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Effect of Tween 20 and linear alkylbenzene sulfonate on microplastic coagulation

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ABSTRACT

Microplastics have surfactant adsorption capability on their surface. As a result, its physical–chemical properties can be affected, leading to a decreased efficiency of microplastic removal by the coagulation process. Based on this, this research aims to verify the effect of the surfactant Tween 20 and linear alkylbenzene sulfonate on the chemical coagulation of polyethylene and expanded polystyrene microplastics. The coagulation/flocculation technique was applied, using turbidity analysis as a measure for the removal efficiency of microplastics. With the use of complete factorial planning at 2 levels, it was possible to find ideal conditions for microplastic coagulation and, therefore, to study the influence of surfactants through ZP, scanning electron microscopy and Fourier-transform infrared spectroscopy analyses. From this, electrostatic repulsion was observed in the polyethylene (PE) and expanded polystyrene (SPE) systems in the presence of linear alkylbenzene sulfonate, and in the presence of Tween 20, the formation of a protective layer in the molecular structure of microplastics prevented their aggregation. Therefore, it is necessary to consolidate methodologies when seeking to remove microplastics by coagulation because surfactants, in addition to changing the surfaces and morphology of microplastics, lead to a decrease in the removal of PE and SPE by the coagulation and flocculation process.

Keywords: Microplastic; Coagulation; Environment; Surfactants; Adsorption

1. Introduction

Pollution by microplastics (MPs) in river waters and coastal environments [1,2] is increasing in a way that they can be more harmful than larger debris, being qualified as emerging pollutants of global concern [3,4]. Microplastics are polymers with low biodegradability that are capable of persisting in the environment withstanding the weather for years [3]. With their specific surface area and hydrophobic surface, they are able to adsorb toxic chemicals, heavy metals and organic compounds present in water [5–7]. Because of this adsorption capacity, substances coexist on their surface and act as contaminant vectors in the environment [8].

MPs are particles smaller than 5 mm that are easily ingested by aquatic animals, and after adsorption of chemical compounds, they are sheltered in aquatic beings, impairing reproductive growth, in addition to inhibiting appetite and altering the behavior of species [2,9,10]. The same species that ingest MPs, such as turtles, crustaceans and fish, can be consumed by humans, reaching human organs through

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the food chain [8,11–13]. MPs enter water bodies directly or by wastewater treatment plant discharges [14].

Physical–chemical treatment processes of coagulation and flocculation are effective techniques for removing MPs, with efficiencies above 80% [3,15]. However, in the presence of surfactants, MP coagulation can be influenced, leading to decreased particle removal efficiency. Therefore, when coexisting with surfactants, the properties of the process can be affected or altered [7].

Surfactants are amphiphilic molecules with hydrophilic and hydrophobic characteristics that are capable of forming micelles in solution from a critical micellar concentration (CMC). Among them, linear alkylbenzene sulfonate (LAS) belongs to the sulfonate base, with anionic characteristics, and polysorbate 20 (Tween 20), derived from the polyoxyethylene sorbitan monolaurate family, has nonionic characteristics. These characteristics are widely used in daily activities and industrial applications; for this reason, surfactants can be found at concentrations greater than 16 $mg·L^{-1}$ in wastewater [16,17], affecting the approximation, transport, aggregation, and sedimentation of particles in aqueous suspensions [18,19].

The presence of sodium dodecyl benzene sulfonate (SDBS) affected the removal of kaolin in water [19], as well as magnetic nanoparticles [18]. Tween 20, in turn, when added to gold nanoparticles, can produce synergistic toxicity in zebrafish species in their embryonic phase [20]. The adsorption of nonionic surfactants on the PS surface can lead to the formation of a hydrophilic flexible layer of polyethylene glycol (PEG), capable of causing the stealth effect of PS in water [7].

Since few studies have assessed all these constraints, this study exhaustively investigated the effect of nonionic and anionic surfactants on the chemical coagulation of polyethylene (PE) and expanded polystyrene (SPE) MPs with sizes below 5 mm to describe the effect of Tween 20 and LAS surfactants on the surfaces of plastic particulate matter.

2. Materials and methods

Prior to surfactant addition, jar test experiments were carried out with deionized water, aluminum sulfate and MPs. A statistical methodology of experimental planning was applied, with the objective of identifying the variables and combinations for the best removal of PE and SPE MPs by chemical coagulation. For this, two complete factorials at 2^k, including two repetitions in the central points, were applied.

After determining which variables and combinations were ideal for removing the MPs, the surfactants Tween 20 and LAS were added to evaluate the influence of these compounds on the chemical coagulation of PE and SPE.

2.1. Materials

PE microspheres (0.6 mm, Bianquimica) and SPE beads (Swepor) with sizes ranging from 1 to 3 mm were used for this study. To obtain MPs smaller than 1 mm for SPE, beads were fragmented with a crusher for 15 min, and then stainless-steel sieves were used to identify the fragmented sizes. An average size of 0.9 mm was identified for this material.

The concentration for the aluminum sulfate stock solution (Perfyl Tech Química) was set to 100 $mg·L^{-1}$. For both Tween 20 (Perfyl Tech Química) and LAS (Neon Comercial) solutions, the concentrations were 1,000 $mg·L^{-1}$. To adjust the pH, solutions of HCl 1 $mol·L^{-1}$ (Chemical Dynamics) and NaOH 1 $mol·L^{-1}$ (Kinetic Reagents and Solutions) were used. All glassware was washed with 1 $mol·L^{-1}$ HCl and rinsed with distilled water to remove impurities.

2.2. Factorial planning

Complete factorial planning at 2 levels with the addition of 2 central points was applied.

The sizes and concentrations of the MPs were defined as constant parameters. Their value was set at 0.6 and 0.9 mm for PE and SPE, respectively, and the concentration of both was 400 $mg·L^{-1}$, since according to [7,21,22], different concentrations did not cause discrepancies in removal efficiency.

The independent parameters were pH values at 4, 5 and 6 and aluminum sulfate at concentrations of 2.5, 4.5 and 6.0 $mg·L^{-1}$ because under these conditions, it is possible to neutralize the particle charges by the positively charged aluminum hydrolyzed species, favoring the adsorption and charge neutralization mechanism.

Turbidity was set as the (dependent) response variable, measured by a PolyControl AP2000 turbidimeter, since it was reported as an indicator for the removal of microplastic particles [23,24].

After defining the process variables, the construction of the PE and SPE experimental matrix was started, inserting the lower and upper levels and the central point of the selected variables, as shown in Table 1.

With the doses of $Al_2(SO_4)_3$ concentrations and pH values defined, the experimental matrix that was applied in the jar tests was obtained (Table 2), with the respective real and encoded values.

Table 1
Actual levels of independent parameters

Parameter	Real levels		
	Lower level (–)	Top level (+)	Center point (0)
$Al_2(SO_4)_3$ ($mg·L^{-1}$)	2.50	6.00	4.25
pH	4	6	5

Table 2
Matrix of independent parameters

Essay	Actual values		Encoded values	
	$[Al_2(SO_4)_3]$ $mg·L^{-1}$ (X_1)	pH (X_2)	$[Al_2(SO_4)_3]$ $mg·L^{-1}$ (X_1)	pH (X_2)
1	2.50	4	–1	–1
2	6.00	4	+1	–1
3	2.50	6	–1	+1
4	6.00	6	+1	+1
5	4.25	5	0	0
6	4.25	5	0	0

2.3. Jar test

Coagulation tests were performed on jar test equipment (Policontrol Floc Control II) free of surfactants in this first stage. Briefly, for the preparation of the suspensions of PE and SPE MPs, 1 L of deionized water was used. Stirring velocities were set to 400 rpm for 1 min, decreased to 100 rpm for 15 min, and the suspension was allowed to settle for 30 min, with a sedimentation rate of 0.1 cm/min, considering a depth of 3 cm from the water surface [22,25].

2.4. Coagulation of microplastics in the presence of surfactants

After completing the stage that identified the concentrations of the coagulant and pH values that most influenced the removal of PE and SPE (Table 3), the same experimental approach was applied in the next assays, this time adding the surfactants to the jars that contained the MPs and stirring for 30 min to have better homogenization and adsorption of Tween 20 and LAS on the surface of PE and SPE [24].

Table 3
Concentrations of $Al_2(SO_4)_3$ and pH values obtained from factorial planning and used in the coagulation of microplastics with surfactants

Surfactants	$[Al_2(SO_4)_3]$ mg·L^{-1}	pH	$[Al_2(SO_4)_3]$ mg·L^{-1}	pH
	Polyethylene		Expanded polystyrene	
Tween 20	4.25	5	6.00	4
Linear alkylbenzene sulfonate	4.25	5	6.00	4

For Tween 20 and LAS, surfactant doses of 20, 80, 140, 200, 260 and 300 mg·L^{-1} were applied, which are considered typical values found in domestic and industrial wastewaters [26–28]. Thus, trials in triplicate were performed, and therefore, a descriptive statistical analysis was applied for each of the surfactants. The values of coagulant concentrations and pH were adjusted according to Table 3. Figs. 1 and 2 schematically present the development of the coagulation process of PE and SPE MPs with surfactants.

2.5. Characterization of microplastics

For the Fourier-transform infrared spectroscopy (FTIR) analysis, 100 mL of the samples taken after the jar test assays were added to a petri dish, dried in a vacuum dryer at a temperature of 60°C for 24 h and cooled in a desiccator. For the analysis of ZP and scanning electron microscopy (SEM), 200 mL of sample was collected and stored in amber vials. Fig. 3 presents a schematic representation of the characteristics of the samples used for FTIR, ZP and SEM analyses.

For FTIR analysis, the samples were mixed with potassium bromide (KBr) at a concentration of 5% by mass and pressed to form small discs. A PerkinElmer Spectrum 400 Model Spectrophotometer was used in the detection range of 400–4,000 cm^{-1}, and eight scans were performed for each

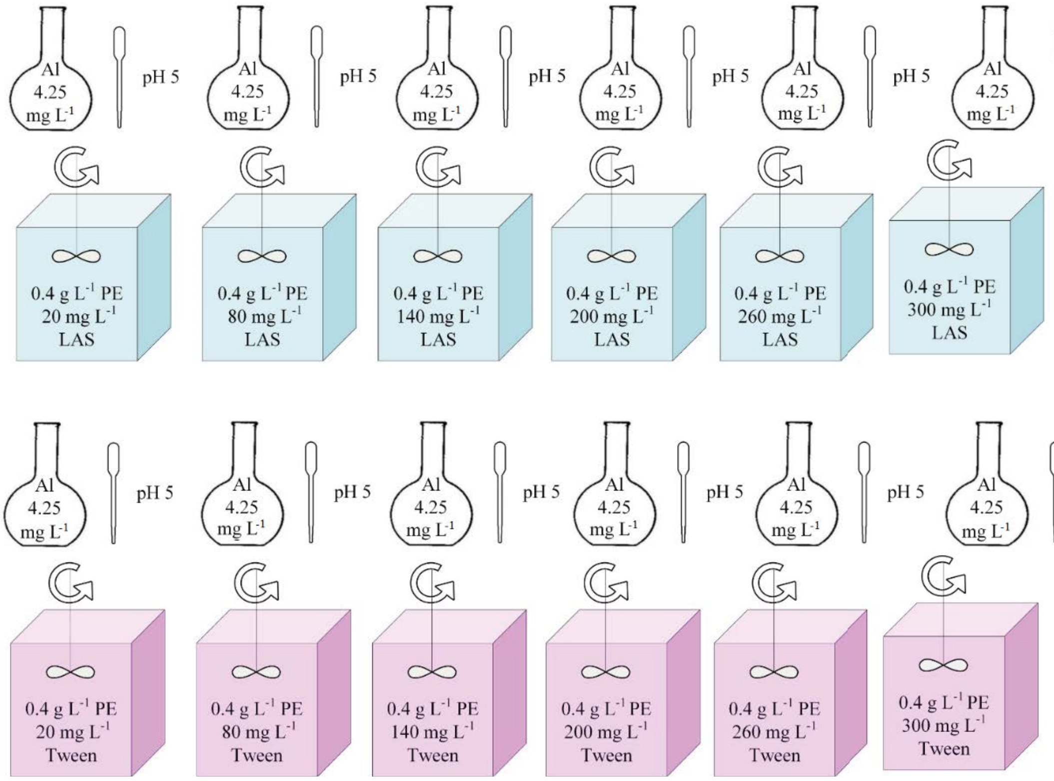


Fig. 1. Representation of the polyethylene coagulation process with surfactants and $Al_2(SO_4)_3$ dosages and pH values.

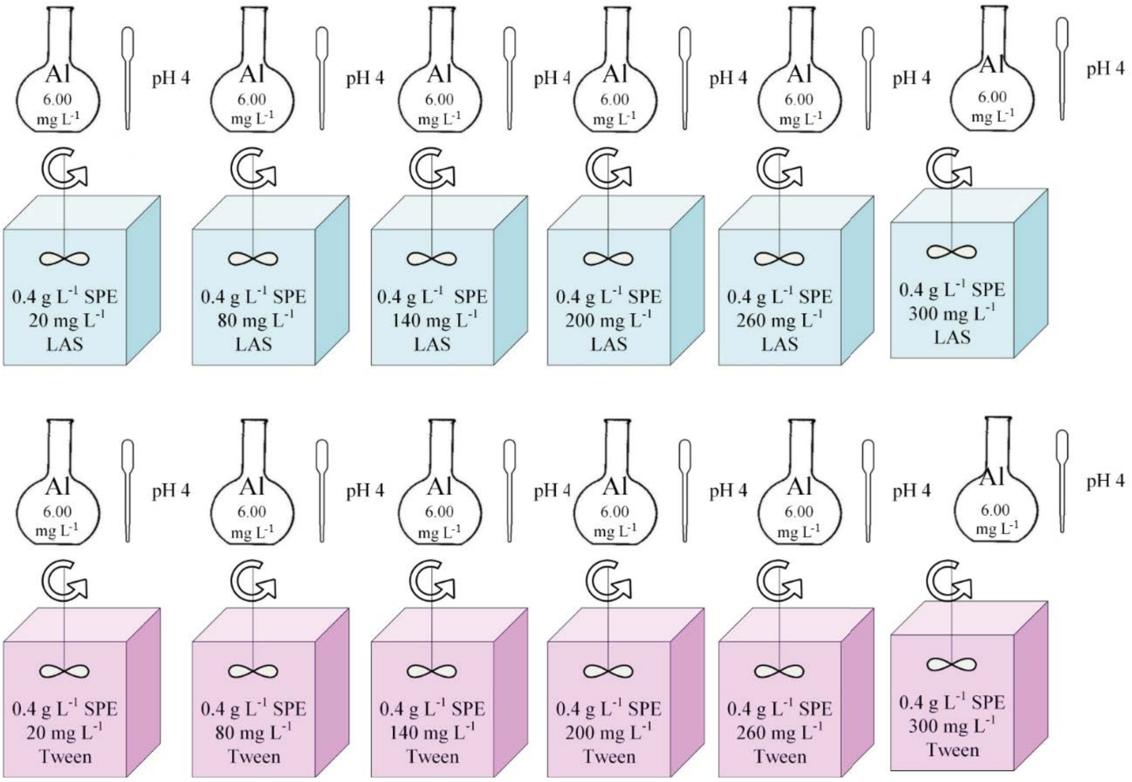


Fig. 2. Representation of the expanded polystyrene coagulation process with surfactants and $Al_2(SO_4)_3$ dosages and pH values.

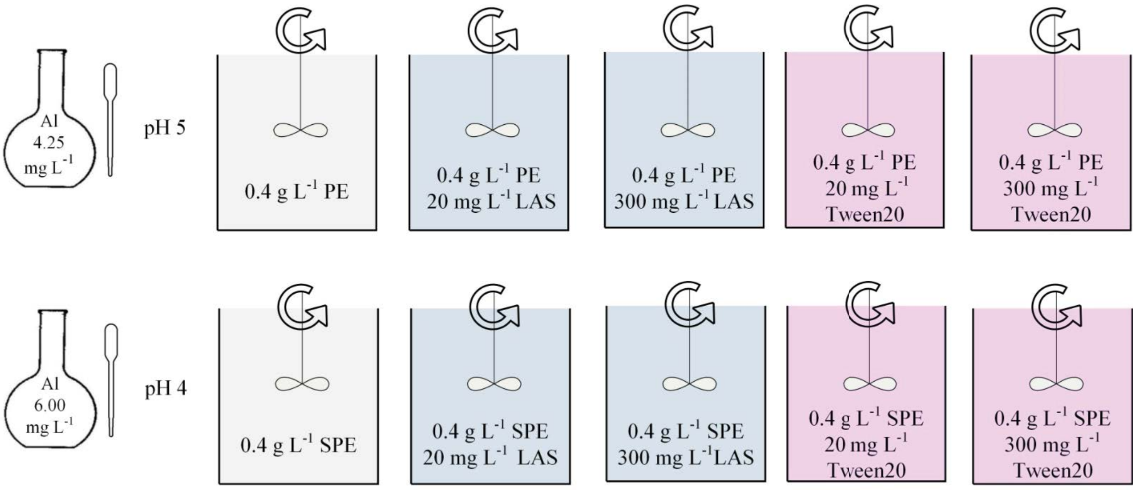


Fig. 3. Schematic of the characteristics of the samples collected after the jar test.

reading to identify the bands associated with intermolecular bonds before and after the reaction with the surfactants Tween 20 and LAS in interferograms.

To determine the ZP, Zetasizer Nano ZS equipment was used, which uses the scattering of electrophoretic light to particles, molecules and surfaces, in addition to a molecular mass analyzer by static light scattering.

SEM analysis was performed with a JEOL JSM-6610 scanning microscope to verify the changes in the morphological characteristics of the surfaces of the MPs under the influence of surfactants. The parameters used were Spectral 28, with an acceleration voltage of 5 kV and 150 and 500 amplifications.

3. Results and discussion

3.1. Factorial planning

Table 4 shows the values of the variables and the responses obtained with PE and SPE.

For PE, the best condition occurred with 4.25 mg·L^{-1} $Al_2(SO_4)_3$ and pH 5, and the removal and remaining turbidity obtained were 96.81% and 0.38 NTUs, respectively. For SPE, the highest removal efficiency occurred in experiment 2 (96.30%), with 6.00 mg·L^{-1} $Al_2(SO_4)_3$ and pH 4, and a remaining turbidity of 0.50 NTU was achieved.

Ionic strength, together with pH, plays an important role in coagulation, exerting influence on the formation of chemical flakes [29]. To investigate the removal of MPs, the initial pH values were adjusted according to the experimental planning using HCl and NaOH solutions; for PE, the values measured were 4.20, 4.20, 5.70, 5.80, 5.30 and 5.20, and for SPE, they were 4.10, 3.90, 5.90, 5.80, 4.80 and 5.00. After the addition of coagulants, the pH values of the suspensions with PE were 5.80, 4.70, 5.40, 5.50, 5.50 and 5.40, and those with SPE were 4.70, 4.00, 5.00, 4.30, 3.70 and 4.20. These values were considered to not lead to the formation of the precipitate $Al(OH)_3$, which, when formed, could interfere in turbidity analyses as well as inhibit the effect of surfactants on particles considered to be electrostatic in origin.

Table 5 shows the initial and final turbidity and pH values of each experiment.

For the pH values defined in the experimental planning, in experiments 1 (pH 4), 2 (pH 4), 5 (pH 5) and 6 (pH 5), higher removal of PE and SPE MPs was observed (Table 5).

Table 4
Values of encoded and uncoded variables and results of the efficiency of microplastic removal

Experiment	Variables		Efficiency removal (%)	
	[$Al_2(SO_4)_3$] mg·L^{-1}	pH	Polyethylene	Expanded polystyrene
1	(–1) 2.50	(–1) 4	96.26	93.33
2	(+1) 6.00	(–1) 4	96.53	96.30
3	(–1) 2.50	(+1) 6	89.23	87.56
4	(+1) 6.00	(+1) 6	89.57	89.62
5	(0) 4.25	(0) 5	96.47	90.08
6	(0) 4.25	(0) 5	96.81	90.08

Encoded values in parenthesis.

Once the hydrolyzed aluminum species are formed, they come into contact with the MPs in the rapid mixing stage, causing destabilization in the system, as well as the approximation and collision of destabilized microplastics. The flakes form and can then be removed by sedimentation.

Examining the results of final turbidity measured with PE in assay 1 (0.40 NTU), 2 (0.43 NTU), 5 (0.41 NTU) and 6 (0.38 NTU); and for SPE, in experiment 1 (0.84 NTU) and 2 (0.50 NTU), the defined parameters were significant for the removal of suspended particles from the concentration ranges and pH values that were defined in the factorial planning.

In trials 3 and 4, fewer MPs were removed, 89.23% and 89.57% for PE and 87.56% and 89.62% for SPE, which may be due to a reduction in the forces of attraction of van der Waals and electrostatic repulsion, which hinders the attraction between the MPs and the Al ions [23], making it difficult to neutralize the electric charge and finally leading to the stabilization of MPs that remain suspended in water [30].

For experiments 1 and 2 in the PE system, when the coagulant concentration increased from levels (–1) to (+1), there was an increase in removal. Similarly, for SPE in experiments 1 and 2 and 3 and 4, the removal efficiency increased from 93.33% to 96.30% and 87.56% to 89.62%, respectively. With these results, it is observed that the system operates as a function of the degree of ionization in the suspension [15,24,31].

Coagulants based on Al and Fe are well documented for the removal of MPs in water. Studies have noted that Al-based coagulants perform better than Fe-based coagulants [31,32]. In addition, $Al_2(SO_4)_3$ with pH values between 5 and 6 was studied by the study of Prokopova et al. [33] at dosages of 20, 50 and 60 mg·L^{-1}, and the effect of the pH was significant at all coagulant concentrations. Therefore, the $Al_2(SO_4)_3$ concentration and the pH value represent important variables for the removal of MP.

The two replicates in the central points considered for the model presented close results. For SPE, the same removal value was obtained for both assays (90.08%), and for PE, the results were 96.47% and 96.81%, indicating good reproducibility of the experiments.

The significance level and regression coefficients of the independent variables, as well as the coefficient of

Table 5
Factorial results with the noncoded variables and the results of turbidity and pH before and after the coagulation and flocculation processes

Experiment	Variables		Turbidity Initial		Turbidity Final		pH Initial		pH Final	
	$Al_2(SO_4)_3$	pH	Polyethylene	Expanded polystyrene	Polyethylene	Expanded polystyrene	Polyethylene	Expanded polystyrene	Polyethylene	Expanded polystyrene
1	2.50	4	10.70	12.60	0.40	0.84	4.20	4.10	5.80	4.70
2	6.00	4	12.40	13.50	0.43	0.50	4.20	3.90	4.70	4.00
3	2.50	6	11.70	12.30	1.26	1.53	5.70	5.90	5.40	5.00
4	6.00	6	11.70	13.00	1.22	1.35	5.80	5.80	5.50	4.30
5	4.25	5	11.60	12.60	0.41	1.25	5.30	4.80	5.50	3.70
6	4.25	5	11.90	12.10	0.38	1.20	5.20	5.00	5.40	4.20

Table 6
Regression coefficients and significance levels of factorial 2^k applied to the coagulation of microplastics

Independent variables	Microplastics polyethylene		Microplastics Expanded polystyrene	
	Coefficient regression	Significance level (p-value)	Coefficient regression	Significance level (p-value)
$Al_2(SO_4)_3$	0.15311	0.910082	1.25434	0.10757
pH	–3.49763	0.067655	–3.11332	0.011245
R^2	0.72413		0.92398	

determination (R^2), for the 6 trials made with each MP, considering a confidence interval of 90.0% ($p < 0.1$), are presented in Table 6.

Regarding the significance level, the pH presented a p value lower than 10.0% ($p < 0.1$), which is statistically significant for systems with microplastics. The concentration of $Al_2(SO_4)_3$ in the experiments with SPE presented a p value close to 10.0%, which was also significant to the system. On the other hand, $Al_2(SO_4)_3$ as a variable in PE coagulation was above the 10.0% level established for the significance level, having no effect on removal efficiency.

After multiple regression analysis with the MPs, it was possible to obtain the models represented by Eq. (1) and (2), which describe the parameters that were significant ($p < 0.1$). These models presented R^2 values of 0.72415 and 0.92398 for PE and SPE MPs, respectively. In addition, the highest R^2 (92.4%) was for the SPE, showing that the model adjusted well to the system, that is, how close the data were to the regression line; however, for the microplastic PE, the R^2 was 72.4%, demonstrating that the experimental data adjusted little to the model.

$$\text{PE removal} = 94{,}14–3{,}5\ \text{pH} \tag{1}$$

$$\text{SPE removal} = 91{,}16 + 1{,}25\text{Al} - 3{,}11\text{pH} \tag{2}$$

Constructed from Eqs. (1) and (2), Fig. 4a and b illustrate the response surfaces and level curves of the systems. Their purpose is to define the regions of higher and lower responses within the studied range, as well as experimental validation, in which the responses in red indicate that the increase in concentrations of $Al_2(SO_4)_3$ and lower pH values provide a higher removal efficiency. This was also stated by the study of Ma et al. [31], indicating that the PE MPs used in their assays had a low removal with low dosages of aluminum-based coagulants. When higher dosages were added, there was an increase in removal efficiency, especially with smaller MPs <0.5 mm. Reports on SPE removal by chemical coagulation were not detected by the end of this study. PS microplastics, on the other hand, were used by the study of Xue et al. [15] in nanometric ranges with alum dosages varying in the range of 10 to 50 mg·L^{-1}, reporting removals up to 85.2% for 30 mg·L^{-1}.

The variables that were significant in the systems can also be observed through the Pareto graph (Fig. 5). The relative importance of independent variables in relation to the response variable is presented through bars in descending order, so the higher the bar is, the greater the influence of the variables. From this, it is inferred that pH is the variable that most influenced the coagulation of MPs, while aluminum sulfate exerted a lower influence.

The concentrations of $Al_2(SO_4)_3$ and pH values obtained from factorial planning and used in the coagulation of microplastics with surfactants are presented in Table 3.

Alum concentrations of 4.25 and 6 mg·L^{-1} and pH values of 4 and 5 applied for both surfactants also favored the occurrence of coagulation following the mechanism of adsorption and charge neutralization impairing sweep coagulation that would interfere in the turbidity determinations because of the presence of chemical flocs. Since the interaction of ions is expected to be the main step in the study of surfactant effects, this acidic environment is considered essential for the development of the experimental approach.

3.2. Effect of surfactants on the coagulation of microplastics

After obtaining the concentrations of $Al_2(SO_4)_3$ and pH values that best fit the coagulation system of the MPs, they were used for all assays with Tween 20 and LAS for both MPs. Figs. 6 and 7 present the effect of Tween 20 and LAS on the coagulation of PE and SPE.

The results presented in Fig. 6 show the increase in turbidity according to the increase in surfactant concentrations in coagulation with PE, beginning with 0.38 NTU, which was the zero-surfactant added value. In this stage, there was an increase in turbidity due to particles in suspension from 0.38 to 2.86 NTU with LAS and from 0.38 to 0.92 with Tween 20. When the concentration of surfactants was raised to 300 mg·L^{-1}, the turbidity reached 19.90 NTU with LAS and 12.67 NTU with Tween 20, showing that LAS caused greater coagulation disturbance to PE microplastics.

A similar result was obtained for SPE coagulation, again showing that LAS had a greater influence than Tween 20. Fig. 7 shows the increase in turbidity according to the increase in the concentration of Tween 20 and LAS. The initial turbidity for these assays was 0.50 NTU, and as soon as 20 mg·L^{-1} surfactants were added, the turbidity increased to 34.5 NTU with LAS, and 25 NTU with Tween 20. Nevertheless, at a concentration of 200 mg·L^{-1} LAS, the system reached its maximum turbidity value equal to 55.0 NTU; however, the maximum value for Tween 20 was 36.0 NTU and occurred at a concentration of 300 mg·L^{-1}.

It can be inferred that this influence of LAS in the PE and SPE systems is due to its anionic characteristic due to the ionization of the sulfonic group [29], which may have been adsorbed on the surface of the MPs, causing a restabilization of the already coagulated MP particles (Fig. 8), unlike Tween 20, which does not present a charge in its polar group.

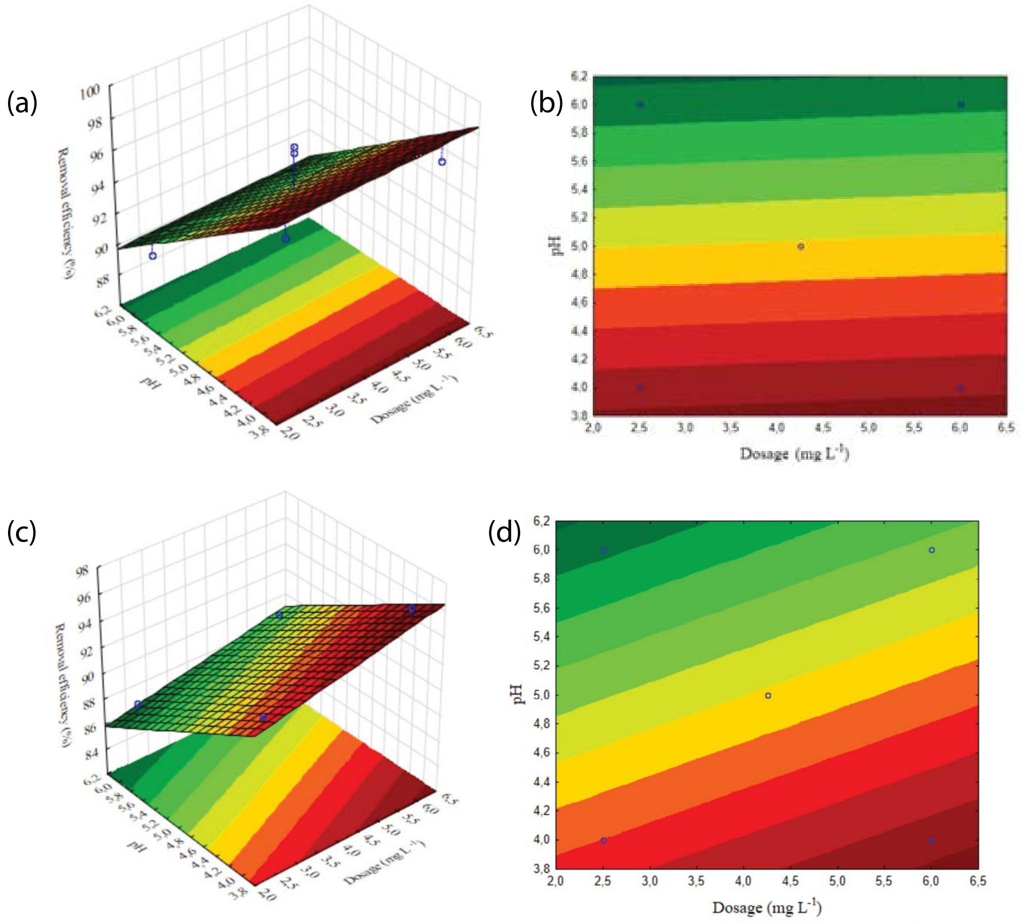


Fig. 4. Response surfaces and level curves: (a) for polyethylene microplastic removal efficiency and (b) for expanded polystyrene microplastic removal efficiency.

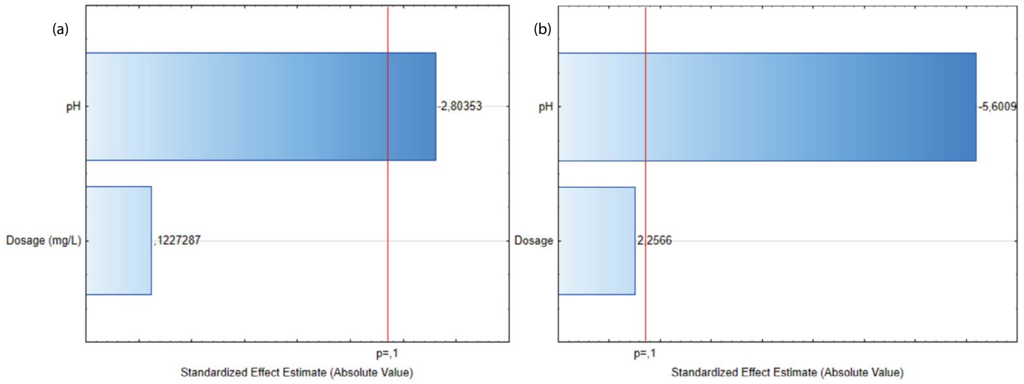


Fig. 5. Pareto diagram of the responses obtained with microplastics polyethylene (a) and expanded polystyrene (b).

When the Tween 20 surfactant is adsorbed on the surface of the MP, the PEG layer is formed on the surface of the MP, forming a micelle-like structure, which prevents the MPs from interacting with the coagulant, thus suggesting that the steric resistance from the PEG layer formed by Tween 20 tends to make PE and SPE stealthy in the coagulation process [7]. A schematic representation of these mechanisms is presented in Figs. 8 and 9.

It is also necessary to consider that it is characteristic of MPs to easily adsorb organic compounds in aqueous media due to their hydrophobic surface. Thus, it is expected that coexistence with surfactants creates disturbances in the liquid medium capable of reducing the efficiency of coagulation removal of MPs [7] since surfactants have amphiphilic behavior, interacting, therefore, with any hydrophobic or hydrophilic contaminants. This was also reported by the

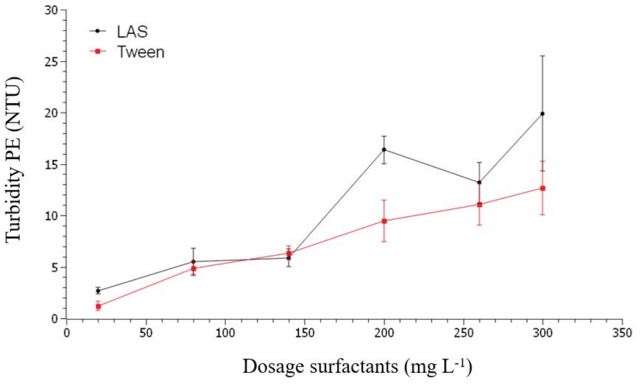


Fig. 6. Effect of Tween 20 and linear alkylbenzene sulfonate surfactants on the coagulation of polyethylene microplastics.

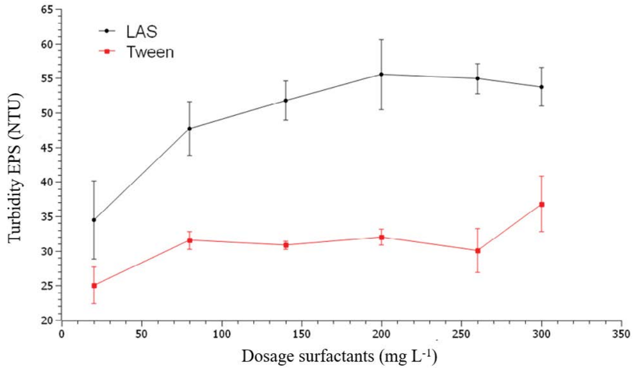


Fig. 7. Effect of Tween 20 and linear alkylbenzene sulfonate surfactants on the coagulation of expanded polystyrene microplastics.

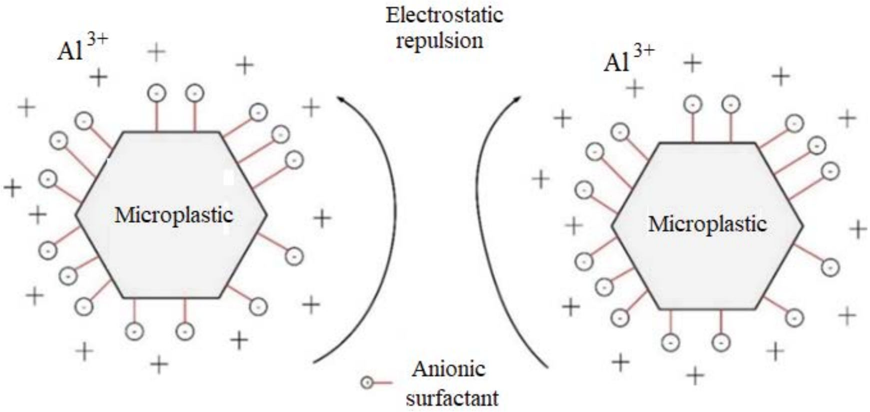


Fig. 8. Schematic representation of the effect of linear alkylbenzene sulfonate on the coagulation of polyethylene and expanded polystyrene microplastics. Adapted from Xia et al. [7].

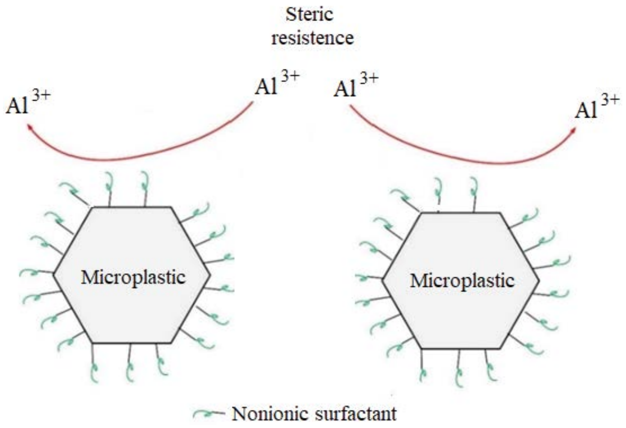


Fig. 9. Schematic representation of the effect of Tween 20 on the coagulation of polyethylene and expanded polystyrene microplastics. Adapted from Xia et al. [7].

study of Li et al. [29] with microfibers in washing wastewater, in which there was a reduction in removal efficiency by more than 10.0%.

For the surfactants Tween 20 and LAS, the critical micellar concentrations are 2,946 mg·L^{-1} [34] and 650 mg·L^{-1} [28], respectively. As micellization is a mechanism that protects hydrophobic groups from contact with water and reduces free energy from the system, the concentration of freely dissolved unimers in solution can never exceed the CMC regardless of the amount of surfactant added to the solution. Thus, the excess surfactant must necessarily be self-associated in the form of micelles.

As the study was carried out by applying concentrations of surfactants always below the CMC, the increase in turbidity in the suspension cannot be expected to be associated with the formation of micelles but mainly to the formation of aggregates consisting of MP particles covered by unimers and the presence of chemical flakes of $Al(OH)_3$ to a lesser extent, considering that the experiments were accomplished in coagulant concentrations and pH values that would favor the formation of ionic species.

3.3. Operating mechanisms in the coagulation of microplastics with surfactants

To explore the effects of Tween 20 and LAS on the coagulation of MPs, ZP, SEM and FTIR analyses were performed on PE and SPE samples in the absence and presence of Tween 20 and LAS surfactants.

In Figs. 10 and 11, it is possible to observe that in the absence of surfactants, after the reaction with $Al_2(SO_4)_3$, the ZP was zeta negative for both PE (–16.10) and SPE (–4.10 mV). Usually, in regard to determining the ZP, the colloidal suspension present in the liquid is unstable when the ZP is approximately zero and stable when the ZP is negative or positive [29]. Thus, it is inferred that when the obtained ZP was close to zero, the particles were able to destabilize. This occurred in the system with the SPE, mainly due to electrostatic repulsion between the ions.

As the LAS concentration increased (Fig. 10) in the PE system, ZP increased, being more zeta negative. Thus, for the concentration of 300 mg·L^{-1}, the ZP was –47.10 mV, and for the concentration of 20 mg·L^{-1}, it was equal to –27.50 mV. Thus, it was observed that at higher concentrations of LAS, inversion of charges occurred, causing the PE particles to be suspended and increasing the turbidity of the water. With Tween 20, the ZP was negative (–7.62 mV) at a concentration of 20 mg·L^{-1} and close to zero (–0.67 mV) at a concentration of 300 mg·L^{-1}. Due to the character of Tween 20 not presenting true charges in its polar region, these values may not be associated with colloidal suspension instability but possibly with steric repulsion. What leads to this steric repulsion is the PEG layer coming from Tween 20, as soon as it is adsorbed into the molecular structure of MP. A PEG layer forms, preventing the metallic coagulant from adsorbing, resulting in the non-aggregation of particles [7]. Therefore, as the ZP seeks to measure the charges of the particles present in the liquid medium, Tween 20, by its characteristic, does not interfere with the result and, rather, causes the steric effect observed in the system.

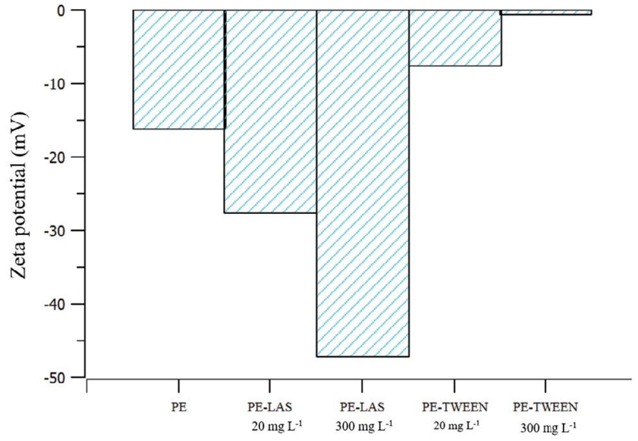


Fig. 10. Results of zeta potential analysis with polyethylene microplastics under different conditions.

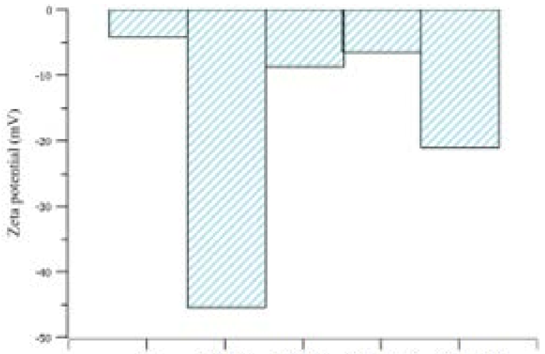


Fig. 11. Results of zeta potential analysis with expanded polystyrene microplastics under different conditions.

The steric repulsion makes it difficult for the particles to aggregate because the ionizable groups dissociate in the liquid phase and the ions from this dissociation add to the steric effect, imposing a dispersion to the system; that is, there was no adsorption of MP with coagulant, but the hydrolyzed species formed together with the particularity of Tween 20 made a protective layer capable of hiding the adjacent particles [29], in addition to foaming, which can affect the sedimentation of MPs.

In the SPE system (Fig. 11) with LAS, the opposite occurred; that is, the ZP at the highest concentration decreased (–8.73), while at the lowest concentration, it became more negative (–45.50), indicating that the electrostatic repulsion was higher at lower concentrations. However, the increase in turbidity occurred gradually with each increase in concentration. With Tween 20, the potential became more zeta negative (–21.00) at a concentration of 300 mg·L^{-1} and lower (–6.49) at a concentration of 20 mg·L^{-1}, which was to be expected by its nonionic type. From these conditions, it is inferred that in the SPE system, surfactants can potentially alter the properties of particles [7,29]. All these mechanisms influence the coagulation of SPE, thus requiring investigations in large concentrations of surfactants and MPs, since the study was the first in the study of the effect of LAS and Tween 20 on SPE coagulation.

The interactions between MPs and surfactants were also evaluated through FTIR spectral analysis. Because PE is a relatively unreactive material, surface interactions between MPs and neutral metal hydroxides from coagulants were expected to be low [25], but it is observed in the spectrum of the PE + $Al_2(SO_4)_3$ system (Fig. 12A and B) that a strong and broad peak between 3,400–3,500 cm^{-1} (3,432 cm^{-1}) could be attributed to the stretching vibration of hydroxyl groups of the Al-based hydrolysis products [34]. The peak at 1,635 cm^{-1} may be attributed to the bending vibration of hydroxyl groups due to the angle vibration of absorbed water and coordinated water, confirming the formation of hydrogen bonds (O–H) between PE and hydrolyzed coagulant species [35]. The peak at 651 cm^{-1} could be attributed to the bending and stretching vibrations of Al–O bonds [36]. The spectra obtained after PE coagulation in the presence of surfactants (LAS – 12A and Tween – 12B) did not show significant changes, indicating little interaction between the PE + $Al_2(SO_4)_3$ system and the surfactant. This result corroborates the lower influence of surfactants on PE coagulation when compared to the influence on SPE coagulation. In Fig. 12C, it is possible to observe the appearance of peaks corresponding to the LAS structure in the spectrum of the SPE + $Al_2(SO_4)_3$ + LAS system, indicating a strong interaction between SPE + $Al_2(SO_4)_3$ and the surfactant. The peaks corresponding to characteristic groups in the molecular structure of LAS were identified by the study of Farshchi et al. [37], with two bands, one at approximately 1,040 cm^{-1} and another close to 1,180 cm^{-1} (1,190 cm^{-1}) corresponding to

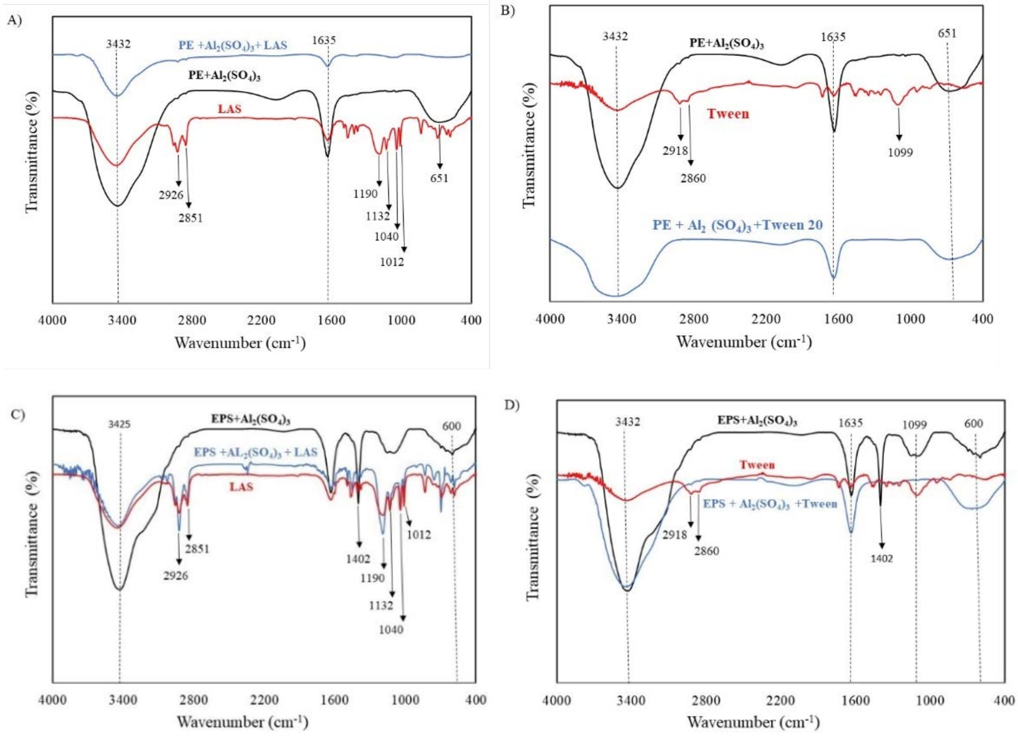
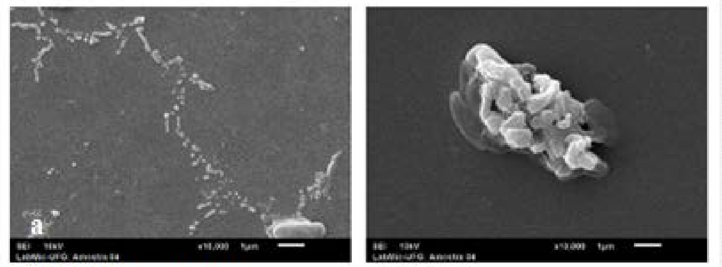
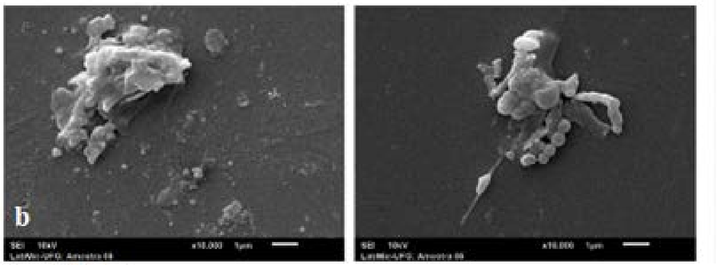


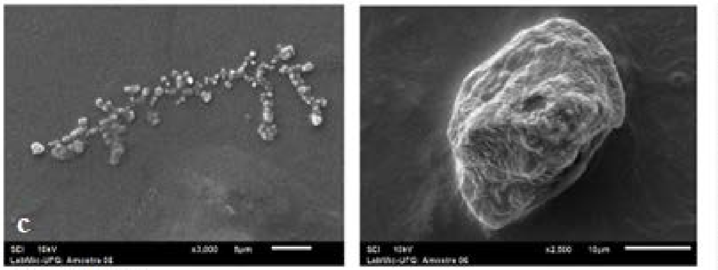
Fig. 12. Fourier-transform infrared spectroscopy analysis of polyethylene and expanded polystyrene.



NO SURFACTANT ADDED

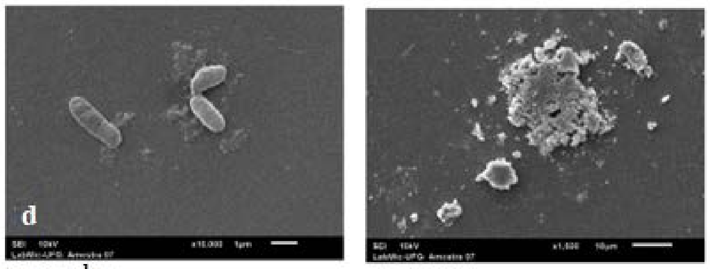


$20\ mg.L^{-1}$ LAS

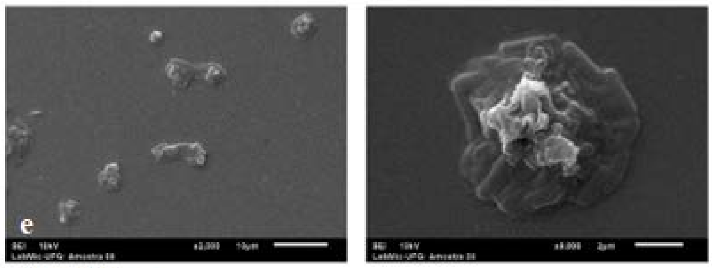


$300\ mg.L^{-1}$ LAS

Fig. 13 (Continued)



$20\ mg.L^{-1}$ Tween



$300\ mg.L^{-1}$ Tween

Fig. 13. Scanning electron microscopy images with polyethylene microplastics and with Tween 20 and linear alkylbenzene sulfonate.

symmetric vibrations of the sulfonate group ($-SO^{3-}$), bands at ~1,010 cm^{-1} (1,012 cm^{-1}) and 1,132 cm^{-1} attributed to aromatic C–H bending vibrations of the benzene ring. The presence of coagulant on the SPE surface can be confirmed by virtue of the presence of the peak at approximately 600 cm^{-1}, which indicates the existence of Al–O bonds [22].

The interaction observed between the studied MPs and $Al_2(SO_4)_3$ may have occurred through the neutralization of charges resulting from the adsorption of amorphous species of $Al(OH)_3$ formed by the hydrolysis of the coagulant. This phenomenon occurs with different intensities depending on the MP characteristics [22].

The morphology of the MPs was observed by SEM analysis. The results indicate changes that occurred on the surface of PE (Fig. 13) and SPE (Fig. 14) when surfactants were added during coagulation. In the PE system, Fig. 13a shows aggregate particles of PE after coagulation without surfactant addition. When receiving 20 $mg\cdot L^{-1}$ LAS (Fig. 13b), the particles began to disaggregate, and when a concentration of 300 $mg\cdot L^{-1}$ (Fig. 13c) was added, the pe surface presented a wavy and irregular aspect. With Tween 20, a pasty (Fig. 13d) and smooth (Fig. 13e) layer is observed, being formed, mainly at the concentration of 300 $mg\cdot L^{-1}$; similar to that obtained by the study of Xia et al. [7], indicating that Tween impaired PE sedimentation.

Fig. 14 presents the different changes in the surfaces of the SPE when surfactants were added at concentrations of 20 and 300 $mg\cdot L^{-1}$. In the absence of them (Fig. 14a), it is possible to observe the particles close to each other, and they agglutinated after the coagulation test. In the SPE and LAS systems, particles form irregular surfaces, showing changes in their shape (Fig. 14b and c). With Tween 20, it is possible to check a set of loose and unsteady particles (Fig. 14d and e), showing that it caused a disturbance in the system, which was initially stable. However, when receiving LAS and Tween 20, the absence of aggregate particles is clear, inferring that they prevent the approximation and deposition of SPE.

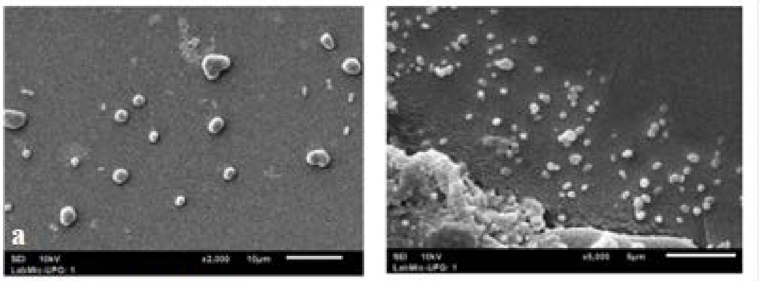
4. Conclusions

Synthetic polymers are difficult to obtain, handle and solubilize, and they can be removed by chemical coagulation with metallic salts. Using complete factorial planning at 2 levels, it was perceived that at concentrations higher than 4.25 $mg\cdot L^{-1}$ alum and with pH values outside the range of chemical precipitates, better removal responses can occur, in addition to reducing time and cost. Moreover, this is a tool capable of assisting in the studies of Tween 20 and LAS surfactants in PE and SPE coagulation.

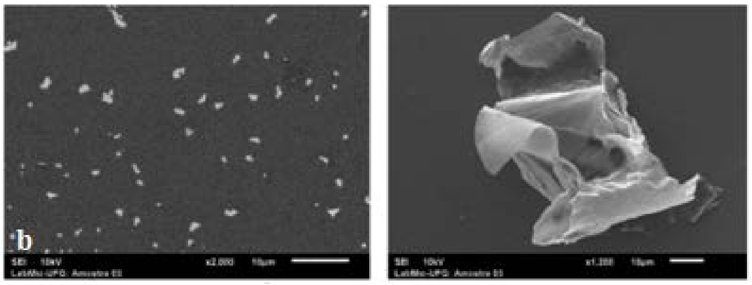
When surfactants coexist with MP, they can be adsorbed on the surface of the MPs, changing their characteristics and removal capacity. Although the turbidity method is sensitive and selective, it can be sufficiently able to analyze the removal of PE and SPE MPs in the presence and absence of surfactants.

Moreover, the ZP analysis allows us to affirm that the higher the mV is, the greater the chances of the diffuse layer being incorporated with the MPs. The morphology of the MPs with the surfactants is perceived to be an irregularly shaped layer; thus, the difference between the morphologies when it is not with the surfactants indicates a field to be explored, considering large concentrations of surfactants. FTIR analysis allows the identification of adsorption of the tensoactive molecule and the formation of the benzene ring group. Therefore, from these analyses, it is possible to identify that surfactants prevent the aggregation and sedimentation of microplastic particles.

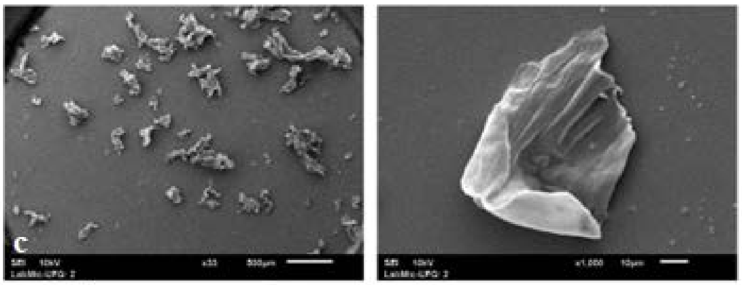
Thus, studying the effect of surfactants on microplastic coagulation explains a challenge for the current situation because surfactants are pollutants found in abundance in the environment and, above all, without effective public



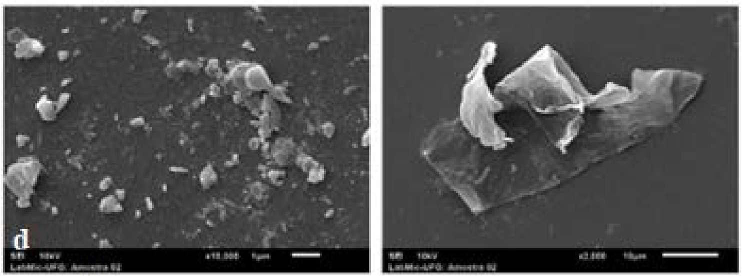
NO SURFACTANT ADDED



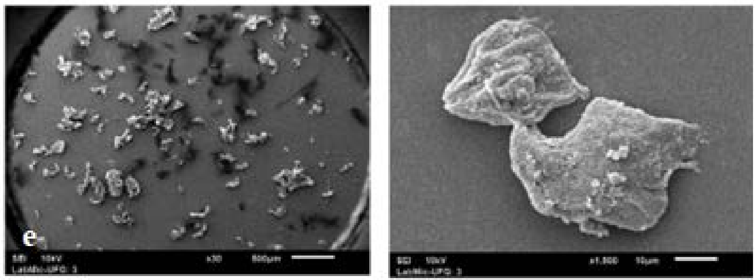
20 mg.L^{-1} LAS



300 mg.L^{-1} LAS



20 mg.L^{-1} Tween



300 mg.L^{-1} Tween

Fig. 14. Scanning electron microscopy images with expanded polystyrene microplastics and with Tween 20 and linear alkylbenzene sulfonate.

policies that ensure the correct management of plastic waste. The technique by coagulation and applied flocculation is satisfactory for the removal and study of MPs and surfactants in the treatment of water; however, it is suggested that more research be conducted with concentrations of coagulant aluminum sulfate, since water treatment stations can considerably increase the MPs in the water, because in addition to changing their surfaces and morphology, coexisting anionic surfactants can lead to electrostatic repulsion, and nonionic surfactants can lead to steric repulsion, capable of a protective layer, leading to a decrease in removal of PE and SPE in water.

Conflicts of interest

The authors declare that there are no conflicts of interest.

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