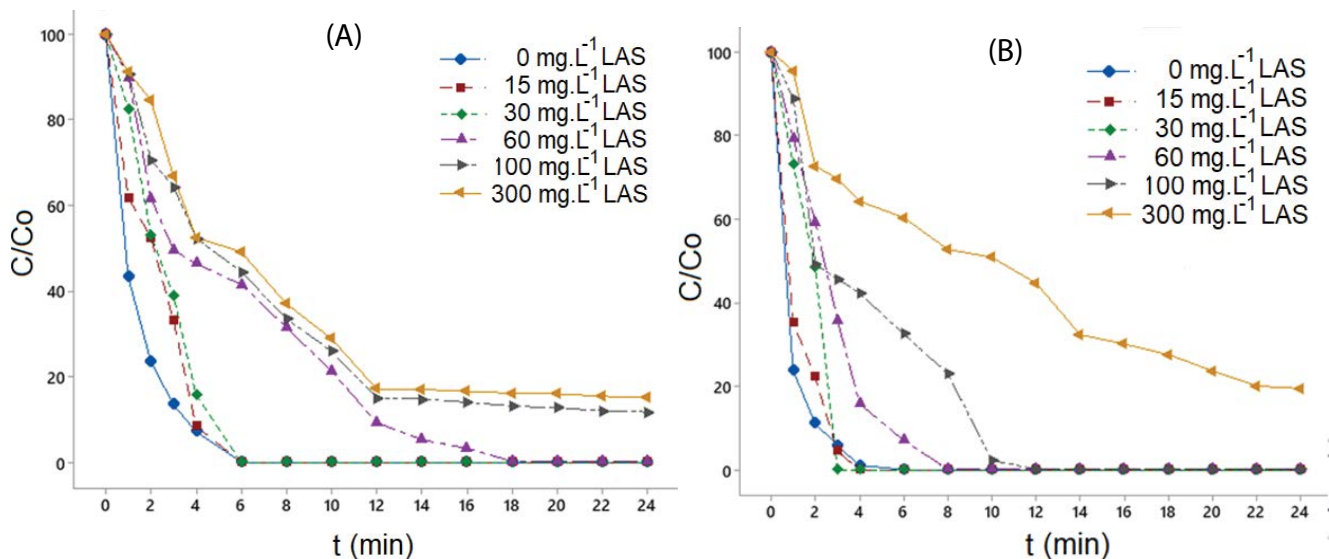


Fig. 2. Effect of surfactant on the sedimentation of zinc oxide aggregates: (A) 50 mg L<sup>-1</sup> NPs ZnO and (B) 100 mg L<sup>-1</sup> NPs ZnO.

functional groups present in surfactants can be absorbed on the surface of NPs and hinder the phenomenon of sedimentation, as it alters the physical-chemical properties of NPs, increasing the stability of NPs in aqueous media [6].

Godinez and Darnault [26] in their work with titanium dioxide nanoparticles demonstrated that the size of TiO<sub>2</sub> aggregates in dispersions containing surfactant was smaller, since by absorbing on the surface of nano-TiO<sub>2</sub>, the surfactants caused electrical repulsion between the nanoaggregates, preventing further aggregation and the increase in particle size. They concluded that the results of this study demonstrated that the surfactant LAS notably affected the aggregation and sedimentation behavior of ZnO nanoparticles. Thus, surfactants can significantly alter the transport and destination of nano-ZnO in the environment, as well as their interaction with contaminants present in it [40,43].

The results obtained from the modeling of sedimentation according to first-order and first-order equations with residuals are presented in Table 1. The graphs that gave rise to these parameters are shown in Figs. 3 and 4.

The variation in the kinetic coefficient *k* as a function of the increase in LAS applied in the jars is shown in Fig. 5.

Fig. 5 shows that the effect of LAS was significant even in the sedimentation velocity of NPs, showing a greater effect when the concentration of NPs was 100 mg L<sup>-1</sup>. When there was no LAS present in the liquid, the coagulation of NPs was more evident in the case shown in graph B due to the greater presence of NPs in the liquid. This concentration, which was twice the concentration applied to the liquid shown in graph A, promoted the best formation of clusters that precipitated at a higher speed. This behavior was maintained for all concentrations applied until the end of the assay. In both cases (graphs A and B), the sedimentation velocity always decreased with the increase of LAS in the liquid medium, except for the last three values of graph A in which it remained with little variation probably due to the low presence of remaining NPs in the liquid medium. These NPs, as shown in Fig. 3 charts E and F and Fig. 4

graph F, remained in suspension in the liquid medium, so they were not removed in the duration of the assay.

### 3.2. LAS effect on zero charge point determination

Electrostatic forces and pH control are two important factors that significantly affect the aggregation and stability of a dispersed aqueous system because pH control is used to influence the surface load of nanoparticles since the zero charge point pH (ZCP) is the electrical state of the surface of an adsorbent solution [26,44,45].

Fig. 6A–F show the influence of surfactant LAS concentrations in relation to the ZCP of nano-ZnO and was determined by the point of intersection of the curve that correlates the initial pH with the final pH with zero abscise value.

The presence of the surfactant at different concentrations did not significantly alter the ZCP when compared to the sample that had no influence of LAS, as shown in Fig. 6A. ZnO nanoparticles presented a ZCP pH of ~7.1 and appeared negatively charged at pH values greater than ~7.2, where the surface density of the negative charge increased with increasing pH. ZnO nanoparticles exhibit positive surface loading at pH values below ~7.1, where the positive surface load increases as the pH decreases.

This behavior coincides with previous studies in which, when in suspension, the nano-ZnO had their surface loads progressively reverted from positive to negative with the increase of pH and that at a pH between 7.0 and 9.0 favored the adsorption of nano-ZnO with anionic surfactants [23,40,46].

### 3.3. Influence of LAS on chemical coagulation

Fig. 7 shows the removal efficiency of nano-ZnO in the chemical coagulation assay with pH variation, using ferric chloride and tannin as coagulants. The test was conducted so that the nano-ZnO present in the solution became less electrically charged and increased the tendency to flocculate and therefore its sedimentation.

Table 1  
First-order fit parameters for all dispersions calculated from experimental sedimentation profiles

Sample	Concentration NP ZnO (mg L <sup>-1</sup> )	Concentration LAS (mg L <sup>-1</sup> )	Equation	Concentration residual (mg L <sup>-1</sup> )	<i>k</i> (min <sup>-1</sup> )	R <sup>2</sup>
(A)	50	0	$C = C_0 e^{-kt}$		$7.4 \times 10^{-1}$	0.99543
(B)	50	15	$C = C_0 e^{-kt}$		$4.3 \times 10^{-1}$	0.95679
(H)	50	30	$C = C_0 e^{-kt}$		$3.8 \times 10^{-1}$	0.95387
(D)	50	60	$C = C_0 e^{-kt}$		$1.8 \times 10^{-1}$	0.97319
(E)	50	100	$C = C_r + (C_0 - C_r)e^{-kt}$	9.06	$1.8 \times 10^{-1}$	0.99317
(A)	50	300	$C = C_r + (C_0 - C_r)e^{-kt}$	11.29	$1.7 \times 10^{-1}$	0.98640
(A)	100	0	$C = C_0 e^{-kt}$		$1.3 \times 10^1$	0.99461
(B)	100	15	$C = C_0 e^{-kt}$		$9.3 \times 10^{-1}$	0.98412
(H)	100	30	$C = C_0 e^{-kt}$		$5.2 \times 10^{-1}$	0.86064
(D)	100	60	$C = C_0 e^{-kt}$		$3.7 \times 10^{-1}$	0.96951
(E)	100	100	$C = C_0 e^{-kt}$		$2.3 \times 10^{-1}$	0.94543
(A)	100	300	$C = C_r + (C_0 - C_r)e^{-kt}$	10.90	$0.9 \times 10^{-1}$	0.97001

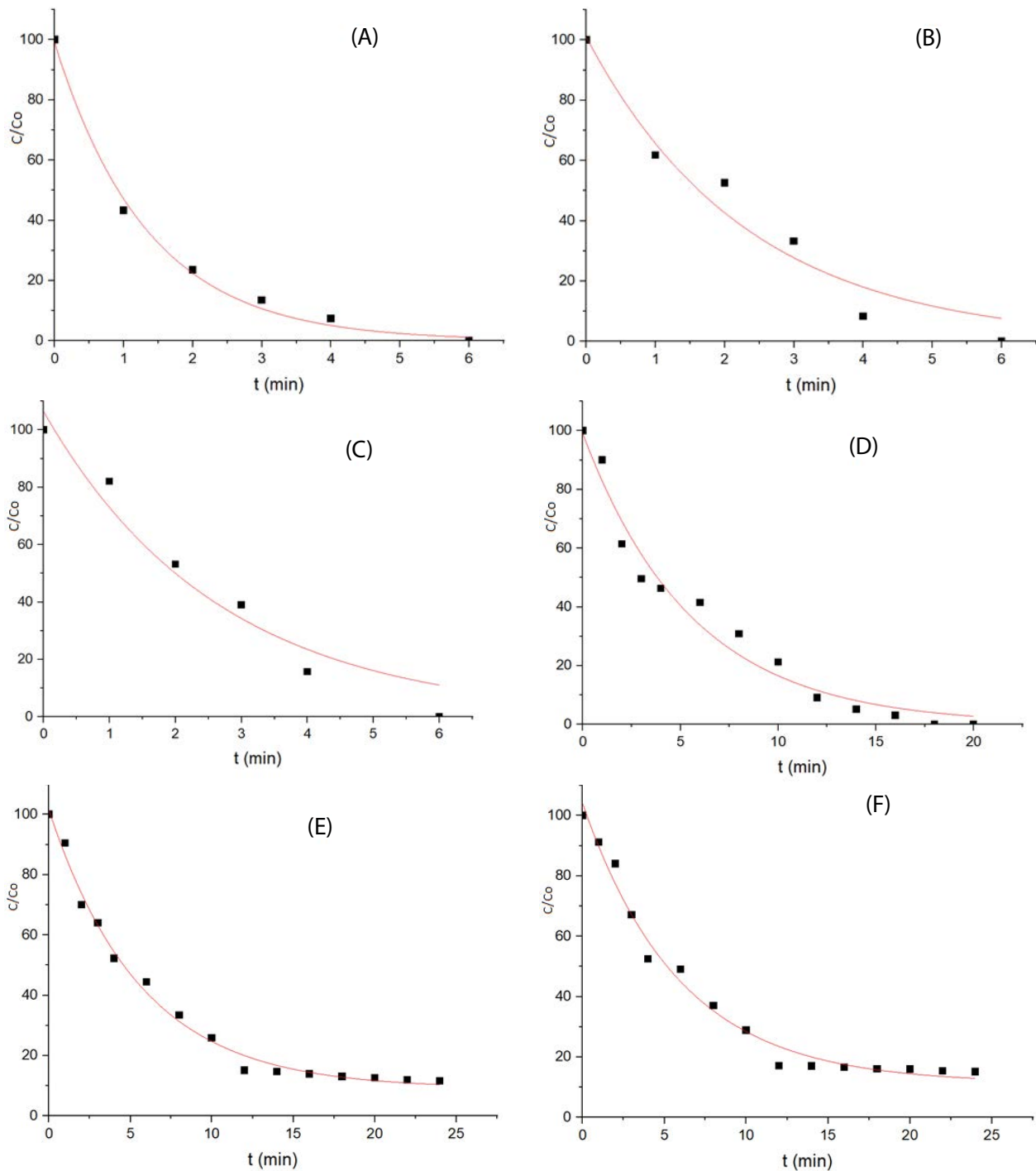


Fig. 3. Normalized graphs showing the variation of the initial concentration of ZnO equal to  $50 \text{ mg L}^{-1}$  as a function of time for LAS concentrations of (A)  $0 \text{ mg L}^{-1}$ , (B)  $15 \text{ mg L}^{-1}$ , (C)  $30 \text{ mg L}^{-1}$ , (D)  $60 \text{ mg L}^{-1}$ , (E)  $100 \text{ mg L}^{-1}$  and (F)  $300 \text{ mg L}^{-1}$ .

Briefly, a concentration of nano-ZnO in a solution of  $50$  and  $100 \text{ mg L}^{-1}$  for samples in the absence of LAS ( $0 \text{ mg L}^{-1}$ ) obtained satisfactory results, since 100% removal of the nanoparticles was attained regardless of the pH value (Fig. 7A–C).

As pH 7 was very close to the pH ZCP ( $\sim 7.1$ ) of the nano-ZnO, it allowed the surface load of the nanoparticles

to decrease at pH 7.0, reducing the electrostatic repulsive force between them, thus favoring the aggregation of the nano-ZnO into suspension. Some authors have reported in their studies that the action of neutralizing the loads with a pH close to or similar to the pH ZCP plays a fundamental role in the process of coagulation of the mixture [23,26,34,40,43].

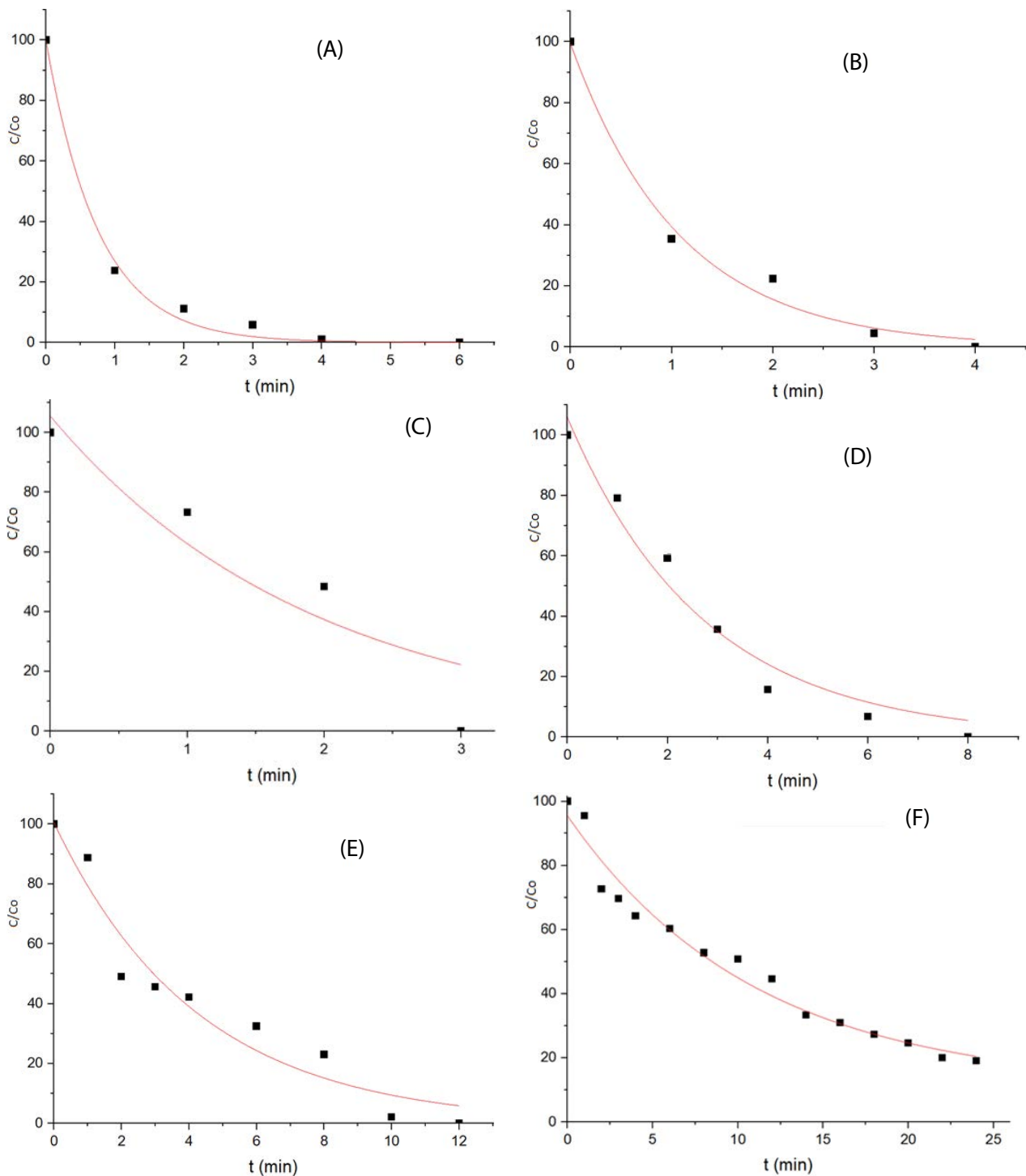


Fig. 4. Normalized graphs showing the variation of the initial concentration of ZnO equal to  $100 \text{ mg L}^{-1}$  as a function of time for LAS concentrations of (A)  $0 \text{ mg L}^{-1}$ , (B)  $15 \text{ mg L}^{-1}$ , (C)  $30 \text{ mg L}^{-1}$ , (D)  $60 \text{ mg L}^{-1}$ , (E)  $100 \text{ mg L}^{-1}$  and (F)  $300 \text{ mg L}^{-1}$ .

Both coagulants presented more significant removal when worked at pH 7.0, and tannin (organic coagulant) with better results in relation to ferric chloride (inorganic), and may be a subject of future studies for the use of tannin on a real scale for the chemical coagulation process, since it enters as an environmentally friendly organic alternative and does not present heavy materials to the process [47,48].

As shown in Fig. 7A–C, the addition of surfactant LAS to the sample reduced the removal rates of nano-ZnO, and the extent to which this concentration increased was significantly reduced at concentrations from  $100 \text{ mg L}^{-1}$ , reaching, in some cases, 100% of the nano-ZnO in suspension after the trial. Khan and Li reported that high concentrations of anionic surfactant hinder the aggregation and

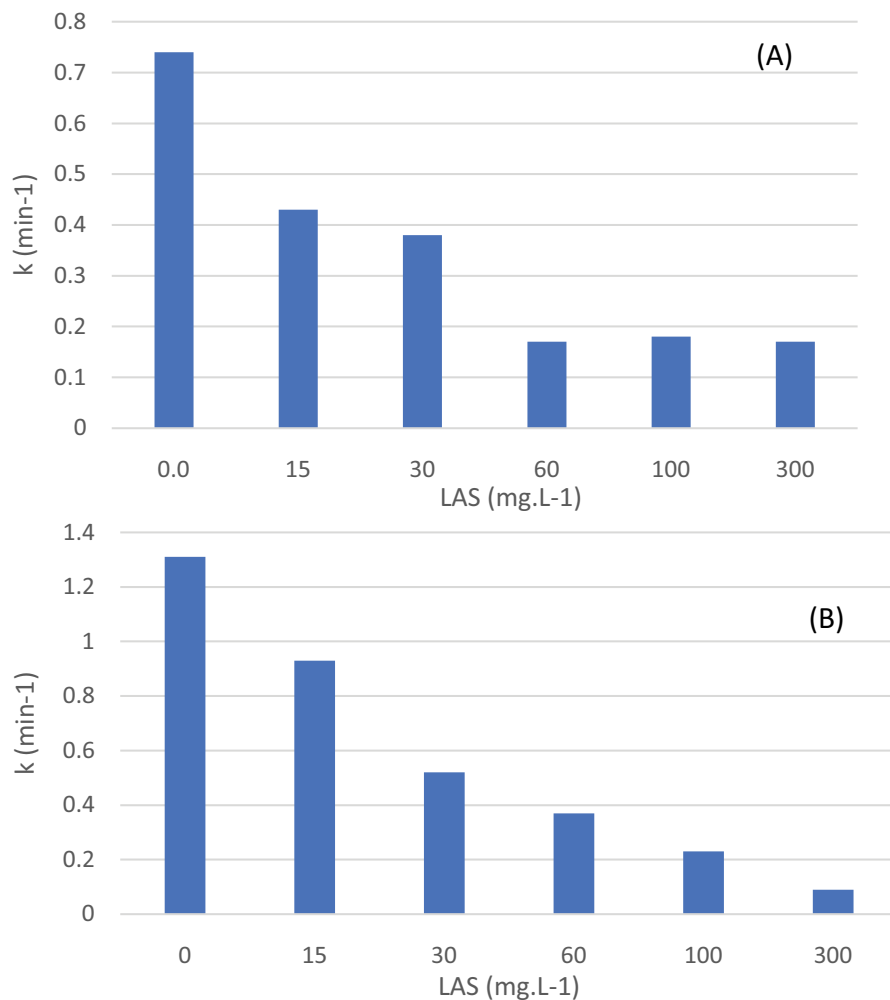


Fig. 5. Variation in the kinetic coefficient  $k$  as a function of LAS concentration for ZnO concentrations of (A) 50 mg L<sup>-1</sup> and (B) 100 mg L<sup>-1</sup>.

sedimentation of nanoparticles, given their strong sorption capacity [6,23].

Brunelli et al. [49] explained that the nanoparticles remain in suspension due to the strong steric resistance (when the adsorption of molecules on the surface forms a kind of protective cover, preventing the particles from getting close enough for the attractive forces of van der Waals to act), generated by the molecules of the anionic surfactant, restricting the aggregation of the nanoparticles and consequently the formation of flakes.

Fig. 8 shows the cause-and-effect flowsheet for the results obtained.

#### 4. Conclusions

In this study, we analyze the influence of a linear alkyl sulfonate anionic surfactant (LAS) on the aggregation, sedimentation, zero load point and coagulation behavior of zinc oxide nanoparticles (nano-ZnO). The presence of LAS affected the aggregation and sedimentation of nano-ZnO, with a more notable difference in concentrations above 100 mg L<sup>-1</sup>, since 20% nano-ZnO, under a concentration of 300 mg L<sup>-1</sup> LAS, was still in suspension after the 24 h trial

period. The surfactant showed no significant influence at the zero charge point of nano-ZnO, even at concentrations above 60 mg L<sup>-1</sup>. The presence of LAS exhibited a pronounced effect on the delay of aggregation and sedimentation of the nanoparticles, hindering the chemical coagulation process. Apparently due to charge inversion, LAS concentrations above 100 mg L<sup>-1</sup> demonstrated low efficiency in the removal of nano-ZnO, having concentrations of 300 mg L<sup>-1</sup>, a more pronounced effect, as they did not reach removal efficiency below 5%, even under different pH values and different coagulants. It may be concluded that the presence of LAS influences the efficiency of the chemical coagulation process for the removal of nano-ZnO. Both coagulants, ferric chloride and tannin, showed better results at pH 7.0, since it is a very approximate value of ZCP (7.1), thus facilitating the formation of aggregates. Future research and efforts should focus on using advanced oxidative processes for the removal of LAS anionic surfactant.

#### Recommendations

Authors recommend that further studies complement this work by means of monitoring z-potential in order to



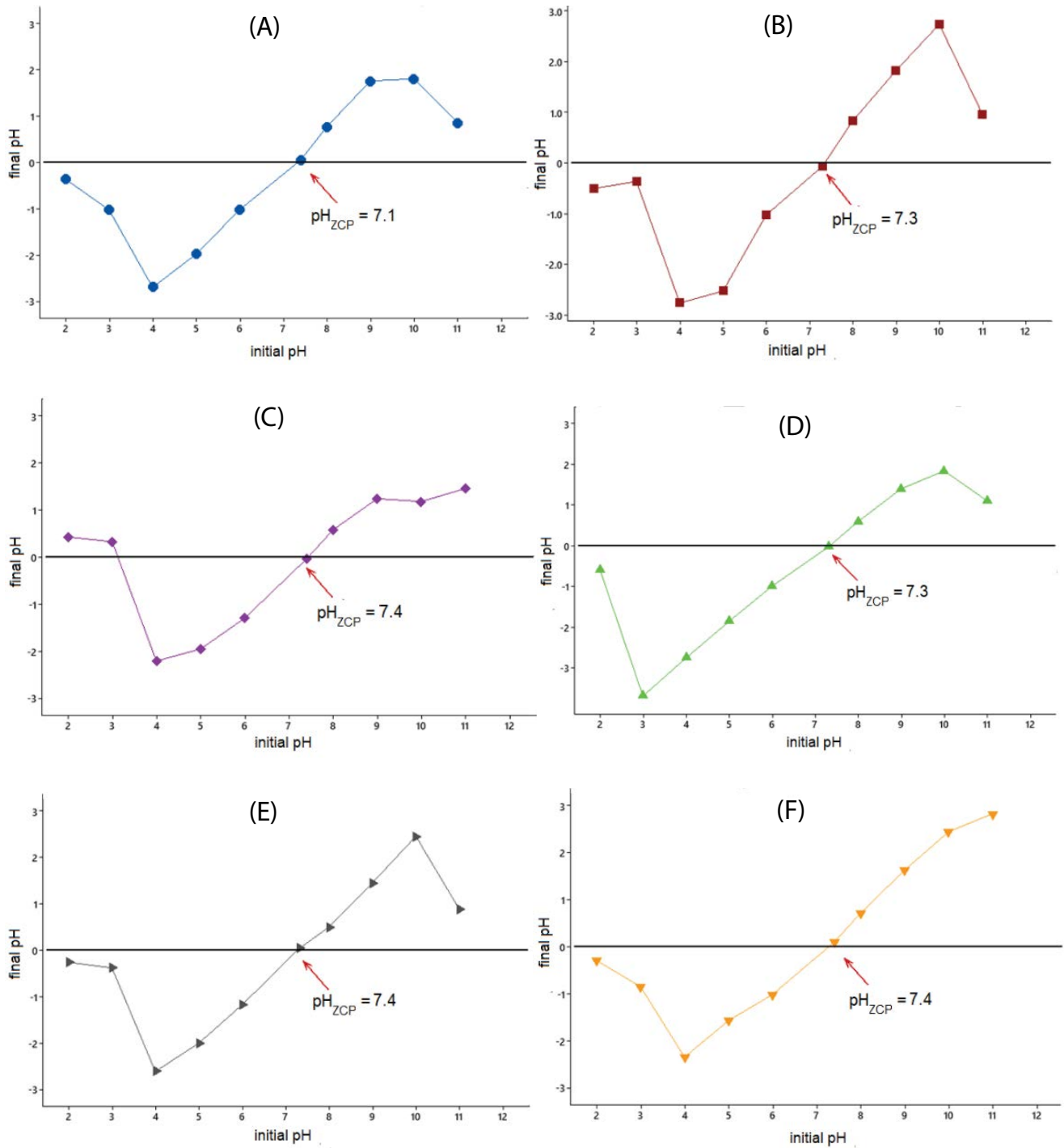


Fig. 6. Effect of surfactant LAS on nano-ZnO ZCP: (A) sample without the presence of LAS, (B) 15 mg L<sup>-1</sup> LAS, (C) 30 mg L<sup>-1</sup> LAS, (D) 60 mg L<sup>-1</sup> LAS, (E) 100 mg L<sup>-1</sup> LAS, and (F) 300 mg L<sup>-1</sup> LAS.

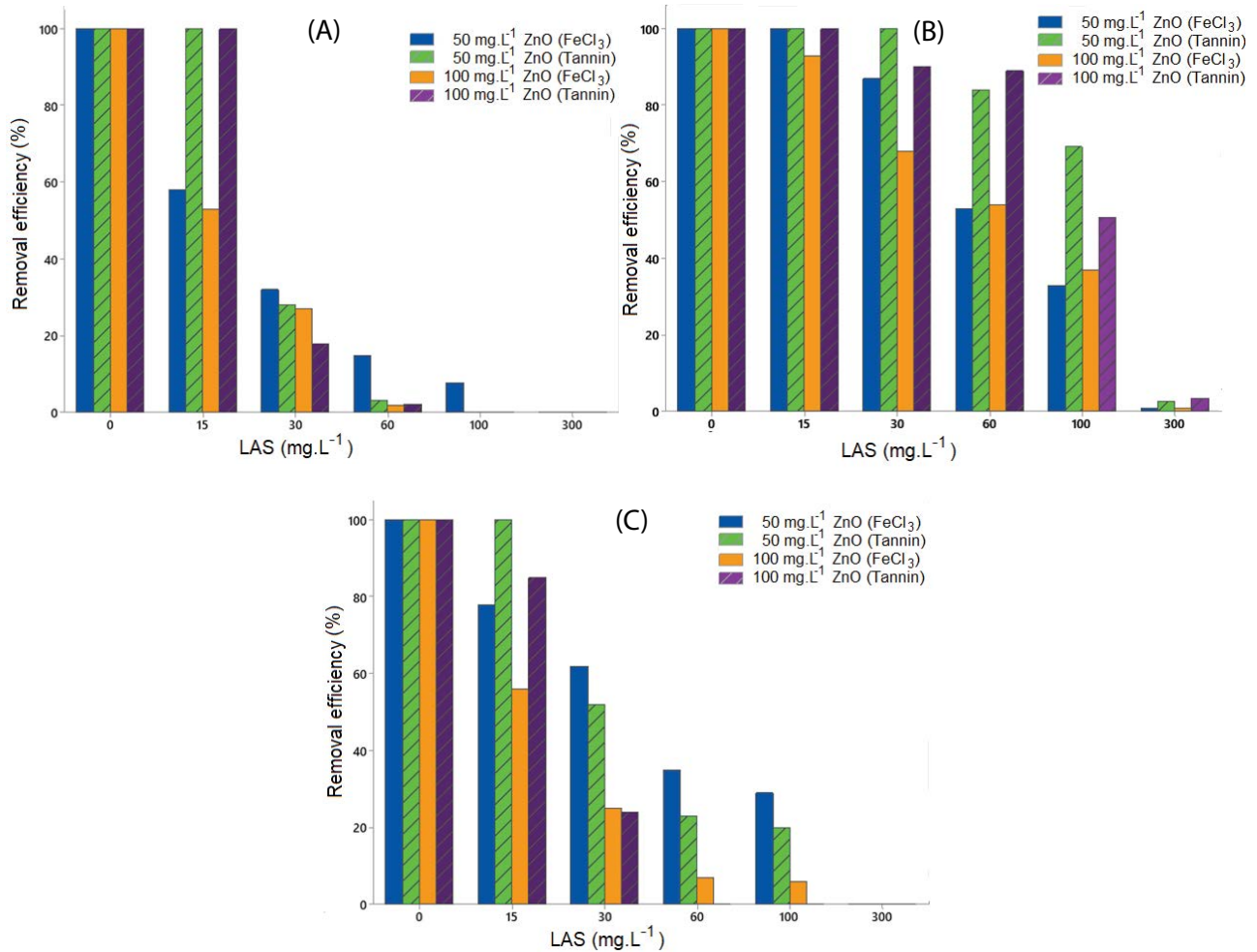


Fig. 7. Effect of LAS on the performance of chemical coagulation of nano-ZnO under different pH values and using ferric chloride and tannin as coagulants: (A) pH 4.0, (B) pH 7.0, and (C) pH 10.0.

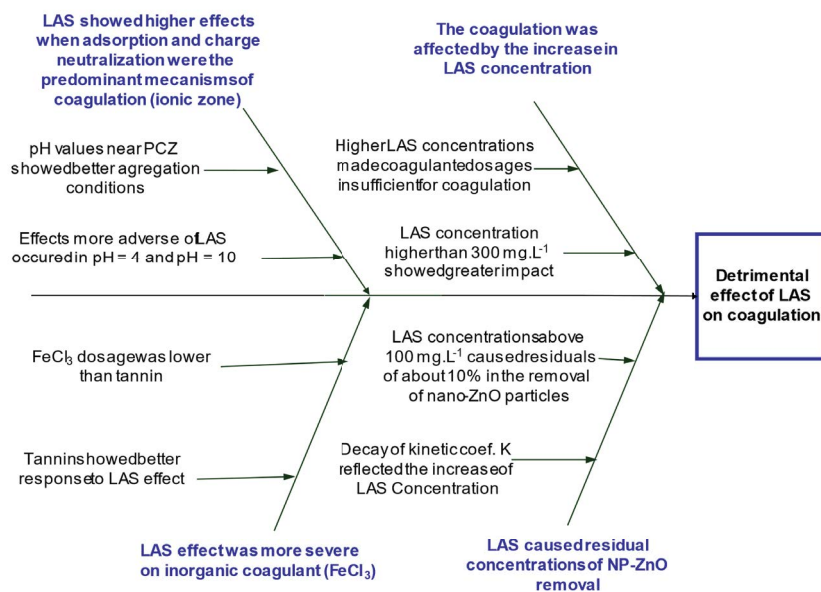


Fig. 8. Cause-and-effect flowsheet.

confirm ZCP results. Also, other suspended pollutants can be tested in order to define threshold limits of coexisting surfactant concentrations. Nonionic surfactants should also be tested for verification of steric resistance.

### Acknowledgments

The authors wish to acknowledge the Foundation for Research Support of the State of Goiás (FAPEG) and the Federal University of Goiás (UFG) that supported this research.

### Conflicts of interest

The author declares that there is no conflict of interest.

### References

- [1] F. Babaei, M.H. Ehrampoush, H. Eslami, M.T. Ghaneian, H. Fallahzadeh, P. Talebi, R.F. Fard, A.A. Ebrahimi. Removal of linear alkylbenzene sulfonate and turbidity from greywater by a hybrid multi-layer slow sand filter microfiltration ultrafiltration system, *J. Cleaner Prod.*, 211 (2019) 922–931.
- [2] H. Eslami, H. Hashemi, R.A. Fallahzadeh, K.R. Khosravi, R. Fouladi-Fard, A. Ebrahimi, Effect of organic loading rates on biogas production and anaerobic biodegradation of composting leachate in the anaerobic series bioreactors, *Ecol. Eng.*, 110 (2018) 165–171.
- [3] K.K. Barnes, D.W. Kolpin, E.T. Furlong, S.D. Zaugg, M.T. Meyer, L.B. Barber, A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States—Groundwater, *Sci. Total Environ.*, 402 (2008) 192–200.
- [4] A.R. Donovan, C.D. Adams, Y. Ma, C. Stephan, T. Eichholz, H. Shi, Detection of zinc oxide and cerium dioxide nanoparticles during drinking water treatment by rapid single particle ICP-MS methods, *Anal. Bioanal. Chem.*, 408 (2016) 5137–5145.
- [5] C.W. Huang, S.W. Li, V.H.C. Liao. Chronic ZnO-NPs exposure at environmentally relevant concentrations results in metabolic and locomotive toxicities in *Caenorhabditis elegans*, *Environ. Pollut.*, 220 (2017) 1456–1464.
- [6] X. Li, M. Yoneda, Y. Shimada, Y. Matsui, Effect of surfactants on the aggregation and sedimentation of zinc oxide nanomaterial in natural water matrices, *Sci. Total Environ.*, 582 (2017) 581–582.
- [7] S.E. Belanger, J.L. Brill, J.M. Rawlings, B.B. Price, Development of acute toxicity quantitative structure-activity relationships (QSAR) and their use in linear alkylbenzene sulfonate species sensitivity distributions, *Chemosphere*, 155 (2016) 18–27.
- [8] Hera: Human and Environmental Risk Assessment on Ingredients of Household Cleaning Products, LAS, 2013, 101 p.
- [9] E. Darvishi, D. Kahrizi, E. Arkan, Comparison of different properties of zinc oxide nanoparticles synthesized by the green (using *Juglans regia* L. leaf extract) and chemical methods, *J. Mol. Liq.*, 286 (2019) 1–7.
- [10] H. Ma, P.L. Williams, S.A. Diamond, Ecotoxicity of manufactured ZnO nanoparticles: a review, *Environ. Pollut.*, 172 (2013) 76–85.
- [11] S.L. Schneider, H.W. Lim. A review of inorganic UV filters zinc oxide and titanium dioxide, *Photodermatol. Photoimmunol. Photomed.*, 35 (2019) 442–446.
- [12] N. Wiesmann, M. Kluecker, P. Demuth, W. Brenner, W. Tremel, J. Brieger, Zinc overload mediated by zinc oxide nanoparticles as innovative antitumor agent, *J. Trace Elem. Med. Biol.*, 51 (2019) 226–234.
- [13] T.E.A. Chalew, G.S. Ajmani, H. Huang, K.J. Schwab, Evaluating nanoparticle breakthrough during drinking water treatment, *Environ. Health Perspect.*, 121 (2013) 1161–1166.
- [14] T. Ivankovic, J. Hrenovic, Surfactants in the environment, *Arh Hig Rada Toksikol.*, 61 (2010) 95–110.
- [15] A. Dereszewska, S. Cytawa, R.T. Wandzel, K. Medrzycka, The effect of anionic surfactant concentration on activated sludge condition and phosphate release in biological treatment plant, *Pol. J. Environ. Stud.*, 24 (2015) 83–91.
- [16] Conama: Conselho Nacional Do Meio Ambiente, Resolução nº 357, Brazil, 2005, 27 p.
- [17] Ministério Da Saúde, Portaria de Consolidação nº 5, Brazil, 2011.
- [18] G.E. Batley, J.K. Kirby, M.J. Mclaughling, Fate and risks of nanomaterials in aquatic and terrestrial environments, *Acc. Chem. Res.*, 46 (2013) 854–862.
- [19] F. Gagne, J. Auclair, P. Turcotte, C. Gagnon, C. Peyrot, K. Wilkinson, *Comparative Biochemistry and Physiology*, 219 (2019) 1–11.
- [20] S. Ranjan, N. Dasgupta, S. Singh, M. Gandhi, Toxicity and regulations of food nanomaterials, *Environ. Chem. Lett.*, 17 (2019) 929–944.
- [21] N.H. Tkachenko, Z.M. Yaremko, C. Bellmann, M.M. Soltys, The influence of ionic and nonionic surfactants on aggregative stability and electrical surface properties of aqueous suspensions of titanium dioxide, *J. Colloid Interface Sci.*, 299 (2006) 686–695.
- [22] Z.L. Wang, Nanostructures of zinc oxide, *Materials Today*, 7 (2004) 26–33.
- [23] R. Khan, M.A. Inam, D.R. Park, S.Z. Zam, S. Shin, S. Khan, M. Akram, I.T. Yeom, Influence of organic ligands on the colloidal stability and removal of ZnO nanoparticles from synthetic waters by coagulation, *Processes*, 6 (2018) 170, doi: 10.3390/pr6090170.
- [24] G. Zhou, Q. Wang, J. Li, Q. Li, H. Xu, Q. Ye, Y. Wang, S. Shu, J. Zhang, Removal of polyethylene microplastics using PAS and FeCl<sub>3</sub> coagulation: performance and mechanism, *Sci. Total Environ.*, 752 (2021) 1–8.
- [25] Z. You, Ch. Zhao, Y. Sun, Ch. Zhuan, Application of PAFC/CPAM for the removal of ZnO microparticles by enhanced coagulation, *Water Sci. Technol.*, 2 (2021) 484–498.
- [26] I.G. Godinez, C.J.G. Darnault, Aggregation and transport of nano-TiO<sub>2</sub> in saturated porous media: effects of pH, surfactants, and flow velocity, *Water Res.*, 45 (2011) 839–851.
- [27] M. Li, D. Lin, L. Zhu, Effects of water chemistry on the dissolution of ZnO nanoparticles and their toxicity to *Escherichia coli*, *Environ. Pollut.*, 173 (2013) 97–102.
- [28] Y. Xia, X. Xiang, K. Dong, Y. Gong, Z. Li, Surfactant stealth effect of microplastics in traditional coagulation process observed via 3-D fluorescence imaging, *Sci. Total Environ.*, 729 (2020) 1–8.
- [29] G.Sh. Boltachev, M.G. Ivanov, Effect of nanoparticle concentration on coagulation rate of colloidal suspensions, *Helyon*, 6 (2020) 1–7.
- [30] E.L. Terechova, G. Zhang, J. Chen, N.A. Sosnina, F. Yang, Combined chemical coagulation-flocculation/ultraviolet photolysis treatment for anionic surfactants in laundry wastewater, *J. Environ. Chem. Eng.*, 2 (2014) 2111–2119.
- [31] J.C.P. Penteado, O.A.E. Seoud, L.R.F. Carvalho, Alquilbenzeno Sulfonato Linear: Uma Abordagem Ambiental e Analítica, *Química Nova*, 29 (2006) 1038–1046.
- [32] E. Liwarska-Bizukojc, M. Bizukojc, Digital image analysis to estimate the influence of sodium dodecyl sulphate on activated sludge flocs, *Process Biochem.*, 40 (2005) 2067–2072.
- [33] J.S. Matthew, N.J. Malcolm, The biodegradation of surfactants in the environment, *Biochimica et Biophysica Acta*, 1508 (2000) 235–251.
- [34] D. Zhou, A.A. Keller, Role of morphology in the aggregation kinetics of ZnO nanoparticles, *Water Res.*, 44 (2010) 2948–2956.
- [35] D. Allen, S. Arthur, H. Haynes, First Order Decay Estimation of SuDS Pollutant Removal Rates, 2nd Infrastructure and Environment Scotland Postgraduate Conference, The University of Edinburgh, Edinburgh, 2014.
- [36] D. Allen, V. Olive, S. Arthur, H. Haynes, Urban sediment transport through an established vegetated swale: long term treatment efficiencies and deposition, *Water*, 7 (2015) 1046–1067.
- [37] M. Irani, T. Mohammadi, S. Mohebbi, Photocatalytic degradation of methylene blue with ZnO nanoparticles: a joint experimental and theoretical study, *J. Mex. Chem. Soc.*, 60 (2016) 218–225.
- [38] R.M.F. Cuba, T.S. Cintra, D.C.C. Paiva, F.J.C. Terán, Influência do etanol como cosubstrato na biorremediação de água contaminada com formulação comercial à base de glifosato, *Eng. Sanit. Ambient.*, 24 (2019) 983–991.

- [39] J.R. Regalbuto, J. Robles, *The Engineering of Pt/Carbon Catalyst Preparation*, University of Illinois, Chicago, 2004.
- [40] R. Khan, M.A. Inam, M.M. Iqbal, M.S. Shoaib, D.R. Park, K. Hoon Lee, S. Shin, S. Khan, I.T. Yeom, Removal of ZnO nanoparticles from natural waters by coagulation–flocculation process: influence of surfactant type on aggregation, dissolution and colloidal stability, *Sustainability*, 11 (2019) 17, doi: 10.3390/su11010017.
- [41] D. Daltin, *Tensoativos: Química, propriedades e aplicações*, 5th ed., Blucher, São Paulo, Brazil, 2011.
- [42] D. Lin, N. Liu, K. Yang, B. Xing, F. Wu, Different stabilities of multiwalled carbon nanotubes in fresh surface water samples, *Environ. Pollut.*, 158 (2010) 1270–1274.
- [43] D.A. Dickson, G.A. Liu, C.B. Li, G.C. Tachiev, Y. Cai, Dispersion and stability of bare hematite nanoparticles: effect of dispersion tools, nanoparticle concentration, humic acid and ionic strength, *Sci. Total Environ.*, 419 (2012) 170–177.
- [44] H.N. Tran, S.J. You, A.H. Bandegharai, H.P. Chao, Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review, *Water Res.*, 120 (2017) 88–116.
- [45] A.H. Zyoud, A. Zubi, S.H. Zyoud, M.H. Hilal, S. Zyoud, N. Qamhieh, A. Hajamohideen, H.S. Hilal, Kaolin-supported ZnO nanoparticle catalysts in self-sensitized tetracycline photodegradation: zero-point charge and pH effects, *Appl. Clay Sci.*, 182 (2019) 105294, doi: 10.1016/j.clay.2019.105294.
- [46] J.D. Hu, Y. Zevi, X.M. Kou, J. Xiao, X.J. Wang, Y. Jin, Effect of dissolved organic matter on the stability of magnetite nanoparticles under different pH and ionic strength conditions, *Sci. Total Environ.*, 408 (2010) 3477–3489.
- [47] Y.T. Hameed, A. Idris, S.A. Hussain, N. Abdullah, H.C. Man, F. Suja, A tannine-based agent for coagulation and flocculation of municipal wastewater as a pretreatment for biofilm process, *J. Cleaner Prod.*, 182 (2018) 198–205.
- [48] Z.Z. Abidin, N.S.M. Shamsudin, N. Madehi, S. Sobri, Optimization of a method to extract the active coagulant agent from *Jatropha curcas* seeds for use in turbidity removal, *Ind. Crops Prod.*, 41 (2013) 319–323.
- [49] A. Brunelli, J. Pojana, S. Callegaro, A. Marcomini, Agglomeration and sedimentation of titanium dioxide nanoparticles (n-TiO<sub>2</sub>) in synthetic and real waters, *J. Nanopart. Res.*, 15 (2013) 3–10.