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Chemical Coagulation Applied for the Removal of Polyethylene and Expanded Polystyrene Microplastics

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ABSTRACT

Microplastics are emerging pollutants, formed through weathering, with sizes equal to or smaller than 5 mm. They can reach surface and groundwater sources, as well as oceans and seas through natural pathways or from the discharge of liquid effluents, causing immeasurable effects on human beings. This study aimed to evaluate the optimal conditions for the removal of polyethylene (PE) and expanded polystyrene (EPS) microplastics through coagulation and flocculation processes using aluminum sulfate. To achieve this goal, two 2^2 full factorial designs were employed, including two replicates at the central points. The sizes of the microplastics were fixed at 0.6 mm and 0.9 mm for PE and EPS, respectively. The selected independent variables were $Al_2(SO_4)_3$ and pH. The experiments were conducted considering rapid mixing parameters (400 rpm for 1 min), slow mixing (100 rpm for 15 min), and sedimentation (30 min), with a velocity of 0.1 $cm \cdot min^{-1}$ in the Jar Test. Turbidity determination was applied to quantify the remaining microplastics. Consequently, it was observed that the highest efficiency occurred for PE microplastics at 4.25 $mg \cdot L^{-1}$ of $Al_2(SO_4)_3$ and pH 5, and for EPS microplastics at 6.00 $mg \cdot L^{-1}$ of $Al_2(SO_4)_3$ and pH 4, resulting in removal rates of 96.81% and 96.30% and turbidity levels of 0.38 and 0.50 NTU, respectively. The removal efficiencies of microplastics were similar, with a decrease at pH 6 for both, as low ionic strength prevents the release of H^+ ions.

Keywords: microplastics, coagulation, water pollution.

INTRODUCTION

Plastics are materials formed from macromolecules known as polymers, from the Greek word "poly" meaning many. They consist of polymeric chains, constituting organic compounds composed of hydrogen and carbon. In their manufacturing, various additives are employed to protect these chains, preventing breakage due to irradiation or weathering, while also enhancing their ductility (Olivatto et al., 2019; Lee et al., 2020).

The characteristics and applications of each plastic polymer vary based on their molecular weight and chain structure–larger molecular weight corresponds to longer polymer chains. The polymerization process takes place under specific pressure, temperature, and catalysis conditions, resulting in two distinct categories: thermoplastics and thermosets (Olivatto et al., 2019; Galloway, 2015). Thermoplastic polymers exhibit linear or branched molecular structures and are heat-sensitive, becoming liquid or viscous upon heating, enabling easy recycling. Thermosetting plastics, on the other hand, possess cross-linked reticulated structures, retaining rigidity at elevated temperatures (Olivatto et al., 2019; Galloway, 2015). It is worth noting that while not all macromolecules are polymers, all polymers are macromolecules–comprising segments of smaller units known as monomers (Olivatto et al., 2019).

As a result of their convenience and durability, plastics have been employed in various utensils, including tires, synthetic fabrics, bags, and packaging, among others. Given their applicability across diverse manufacturing sectors, humans have become reliant on this material for numerous activities (Melchior, 2019). However, the lack of concrete public policies has led to improper plastic disposal, causing environmental harm.

Issues such as choking, entanglement, digestive tract obstruction, and reproductive impairment in animals, as well as damage to maritime equipment and release of toxic gases during combustion, have become prevalent. Improper plastic disposal is a leading cause of landfill saturation and contributes to drainage system blockages, resulting in floods and environmental damage, as well as hindering water and wastewater treatment efficiency.

Numerous plastic polymers exist in the environment, with certain types being more concentrated due to increased supply and productivity in manufacturing. These include polyethylene (PE), polypropylene (PP), polystyrene (PS), expanded polystyrene (EPS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC) (Pyra et al., 2020).

Microplastics (MPs) are particles smaller than 5 mm, formed through the mechanical breakdown of plastics, resulting from the friction of seawater, rainwater, and even wind. These emerging pollutants can reach surface and groundwater sources, oceans, and seas through natural pathways or liquid effluent discharge, persisting in the environment and enduring weathering for years (Thompson et al., 2004; Barboza et al., 2015; Kokalj et al., 2017; Neto et al., 2019). They can adsorb organic compounds, heavy metals, and highly toxic substances on their surfaces (Ma et al., 2019; Wei et al., 2020; Zhang et al., 2021).

Referred to as emerging pollutants (Barboza; Gimenez, 2015), microplastics can reach surface and groundwater sources, oceans, and seas via natural pathways or liquid effluent discharges (Neto et al., 2019). Due to their physical and chemical stability, they persist in the environment, enduring weathering for years (Kokalj et al., 2018), and can act as contaminant carriers, adsorbing persistent organic pollutants (POPs), heavy metals, and other toxic substances on their surfaces (Mizukawa et al., 2013), posing risks to aquatic environments (Silva-Cavalcanti et al., 2016) and human health (Amanto-Lourenço et al., 2021).

Microplastics (MPs) are primarily found in wastewater treatment plants (Murphy et al., 2016), emphasizing the importance of monitoring and effective public policies to reduce contamination. Due to their small size, aquatic animals readily ingest them (Li et al., 2015), yet the toxicity present on MP surfaces can affect aquatic organisms (Cole et al., 2013), impair reproductive growth (Coppock et al., 2017), reduce appetite, and alter species behavior (Pan et al., 2019). Through the food chain, MPs can reach human organs. However, the potential risks of MPs on human health require further investigation (Zhang et al., 2020; Ragusa et al., 2021).

As MPs are ingested by various species, they can reach human tissues and organs, potentially causing effects that are often challenging to quantify, stemming from the presence of persistent organic pollutants and adsorbed metals on MPs. Yet, assessing the potential health effects of microplastics and their additives remains complex, lacking conclusive evidence on their full impact on human health. It can be asserted that ingestion and inhalation are the pathways through which microplastics reach human organs (Galloway, 2015; Ma et al., 2016; Zhang et al., 2020).

In a study by Ragusa et al. (2021), microplastics were found in placentas of six patients, possibly releasing toxic contaminants present in the particles, potentially impacting pregnancy. Microplastics were also detected in lung samples from twenty autopsied human cadavers, constituting 87.5% of the samples, with an average size of 3.92 μm (Amanto-Lourenço et al., 2021). Zhang et al. (2021) monitored the consumption of beverages such as water, milk, and beer for eight days, subsequently collecting fecal samples from 26 young Beijing students, identifying PP, PET, and PS MPs (Zhang et al., 2021).

Despite the lack of exact knowledge regarding the potential human health risks posed by microplastics, Chang et al. (2019) conducted experiments on rodents for five weeks to identify the potential causes of microplastics in human organs. They found that the lipid metabolism in rat livers was disrupted, raising concerns about the potential effects in humans.

Hence, optimizing treatment technologies for water containing such pollutants holds significant importance today. Among these technologies, physicochemical treatment offers the advantage of technique mastery and availability of involved chemical products.

Coagulation and flocculation represent a physicochemical process enabling the separation of particles existing in suspensions, dissolved, and/or colloidal forms in water or effluent, originating from the liquid mass. This process can function independently or as a precursor to any treatment technology. Therefore, it must be maintained in optimal condition to prevent inefficiencies in subsequent units and enhance the overall process efficiency. Achieving effective treatment from a technical standpoint often involves undergoing treatability studies, employing the Jar Test apparatus to determine the appropriate coagulant dosage, agitation speed, and sedimentation time.

Coagulant agents are employed to destabilize the particles present in the liquid. This process results in two phenomena: hydrolysis and the transport of hydrolyzed species to facilitate contact with the particles. This step is termed rapid mixing and generally occurs within second intervals. Subsequently, there is a reduction in mixing speed, referred to as slow mixing, lasting 15 to 20 minutes, leading to the formation of larger aggregates. This marks the transition to the flocculation stage, where these aggregates are subsequently separated through the action of gravity.

Flocculation represents a physical process heavily reliant on coagulation efficiency. Through flocculation, it is possible to diminish repulsive forces, enabling collisions between the particles previously destabilized by coagulants. This aims to form flocs that are subsequently removed through sedimentation.

Three phenomena can occur during the transport of particles for floc formation: Brownian motion (perikinetic flocculation), differences in fluid flow current velocities (orthokinetic flocculation), and distinct sedimentation velocities of flocs (differential sedimentation).

Brownian motion involves random movement that brings particles into contact. In this phase, destabilized colloidal particles come into contact and aggregate, forming flocs. Orthokinetic flocculation occurs as an extension of Brownian motion, involving the introduction of external energy that aids in floc formation, taking into account the velocity gradient and time. Differential sedimentation involves variations in volume and density among flocs, leading to different sedimentation velocities. At this point, the descending motion causes particles to form heavier flocs due to prolonged contact, lasting at least 30 min.

Chemical coagulation represents a specific technique for the removal of suspended and colloidal particles in water, thereby serving as an effective method for microplastic (MP) removal in wastewater treatment plants–a significant MP source (MURPHY et al., 2016). MP removal efficiencies above 80.0% have been observed through chemical coagulation (XUE et al., 2021).

Considering the presence of microplastics in aquatic environments and their adverse effects on ecosystems, the purpose of this study was to evaluate the optimal conditions for the removal of polyethylene (PE) and expanded polystyrene (EPS) microplastics through coagulation and flocculation processes, utilizing aluminum sulfate. It is essential to emphasize that in the context of chemical coagulation, experimental planning enables better choices for pH values and coagulant concentrations in pollutant removal.

MATERIALS AND METHODS

The PE microplastics used were Bianquimica brand microspheres, sized at 0.6 mm. The EPS (expanded polystyrene) microplastics were obtained from commercial styrofoam beads, ranging in sizes from 1 to 3 mm. To achieve sizes smaller than 1 mm, they were fragmented using a crusher for 15 min. Stainless steel sieves with top and bottom lids were then employed to identify the fragmented sizes. The average size of 0.9 mm ($0.6 < d < 1.19$ mm) was determined based on the greater mass retained by the sieves. Each EPS fraction captured by the sieves was separated, stored in glass beakers, and weighed using a semi-analytical balance.

The reagents used in the study were of analytical grade: $Al_2(SO_4)_3$ (Perfyl Tech Química), HCl (Dinâmica Química Contemporânea), NaOH (Cinética Reagentes e Soluções). The defined concentration for the aluminum sulfate stock solution was 100 $mg \cdot L^{-1}$, limited by the solubility of the analytical reagent. Solutions of 1 $mol \cdot L^{-1}$ HCl and 1 $mol \cdot L^{-1}$ NaOH were used for pH adjustment. The concentration of MPs (microplastics) was set at 400 $mg \cdot L^{-1}$, as Zhou et al. (2021) evaluated concentrations ranging from 200 to 800 $mg \cdot L^{-1}$ and found no significant discrepancy in removal efficiency.

To optimize the dosage of aluminum sulfate coagulant, an experimental design was conducted to identify the optimal variables and combinations for MP removal. Two full 2k factorial designs were applied, each including two repetitions at central points (pc) for error estimation, one for each type of microplastic (PE and EPS). The MP sizes were fixed at 0.6 mm and 0.9 mm for PE and

EPS, respectively. The selected independent variables were $Al_2(SO_4)_3$ concentrations of 2.50, 4.50, and 6.00 $mg \cdot L^{-1}$, and pH values of 4, 5, and 6. For the response variable, MP removal efficiency was assessed through turbidity analysis using a PoliControl AP2000 turbidimeter, as Lapointe et al. (2020) and Skaf et al. (2020) provided pertinent observations on turbidity as an indicator of suspended particle removal efficiency.

Following the determination of the process variables, the experimental matrix for PE and EPS was constructed, incorporating lower and upper levels, as well as central points for the selected variables, as presented in Table 1.

The experimental matrix for the Jar Test trials was established based on the predetermined levels of $Al_2(SO_4)_3$ concentrations and pH values, as depicted in Table 2. The matrix encompassed both the actual and encoded values utilized in the experiments.

The experiments were conducted utilizing a Jar Test apparatus (Policontrol Floc Control II) and laboratory-generated liquid effluent. The test parameters included rapid mixing (400 rpm for 1 min), slow mixing (100 rpm for 15 min), and sedimentation (30 min), with a settling velocity of 0.1 $cm \cdot min^{-1}$. Following the sedimentation period, a 50 mL sample was withdrawn from each jar using a syringe. Turbidity determination was employed for quantifying residual microplastics. It is noteworthy that, to ensure the reliability of the nephelometric method, disturbances to the systems were avoided during each sample collection.

RESULTS AND DISCUSSION

Through the 2k factorial scheme, the significance of the variables pH and aluminum sulfate ($mg \cdot L^{-1}$) in the coagulation of PE and EPS microplastics was identified, along with the combinations yielding optimal microplastic removal efficiency. Table 3 presents both coded and uncoded variable values, along with the obtained responses, as well as the coefficient of determination (R^2) for the respective microplastics.

On the basis of the obtained results, reduced models represented by Equations 1 and 2 were derived, describing the significant parameters ($p<0.1$). These models exhibited the R^2 values of 0.72415 and 0.92398 for PE and EPS microplastics, respectively. These R^2 values can also be expressed in percentage terms; the higher R^2 value (92.4%) was observed for EPS, indicating a strong alignment of the model with the system, i.e., how closely the data points adhere to the regression line. However, for PE microplastics, the R^2 value was 72.4%, suggesting a reasonable, yet comparatively lower fit to the experimental data.

$$PE = 94{,}14 - 3{,}50pH \tag{1}$$

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

The residual turbidity, quantified following the jar test, proved to be a viable metric for monitoring the efficiency of MP removal in coagulation

Table 1. Values of independent variables

Variables	Real levels		
	Lower level (-)	Upper level (+)	Central point (0)
$Al_2(SO_4)_3$ (mg L^{-1})	2.50	6.00	4.25
pH	4	6	5

Table 2. Independent variables

Test	Real values		Coded values	
	$Al_2(SO_4)_3$ (mg L^{-1}) (X1)	pH (X2)	$Al_2(SO_4)_3$ (mg L^{-1}) (X1)	pH (X2)
1	2.50	4.00	-1	-1
2	6.00	4.00	+1	-1
3	2.50	6.00	-1	+1
4	6.00	6.00	+1	+1
5	4.25	5.00	0	0
6	4.25	5.00	0	0

Table 3. Total factorial planning results 2^2 for removal of MP by coagulation

Test	Variables real values		Variables coded values		Removal efficiency results (%)	
	$Al_2(SO_4)_3$(mg L^{-1})	pH	$Al_2(SO_4)_3$(mg L^{-1})	pH	MPs PE	MPs EPS
1	2.50	4.00	-1	-1	96.26	93.33
2	6.00	4.00	+1	-1	96.53	96.30
3	2.50	6.00	-1	+1	89.23	87.56
4	6.00	6.00	+1	+1	89.57	89.62
5	4.25	5.00	0	0	96.47	90.08
6	4.25	5.00	0	0	96.81	90.08
				R^2	72.4%	92.4%

Table 4. Turbidity and pH values for PE e EPS microplastics before and after the jar test

Test	Initial turbidity (NTU)		Final turbidity (NTU)		Initial pH		Final pH	
	MPs PE	MPs EPS	MPs PE	MPs EPS	MPs PE	MPs EPS	MPs PE	MPs EPS
1	10.70	12.60	0.40	0.84	4.20	4.10	5.80	4.10
2	12.40	13.50	0.43	0.50	4.20	3.90	4.70	3.90
3	11.70	12.30	1.26	1.53	5.70	5.90	5.40	5.90
4	11.70	13.00	1.22	1.35	5.80	5.80	5.50	5.80
5	11.60	12.60	0.41	1.25	5.30	4.80	5.50	4.80
6	11.90	12.10	0.38	1.20	5.20	5.00	5.40	5.00

experiments, as corroborated by the findings from Skaf et al. (2020).

In Table 4, turbidity values in NTU alongside pH are presented. It is emphasized that a concentration of 400 mg·L^{-1} was considered for both MPs.

In the corresponding pH range, an increase in suspended particles of PE MPs expressed as turbidity is evident – from 0.40 to 1.26 NTU as pH increases from 4.20 to 5.70 and subsequently from 0.43 to 1.22 NTU within the same pH range, 4.20 and 5.80, respectively. The same trend was observed for EPS MPs, where turbidity increased from 0.84 to 1.53 NTU and then from 0.50 to 1.35 NTU. This behavior could be attributed to low ionic strength. preventing strong cation-oxygen bonding, thus restraining the release of H^+ ions, allowing the particles responsible for turbidity to remain suspended due to decreased electrostatic repulsion (Sembiring et al. 2021). Hence, charge adsorption and neutralization may be the governing mechanism within these pH ranges, coinciding with coagulant dosing.

CONCLUSIONS

The presence of PE and EPS constitutes a substantial proportion of MPs in wastewater treatment plants and terrestrial ecosystems. Mitigation of these micropollutants can be achieved through conventional treatment techniques, such as coagulation and flocculation, with primary use of aluminum sulfate as the coagulant. The coagulation process, coupled with experimental design, provides optimal conditions for the removal of 0.6 mm-sized PE MPs and 0.9 mm-sized EPS MPs. It was observed that the concentrations exceeding 4.25 mg·L^{-1} of coagulant and pH values outside the optimal chemical precipitation range could yield improved removal responses.

This study concludes that through a full 2k factorial design the variables $Al_2(SO_4)_3$ and pH exert influence on the removal of PE and EPS MPs. The coagulation and flocculation technique, applied with experimental design tools, yields reasonable results, particularly given that the classified polymers in the polymerization process are condensation polymers, soluble primarily in organic compounds. Furthermore, despite turbidity being a sensitive and selective method, it effectively assesses MP removal. However, further research into aluminum sulfate coagulant concentrations is recommended, as water treatment plants can significantly contribute to MP concentrations in water.

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