RGSA – Revista de Gestão Social e Ambiental
ISSN: 1981-982X
Data de submissão: 01/15/2023
Data de aceite: 03/15/2024
DOI: https://doi.org/10.24857/rgsa.v18n8-033
Organização: Comitê Científico Interinstitucional
Editor Chefe: Christian Luiz da Silva
Avaliação: Double Blind Review pelo SEER/OJS

STUDY OF THE EFFECT OF THE SURFACTANT LINEAR ALKYLBENZENE SULFONATE (LAS) ON THE COAGULATION OF AGED MICROPLASTIC

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ABSTRACT

Objective: Evaluate the effect of linear alkylbenzene sulfonate (LAS) surfactant on the coagulation of aged microplastic.

Theoretical Framework: Chemical coagulation is one of the steps adopted in water treatment that can help remove microplastics. During coagulation, suspended particles agglomerate, increasing the efficiency of removing these particles in the sedimentation stage. However, when coagulation occurs in the presence of surfactants, evidence points to deficits in removal capacity.

Method: Using Jar Test tests, the optimal parameters for microplastic removal were determined with aluminum sulfate as a coagulating agent in the presence and absence of the surfactant linear alkyl benzene sulfonate (LAS). The LAS concentrations studied were in the range of 20 mg/L to 300 mg/L. Microplastic removal efficiency was evaluated by measuring turbidity.

Results and Discussions: The combination of pH and coagulant concentration values that best suited the system were 5.0 and 4.25 mg/L, respectively. Due to the addition of surfactants, a decrease in removal efficiency was observed, with an average value ranging from 94.79% to 76.50% due to the interaction of polyethylene spheres with the surfactant.

Research Implications: As explained, due to the coexistence of microplastics and surfactants in the aqueous environment, studies that describe chemical coagulation under these conditions have great value for optimizing treatment systems and technologies.

Research Originality/Value: The use of aged microplastics aims to approximate their natural occurrence.

Keywords: Microplastic, Surfactant, Chemical Coagulation, Jar Test.

ESTUDO DO EFEITO DO SURFACTANTE ALQUILBENZENO SULFONATO LINEAR (LAS) SOBRE A COAGULAÇÃO DE MICROPLÁSTICO ENVELHECIDO

RESUMO

Objetivo: Avaliar o efeito do surfactante alquilbenzeno sulfonato linear (LAS) na coagulação de microplástico envelhecido

Referencial Teórico: A coagulação química é uma das etapas adotadas no tratamento de água que pode auxiliar na remoção de microplásticos. Durante a coagulação ocorre a aglomeração de partículas suspensas aumentando a

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eficiência de remoção destas partículas na etapa de sedimentação. Porém quando a coagulação ocorre na presença de surfactantes, as evidências apontam para déficits na capacidade de remoção.

Método: Por meio de ensaios de Jar Test foram determinados os parâmetros ótimos para remoção do microplástico com o sulfato de alumínio como agente coagulante na presença e ausência do surfactante alquil benzeno sulfonato linear (LAS). As concentrações de LAS estudadas estiveram na faixa de 20 mg/L a 300 mg/L A eficiência de remoção do microplástico foi avaliada por meio da medida de turbidez.

Resultados e Discussões: A combinação dos valores de pH e concentração do coagulante que melhor se ajustaram ao sistema foi 5,0 e 4,25 mg/L, respectivamente. Devido a adição dos surfactantes, notou-se diminuição da eficiência de remoção, com valor médio variando de 94,79% para 76,50% devido a interação das esferas de polietileno com o surfactante.

Implicações da Pesquisa: Conforme exposto, devido a coexistência de microplásticos e surfactantes no meio aquoso, estudos que descrevem a coagulação química nessas condições têm grande valor para otimização dos sistemas e tecnologias de tratamento.

Originalidade/valor: Utilização do microplástico envelhecido, de modo a se aproximar da forma como este ocorre na natureza.

Palavras-chave: Microplástico, Surfactante, Coagulação Química, Jar test.

ESTUDIO DEL EFECTO DEL TENSIOACTIVO SULFONATO LINEAL DE ALQUILBENCENO (LAS) SOBRE LA COAGULACIÓN DE MICROPLÁSTICOS ENVEJECIDOS

RESUMEN

Objetivo: Evaluar el efecto del surfactante lineal sulfonato de alquilbenceno (LAS) sobre la coagulación de microplásticos envejecidos.

Referencia Teórica: La coagulación química es una de las etapas adoptadas en el tratamiento del agua que puede ayudar en la eliminación de microplásticos. Durante la coagulación, las partículas en suspensión se aglomeran, aumentando la eficiencia de remoción de estas partículas en la etapa de sedimentación. Sin embargo, cuando la coagulación se produce en presencia de agentes tensioactivos, la evidencia apunta a déficits en la capacidad de eliminación.

Método: Los parámetros óptimos para la remoción de microplásticos con sulfato de aluminio como agente coagulante en presencia y ausencia del tensioactivo lineal alquilbenceno sulfonato (LAS) se determinaron mediante ensayos Jar. Las concentraciones de LAS estudiadas estuvieron en el rango de 20 mg/L a 300 mg/L. La eficiencia de remoción del microplástico fue evaluada mediante la medida de turbidez.

Resultados y Discusiones: La combinación de valores de pH y concentración de coagulantes que mejor se ajustaron al sistema fue 5,0 y 4,25 mg/L, respectivamente. Debido a la adición de tensioactivos, se observó una disminución en la eficiencia de remoción, con valores medios que oscilaron entre 94,79% y 76,50% debido a la interacción de las esferas de polietileno con el tensioactivo.

Implicaciones de la Investigación: Como se explicó, debido a la coexistencia de microplásticos y surfactantes en el medio acuoso, los estudios que describen la coagulación química en estas condiciones tienen un gran valor para la optimización de sistemas y tecnologías de tratamiento.

Originalidad/valor: Uso del microplástico envejecido para aproximarse a la forma en que se produce en la naturaleza.

Palabras clave: Microplástico, Surfactante, Coagulación Química, Prueba de Tarro.

1 INTRODUCTION

Plastics are synthetic organic polymers with applications in various production sectors worldwide, with production of approximately 2.4 billion tons per year (Ma et. al., 2019). As a result of human activities and/or environmental stressors, such as photo-oxidative degradation and mechanical actions, macroplastics are disintegrated into fragments of less than 5 mm and renamed as microplastics (Kokalj et al., 2018).

Microplastics - MPs - are considered emerging pollutants and due to their physical and chemical stability, these products are able to persist in the environment for long periods and support chemical and biological changes over the years (Kokalj et al., 2018).

MPs are commonly found in surface, underground, marine, and oceanic sources, with the main source being liquid effluent discharge. (Murphy et al., 2016). According to Olivatto et al (2018), microplastics can be ingested by aquatic organisms, affecting the growth of species, as well as acting as vehicles of contamination, due to the adsorption of persistent organic pollutants (POPs), heavy metals and other toxic substances on their surface, which amplifies the risks to the various trophic levels that come into contact with these particles (Ma et al., 2019).

In the literature, different studies aimed at removing MPs from the aquatic environment are presented: Araújo et al (2020) evaluated their removal through filtration in granular medium covered with silver nanoparticles; Shen et al (2022) used the electrocoagulation technique, presenting removal bands close to 90%; Zhou et al (2021) used chemical coagulation with aluminum sulfate as a coagulant agent and presented removal efficiencies higher than 80%.

Although chemical coagulation has been shown to be a process with good levels of efficacy for removing microplastics (Xue et. al., 2021), according to Xia (2020), its performance is tied to the characteristics of raw water, in the presence of other compounds, such as surfactants, which can interact with the MPs, and also, as a result of changes in the surface physical-chemical characteristics of the MPs due to their exposure to solar radiation.

In order to analyze the effects of surfactants in the removal of particulate materials in conventional water treatment processes and the evidence of superficial alterations in MP's particles plastic microspheres of polyethylene (PE) exposed to UV radiation for their aging, with dimensions of less than 5 mm, were submitted to the action of Linear Alkylbenzene Sulfonate (LAS), during chemical coagulation process in accordance with the recent studies of Guimarães et al. (2022) Oliveira et al. (2023) Zhou et al. (2021) and Ma et al. (2020).

2 BIBLIOGRAPHIC REVIEW

The term "microplastic" was first used in 2004, associated with the size of plastic particles. To be considered a microplastic, the polymeric matrix or its fragment must be between 1 µm and 5 mm in size (Thompson, 2004). They are characterized by their large specific surface area, low density and small size (Andrady, 2017).

Microplastics are present in all media. Due to its wide range of uses associated with poor management of effluent discharges and insufficient capacity to dispose of effluent in industrial and domestic effluent treatment plants, it is common to find them recurrently in rivers, lakes, seas and oceans, which causes great concern to the scientific and environmental communities (Xia et. al., 2019). Due to the chemical characteristics of their surface, microplastics can be vectors of toxic substances or persistent organic pollutants due to the adsorption capacity of environmental toxins (Li et. al., 2022).

MPs are divided into primary and secondary, depending on their origin. Primary microplastics are those manufactured in a certain size (less than 5mm) to meet some demand, associated with cosmetics and personal care products or in blasting technologies (Teotônio, 2020). Secondary are fragments of macroplastics formed through degrading processes that contribute to fragmentation in progressively smaller dimensions that may even become undetectable to the naked eye (Andrady,2017; Browne et al., 2007).

Various activities and practices intentionally or unintentionally use and release plastic waste into the environment. Plastic waste related to these activities is the main source of PMs for the environment, whether primary or secondary. (Montagner et al., 2021).

The plastic microspheres, known as "pellets", contained in cosmetics can reach concentrations of more than 50,000 particles per gram of product. (UNEP, 2015). These are usually introduced into the nature by discarding effluents whose treatment is not fully effective in removing these particles, thus reaching surface water bodies (Teotonio, 2020).

Once they enter the environment, microplastic particles can undergo various aging processes (Huffer et al., 2018). However, in the environment, MP's undergo the action of solar radiation, which generates physical and chemical alterations in their surface, favoring their capacity for surface adsorption in relation to other substances present in the environment (Santana, 2023). The aging of MPs with ultraviolet radiation is an experimental alternative to the natural aging of these materials. This technique can naturally reduce aging time and help in obtaining aged MPs (EWM) and application in experiments (Li et al., 2020). Huffer et al. (2019) noted that aging of MPs contributed to the increase in functional groups containing oxygen as carbonyl and hydroxyl groups. Guan et al (2022) observed that when interacting with aged microplastics (MPE), lead (2) had its mobility in the environment reduced in relation to interaction with new microplastics.

During the processes of fragmentation of polymers, such as from macroplastics to MPs, the release of the chemical additives that make up these materials, such as dye stabilizers, flame retardants, etc., which are used during the production process of these materials, also occurs. Such compounds can be leached into the environment by diffusion to the surface of MPs (COLE et al., 2011).

Similar processes occur with other contaminants, of anthropic or non-anthropic origin, which are fixed by adsorption to the surfaces of the microplastics and are transported, mainly in aquatic environments, where the MPs act as vectors of contaminants. (International Pellet Watch, 2006).

Recent studies point to intensified migration and persistence of microplastics, especially due to changes in their surface properties caused when they occur together with surfactant substances such as surfactants (Jiang et al., 2021).

Jardak et al. (2016), surfactants are compounds with widely consumed cleaning and solubilization properties that reduce surface tension between two immiscible liquids. They are discarded in large quantities in domestic and industrial effluents, regarded as undesirable pollutants for both the aquatic and the terrestrial environment. Its molecular structure is characterized by the presence of a hydrophilic part, which includes groups such as sulfate, carboxyl or phosphate, and a hydrophobic part, designed to be adsorbed at the oil/water interfaces, composed of hydrocarbon or branched chains, which may contain aromatic groups (MungraY; Kumar, 2008).

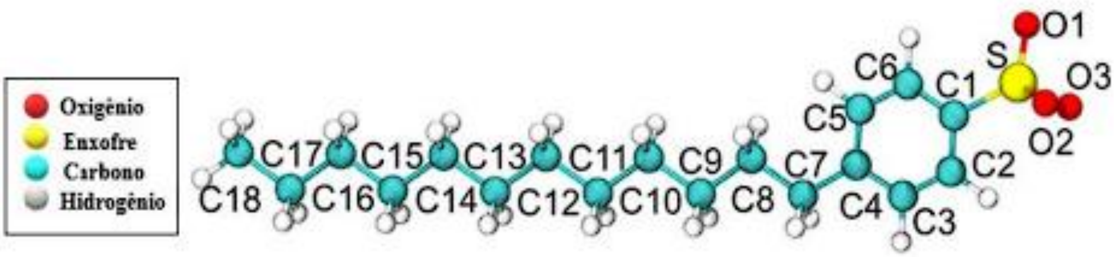
Not infrequently, these compounds are found in concentrations higher than 16 mg/L (XIA et. al., 2020), with the ability to significantly affect the approximation, transport and sedimentation of particles under coagulation/flocculation treatment (Tang et. al., 2016; LI et. al., 2017).

Due to their amphilic nature, these molecules are designed to be adsorbed at the oil/water interfaces, and have been widely used as detergents or in detergent composition and in industrial applications (Buurma, 2017). As a result of the release of effluents, these are one of the main pollutants found in aquatic environments (Scott; Jones, 2000).

Commercial linear alkylbenzene sulfonate (LAS) usually consists of a combination of several isomers (carbon chains of different sizes - C10-C14). Each isomer contains a sulfonated aromatic ring attached to the linear alkyl chain in any position except at the end carbons. Figure 1 shows the LAS structural formula.

Figure 1

Chemical structure of Linear Alkylbenzene Sulphonate (LAS)



Source: Takeda et al. (2019)

Due to its linear structure, LAS has good cleaning and detergent properties, evidenced by its affinity with oils and fats. The presence of the sulfonate group gives it anionic character and high solubility in water (Scott; Jones, 2000).

Studies (PenteadO et al., 2006; Scott; Jones, 2000) report the difficulty of biodegradation of these compounds that confer a degree of acute toxicity, mainly aquatic biota and water supply. Although LAS is considered to be a biodegradable surfactant, its high surface surfactant capacity favors its sorption in particulate materials (such as microplastics), and as a consequence its biodegradability is reduced as well as the difficulty of removing these associated particles (Boluda-Botella et al., 2010)

Among the existing technologies for the removal of microplastics in water and effluent treatment, chemical coagulation is the most widespread technology for the removal of suspended pollutants in water supply, with removal efficiency above 80% for microplastics (Xue et al., 2021; Zhou et al., 2021). However, when they occur together with surfactants, microplastics may have altered behavior of surface interactions, causing impairment of their removal by chemical coagulation mechanisms (Tang et al., 2016).

Chemical coagulation is a process used during the treatment of replenishing water or effluents for the removal of particles and colloidal substances in suspension. The process of chemical coagulation involves the addition of chemicals (coagulants) to the liquid medium that act on the surface charge of the suspended particles, destabilizing them, allowing the formation of larger flakes. These flakes can be removed more easily in subsequent steps, such as sedimentation or filtration. (Di Bernardo, 2005).

In general, the coagulants used commercially are based on salts of aluminum or iron, releasing ions into the medium, which interact with the charges with colloids in suspension. The destabilized colloidal suspension has its attractive forces reduced, thus lowering the energy barrier and allowing these particles to later aggregate (Metcalf; Edy, 2016).

Aluminum sulfate is among the chemical coagulants most used in water treatment plants - ETAs - and sewage treatment plants - ETEs - throughout Brazil, due to its low cost and high availability (Di Bernardo 2005). It has the molecular formula Al2(SO4)3, belonging to the group of metallic salts. Depending on the physical and chemical properties of the solution, pollutant and coagulant, chemical coagulation occurs according to the following mechanisms: adsorption/neutralization of charges; compression of the double electric layer; sweep coagulation and chemical bridge formation (Metcalf; Eddy, 2016).

In view of the above, it is believed that the presence of LAS in the liquid medium will negatively interfere in the removal capacity of the MP during the coagulation and flocculation stages and the effect potentialized in the aged MP due to the possibility of further interaction between MP and LAS.

3 METHODOLOGY

The coagulation/flocculation/sedimentation experiments were performed in a Jar Test apparatus with a microplastic suspension, which was composed of deionised water and MPEs. According to a methodology proposed by Oliveira (2023), the surfactant LAS was added to the suspension to evaluate the influence of this compound on the chemical coagulation of the aged polyethylene.

The experiments at Jar Test were entirely carried out at the Sanitation Laboratory of the School of Civil and Environmental Engineering, belonging to the Federal University of Goiás - UFG.

3.1 MATERIALS AND REAGENTS

The PE microplastics used were of the brand Bianquímica, in the format of microspheres with a size of 0.6 mm.

The aging process of microplastics was achieved by exposing them to ultraviolet radiation for a period of 15 days, as did Guan et al. (2022). To carry out this process, a wooden chamber was used, with dimensions of 50 cm in width, 50 cm in length and 70 cm in height, internally coated with reflective paper. Inside the chamber, two ultraviolet lamps were installed, emitting UV wave radiation with a peak wavelength of 254 nm (UV-C) and power of 15 W each. This configuration is designed to simulate the degradation of microplastics over time and their exposure to sunlight.

The coagulant agent used in the research was Al2(SO4)3 (Perfyl Tech Química) aluminum sulfate, at a concentration of 100 mg L-1, obtained from a standard solution of 1% aluminum sulfate, as used by Oliveira (2023). To correct the pH of the microplastic suspension, solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used, both with 1M concentration (Kinetic Reagents and Solutions).

In experiments containing LAS (Neon Chemistry) concentrations ranging from 20 to 300 mg L-1 obtained by diluting a standard solution with a concentration of 1,000 mg L-1 were tested (XIA et. al., 2020).

The coagulation tests were carried out on the Jar Test (Policontrol Floc Control II) equipment, which has six jars with a volumetric capacity of 2 L each. The removal efficiency of the microplastic through chemical coagulation was evaluated by the turbidity analysis using the PoliControl AP2000 turbidimeter.

3.2 DETERMINATION OF THE COAGULATION AND FLOCCULATION CONDITIONS OF PM BALLS

To evaluate the influence of the LAS on the coagulation and flocculation stage of the PM, the optimal coagulation conditions were first determined, by means of the mechanism of adsorption and neutralization of charges, for conditions in the absence of the LAS. The parameters obtained in this test were coagulation pH values and optimal concentrations of aluminum sulfate. The starting point for this test was the values of these parameters obtained by Oliveira (2023) who studied the removal of PE in natura in the presence and absence of LAS. In this sense, for batches, the following values were adopted:

pH: 4, 5 e 6;

$Al_2(SO_4)_3$: 2,50; 4,25; 6,00 mg L^{-1}

The concentration of PM in the suspensions was determined according to results presented by Zhou et al. (2021), evaluated MPs concentrations in the 200 to 800 mg L-1 ranges in coagulation studies with microplastic in natura, having not noticed significant variations above 500 mg L-1. Thus, the trials to be conducted in this study used a concentration of 400 mg L-1, the same concentration used by Oliveira (2023), in order to conduct a comparative study.

3.2.1 Preparation of the microplastic suspension

Deionized water plus aged polyethylene microspheres (MPE) was used for the microplastic suspension. Thus, each of the six jars was filled with 1L of deionized water and later added 400 mg of microspheres of PE aged in equal quantity for each bottle, thus the suspension obtained presented MPE concentration of 400 mg L-1. The micro-plastic suspension used in the tests was tested in the process of achieving optimal coagulation conditions for removal of PE.

After the addition of the MPE spheres, the microplastic suspension was rotated slowly (<100 RPM) to homogenize the material, then the pH was measured and corrected to the above concentrations and then an aliquot was taken from which the pH, temperature and initial turbidity were measured.

3.2.2 Jar Test Testing

For the coagulation/flocculation assays in JarTest, aluminum sulfate was dosed at the different concentrations noted in section 3.2, under the different pH levels mentioned above, in order to obtain the optimal coagulation/flocculation condition. After this determination, the tests with the surfactant LAS on the conditions obtained at the first moment were performed. In the following items, the particularities of each stage are described.

3.2.3 Coagulation of PE microspheres

With the jars filled with the micro-plastic suspension, the coagulant was added and subjected to a stirring speed of 400 rpm set to simulate a first rapid mixing step for 1 min and then slow mixing for 15 min at a speed of 100 rpm. After the mixing stage, the suspension present in the jars (deionized + MP + coagulant) was subjected to sedimentation for at least 30 min (Zhou et al., 2021; Oliveira, 2023).

At the end of the sedimentation period, samples of the supernatant material from each jar were carried out for analysis of turbidity and pH after the test. It should be noted that in order to maintain the integrity of the tests in relation to the analysis of turbidity, system disturbances were avoided in each sample withdrawal. For optimal chemical coagulation conditions (pH and coagulant concentration), quintuplicates of assays were performed where pH and concentration values were varied as shown in Table 1.

Table 1

Al2(SO4)3 concentrations and pH values used to obtain optimal coagulation conditions for microplastics

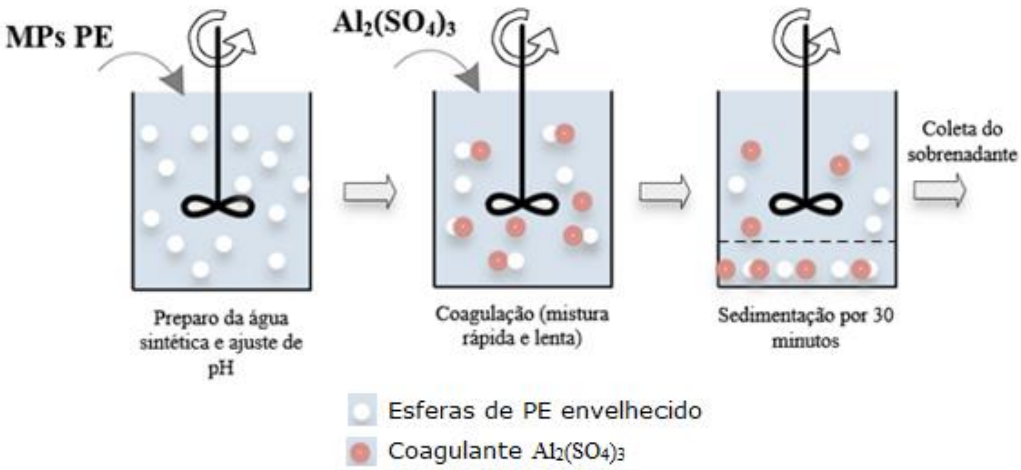
Jug	pH	Polyethylene concentration (mg/L)	Concentration of [$Al_2(SO_4)_3$] (mg/L) – 0,1%
1	4,0	400	2,50
2	4,0	400	6,00
3	6,0	400	2,50
4	6,0	400	6,00
5	5,0	400	4,25
6	5,0	400	4,25

Source: Prepared by the authors (2024)

A Figure 2 apresenta o esquema da realização da coagulação no Jar Test.

Figure 2

Schematic representation of coagulation test in laboratory



Source: The authors (2024), adapted from Oliveira (2023)

3.3 COAGULATION OF PE MICROSPHERES IN THE PRESENCE OF LAS

Once the optimal coagulation conditions of the aged PE in relation to the pH and concentration of aluminum sulfate in the absence of LAS were identified, more batches were performed in the Test Jar to evaluate the influence of the surfactant on the coagulation of the polyethylene spheres. To this end, the microplastic suspension has been prepared as described in section 3.2.1 and the LAS has been added in concentrations ranging from 20 to 300 mg L-1. These values include the ranges of typical domestic sewage concentrations up to concentrations found in industrial effluents (Oliveira, 2023 apud Liwarska-Bizukojc; Bizukojc, 2005; Terechova et al., 2014).

Three batches were performed, the coagulant concentrations and pH values were adjusted according to the optimal conditions obtained from the described in item 3.2.3 and the calculation of the removal efficiency of PE in the presence of the initial and final LAS was determined according to equation 1.

3.4 EXPERIMENTAL ANALYSIS

To evaluate the effect of the surfactant LAS on the coagulation of the aged PE, an analytical method was used by varying the turbidity values. Skaf et al. (2020) and Oliveira (2023) observed that this is a relevant parameter to indicate the amount of PM suspended particles.

To determine the removal efficiency of PE, the nephelometric turbidity unit (NTU) was analyzed before and after testing by means of equation 1.

$$E = \frac{C_O - C_F}{C_O} \times 100 \qquad (1)$$

Where:

E is the removal efficiency;
C_O is an initial measurement of NTU;
C_F is the final measurement of NTU.

4 RESULTS AND DISCUSSIONS

The mean of the tests performed in the absence of the surfactant are presented in Table 2.

Table 2

Average of test results for determination of optimal coagulation conditions

Jars	$(Al_2SO_4)_3$ (mg/L)	pH average initial	Turbidity average initial	pH average end	Turbidity Average end	σ - Turbidity	Removal Efficiency (%)	σ - Efficiency
1	2,50	4,0	9,43	4,23	0,60	0,08	93,58	0,80
2	6,00	4,0	6,78	4,22	0,27	0,08	95,66	1,66
3	2,50	6,0	13,69	6,07	1,14	0,37	91,77	1,99
4	6,00	6,0	12,22	5,87	0,78	0,32	93,52	2,83
5 e 6	4,25	5,0	10,01	4,84	0,31	0,29	97,07	1,67

Source: Prepared by the authors (2024)

Ion attraction forces, together with pH, are determinants in coagulation/flocculation treatment, since the formation of chemical flakes depends on the destabilization of such forces (Li; Dagnew; Ray, 2022). Due to the susceptibility of water traceability tests to pH, it was corrected before the addition of aluminum sulfate and calibrated after the addition of aluminum sulfate in order to avoid the formation of the Al (OH)3 precipitate.

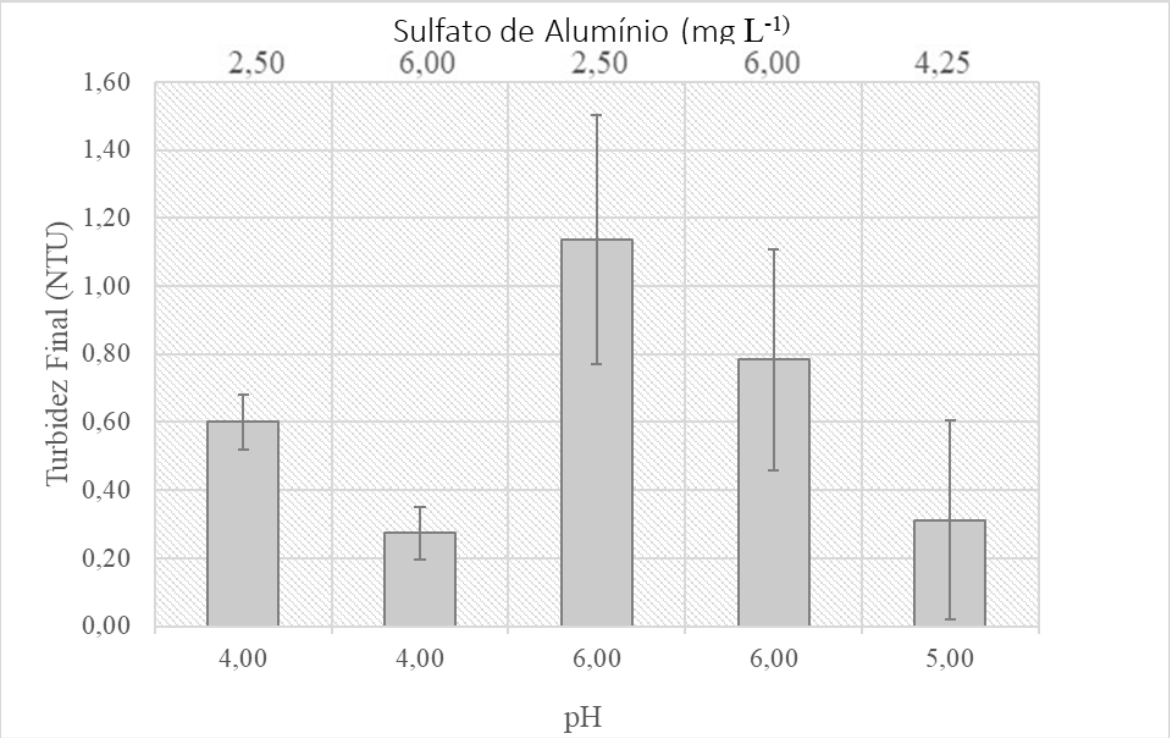
Thus, after the coagulant mixture, pH variations were observed under different conditions. Libanium (2010) points out that alterations of such nature are common due to the acid character of aluminum sulfate, which when released into water forms bonds with oxygen atoms, releasing H+ ions, leading to a decrease in pH. However, this phenomenon is not commonly observed when the pH is close to 4.

Analyzing the results, from the mean value in each jar, what presented the lowest efficiency was the combination of pH 6 and $(Al_2(SO_4)_3)$ of 2.50 mg/L with an average of 91.77% turbidity removal and standard deviation of 1.99. On the other hand, with pH of 5.0 and concentration of aluminum sulfate of 4.25 mg/L, removal efficiency of 97.07% was achieved, with average residual turbidity of 0.29 NTU.

The values of turbidity found (Figure 3) are at their highest in final turbidity bands lower than 1.0 NTU, results also found by Skaf et al. (2020) and Oliveira (2023), supporting the calculated removal efficiencies. As evidenced in the studies of Oliveira (2023), Zhang et al (2020), Ma et al. (2019), who also used aluminum salt coagulants, showed good performance when removing microplastics in aqueous media, in addition, Phokopova et al. also showed the influence of pH variation in different concentrations of aluminum sulfate dosing, reinforcing what this study presents.

Figure 3

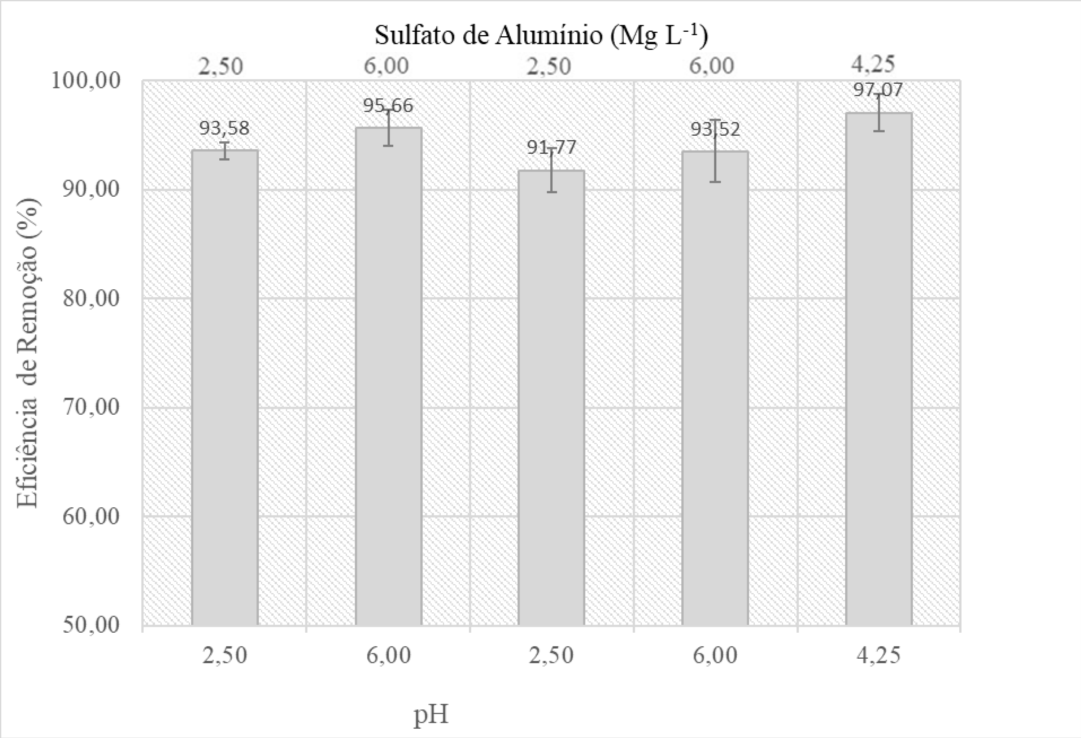
Residual turbidity of coagulation assays in the absence of AML



Source: The authors (2024)

Figure 4

MP removal efficiency in the absence of LAS



Source: The authors (2024)

In the absence of LAS (Figure 4), turbidity removal efficiencies are influenced by the combination of pH range and coagulant dosing. In this scenario, the mean value of turbidity removal was 94.79%, according to results presented by Zhang and collaborators (2020) and Oliveira (2023).

After obtaining the optimal coagulant and pH concentrations that showed the best response in the coagulation assays, they were used for all ASL assays. Table 3 presents the input parameters and results obtained in Jar Test.

Table 3

Results of clotting tests in the presence of LAS

1ª Batch									
Jug	**$(Al_2SO_4)_3$ (mg/L)**	**LAS (mL)**	**Turbidity initial**	**pH initial**	**Temp. initial**	**Turbidity final**	**pH final**	**Temp. final**	**Removal Efficiency (%)**
1	4,25	20	6,48	5,10	23,30	0,86	4,10	22,50	86,73
2	4,25	80	31,00	4,90	22,90	2,05	4,60	21,90	93,39
3	4,25	140	4,80	5,10	23,10	3,01	4,80	22,00	37,29
4	4,25	200	7,45	4,70	22,90	1,62	5,10	21,80	78,26
5	4,25	260	8,46	5,10	23,10	2,18	5,10	21,20	74,23
6	4,25	300	57,80	5,00	22,50	2,03	5,20	21,90	96,49
2ª Batch									

Jug	$(Al_2SO_4)_3$ (mg/L)	LAS (mL)	Turbidity initial	pH initial	Temp. initial	Turbidity final	pH final	Temp. final	Removal Efficiency (%)
1	4,25	20	3,44	5,20	26,10	0,54	4,20	23,70	84,30
2	4,25	80	18,20	5,20	25,90	1,76	4,40	23,10	90,33
3	4,25	140	43,00	5,10	25,20	3,21	4,10	23,10	92,53
4	4,25	200	2,83	5,20	24,90	1,54	4,80	22,80	45,58
5	4,25	260	8,99	5,20	24,70	2,02	5,00	23,10	77,53
6	4,25	300	7,55	5,20	24,10	0,71	5,10	22,90	90,60
3ª Batelada									
Jug	**$(Al_2SO_4)_3$ (mg/L)**	**LAS (mL)**	**Turbidity initial**	**pH initial**	**Temp. initial**	**Turbidity final**	**pH final**	**Temp. final**	**Removal Efficiency (%)**
1	4,25	20	18,70	5,10	24,70	0,54	4,40	23,60	97,11
2	4,25	80	4,73	5,00	24,60	2,91	4,40	23,40	38,48
3	4,25	140	3,52	5,00	24,20	2,16	4,70	22,70	38,64
4	4,25	200	4,74	5,00	24,00	1,29	5,00	22,60	72,78
5	4,25	260	11,20	5,00	23,70	1,20	4,90	22,90	89,29
6	4,25	300	32,30	5,10	23,50	2,12	5,00	22,70	93,44

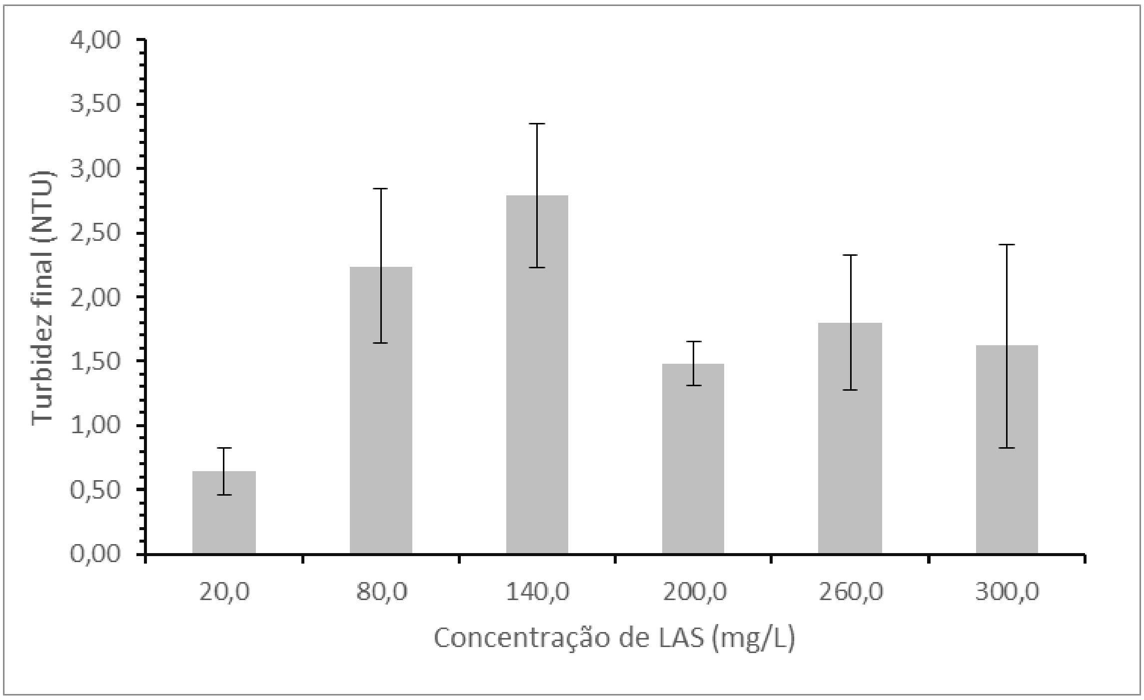
Source: Prepared by the authors (2024)

Figure 5 shows the variation in turbidity caused by the effect of LAS on the coagulation of polyethylene microplastics. In summary, a progressive increase in final turbidity is observed as the surfactant concentration increases. There was a minimum increase of 0.4 NTU and maximum of 23.84 NTU compared to the scenario where the surfactant is absent.

It is possible to associate such influence with the anionic characteristic of LAS, due to the ionization of the sulphonic group (Li; Dagnew; Ray, 2022), being adsorbed on the surface of the polyethylene spheres, causing a re-stabilization of the already coagulated PE particles.

Figure 5

Variation of turbidity as a function of surfactant concentration



Source: The authors (2024)

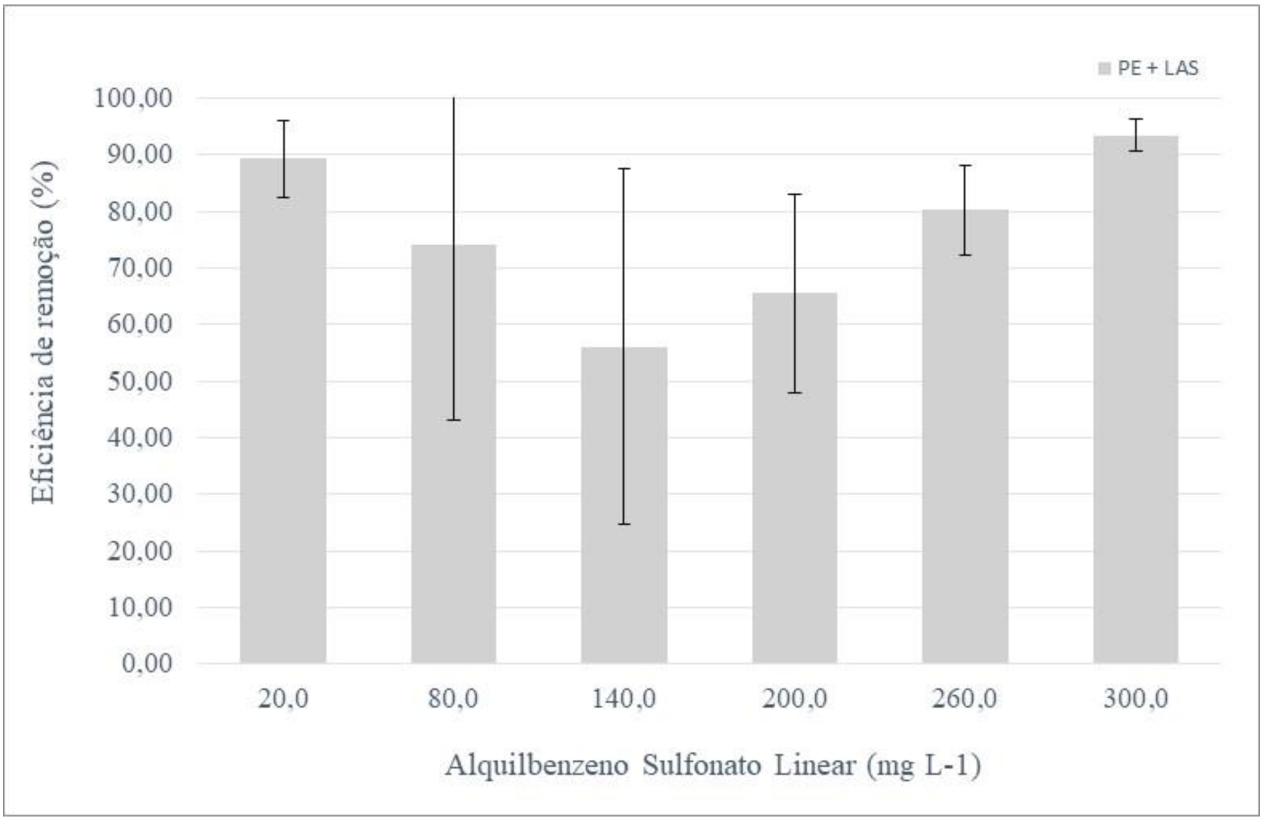
Recent studies, such as that of Xia and collaborators (2019) point to the "stealth" effect of surfactants, which can result in an apparent decrease in removal efficiency by coagulation and possibly increase the amount released up to tens of times in effluent. In addition, due to the properties of MPs, they can easily adsorb other pollutants, especially in aqueous media, as a function of surface hydrophobia. Therefore, in the presence of substances such as surfactants, it is reasonable to expect the occurrence of disturbances that may result in a substantial decrease in the coagulation of MPs (XIA et al., 2020), given that surfactants are amphilic in nature, interacting with both hydrophobic and hydrophilic contaminants (Olivera, 2023).

Figure 6 shows an initial drop in removal efficiency, possibly due to increased repulsion forces caused by interaction of surfactant loads with the surface of microplastics. However, from the concentration of

140 mg/L is an increase in removal efficiency, possibly associated with chemical bridging due to the nature of surfactants. The negatively charged hydrophilic head is attracted to the coagulant ions, while the hydrophobic tail is normally attracted to the hydrophobic surfaces of the suspended particles, which allows the surfactant molecules to form bridges between adjacent particles within the coagulated structure.

Figura 6

MP removal efficiencies in the presence of LAS



Note: concentration (Al2SO4)3 = 4,25 mg L-1; pH value = 5,00
Source: The authors (2024)

In the light of the above, a significant drop in removal efficiency can be seen, in particular in the intermediate dosing values of the surfactant - between 80 and 200 mg/L - with an average value of 76.50% of removal efficiency of the microplastic when it occurs jointly with the surfactant.

This phenomenon can be associated with the creation of agglomerates composed of polyethylene (PE) particles coated by monomers and the presence of Al (OH)3 chemical flakes to a lesser extent (Oliveira, 2023). It should be noted that this work has been conducted with coagulant concentrations and pH levels that are outside the typical ranges for the formation of chemical precipitates. In this case, when the microplastic has its surface covered, the process of destabilizing the surface electrical forces does not occur, jeopardizing the formation of flakes.

5 CONCLUSIONS

In this study, the evaluation of the chemical coagulation process from aluminum sulfate to remove microplastic in an aqueous medium proved to be efficient, since the most favorable conditions for the removal of PE MPs were obtained. From this, it was possible to realize that pH values close to 5.0 combined with concentrations of aluminum sulfate close to 4.25 mg/L presented the best removal efficiencies when comparing the turbidity parameter.

On the other hand, the presence of the surfactant linear alkylbenzo sulfonate (LAS) affected the aggregation and sedimentation processes of the microspheres, which is reflected in higher values of turbidity compared to the tests carried out in the absence of such substances. When the MPs coexist with the surfactants, the mean value for the removal of turbidity varied from 94.79% to 76.50% due to the interaction of the polyethylene spheres with the surfactant. The characteristics of these compounds alter the surfaces and characteristics of MPs, therefore, it can be inferred that surfactants have the capacity to stealthily generate microplastics in water and can trigger effects that lead to a drop in the ability to remove these and other pollutants in water treatment systems for human supply, thus necessitating consolidated methodologies when seeking to remove MPs by coagulation especially in the presence of surfactant substances.

The authors suggest that more tests are carried out to verify the variation of the results, and tests can be carried out by varying the concentration of the micro-plastic in suspension.

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