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REMOVAL OF MICROPLASTICS FROM NATURAL AND WASTEWATER MATRICES BY COAGULATION AND FLOCCULATON: EFFECT OF MICROSAND AND COAGULANT TYPE

Research paper

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Abstract: Microplastics are emerging pollutants with widespread occurrence in both natural and wastewater environments, posing ecological and health risks. This study investigated the removal of powdered polyethylene (PE, 500 µm) and polyvinyl chloride (PVC, 171–279 µm) from Danube River water and municipal wastewater effluent using coagulation–flocculation processes. Ferric chloride ($FeCl_3$) and polyaluminum chloride (PACl) were applied as coagulants, and the effect of microsand addition (10 mg/L) on removal efficiency was evaluated. Jar test experiments were conducted under controlled laboratory conditions with optimal coagulant doses ranging from 20–220 mg/L for $FeCl_3$ and 10–50 mg/L for PACl. Results showed that $FeCl_3$ demonstrated broad applicability and stable performance across both water matrices, achieving high removal efficiencies for PE and PVC. PACl achieved comparable or higher efficiencies at lower doses, particularly in the presence of microsand. The addition of microsand selectively enhanced microplastic removal, improving PE sedimentation in both matrices, while its effect on PVC was limited due to higher density and weaker interactions with flocs. Optimal removal depended on the specific properties of the microplastics, the coagulant type, and the characteristics of the water matrix. These findings highlight the potential of coagulation–flocculation, with or without microsand, as an effective strategy for microplastic removal from diverse water matrices. They also emphasize the importance of process optimization considering pollutant characteristics, coagulant selection, and auxiliary agents, providing guidance for sustainable water treatment applications.
Key words: microplastics, water treatment, coagulation and flocculation, microsand

INTRODUCTION

One of the most significant challenges in environmental protection is plastic waste pollution. Due to its characteristics such as low cost, light weight, durability, and resistance to water and corrosion, plastics are widely used for commercial, industrial, and general purposes (Andrady, 2011). However, these same properties also contribute to their slow degradation. The increasing production of plastics, coupled with inadequate waste management, has resulted in the rapid accumulation of plastic waste in terrestrial and aquatic ecosystems (Bames et al., 2009; Jambeck et al., 2015). Over time, through processes such as photo-oxidative and thermo-oxidative degradation, plastics break down into smaller particles known as microplastics. Microplastics originate from various sources, including the degradation of plastic waste, the release of synthetic fibers during textile washing, plastic microbeads from personal care products, and industrial plastic pellets. Most microplastics eventually end up in the oceans, either via rivers or through direct discharge. Major sources of microplastics also include plastic products such as bags, bottles, medical devices, adhesives, and electronics (Mitrano and Wohlleben, 2020).
Wastewater treatment plants (WWTPs) can also contribute to the release of microplastics into the environment, despite retaining a certain portion of plastic fragments in oxidation basins or sewage sludge (Browne et al., 2011). Nevertheless, significant amounts of microplastics still enter aquatic systems from wastewater treatment plants consisting of primary and secondary treatment, which process water from both urban and industrial sources, thereby concentrating

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and filtering microplastics that arrive through stormwater and urban drainage. Although some studies indicate that WWTPs can remove microplastics with efficiencies of up to 99% (Lares et al., 2018; Gan et al., 2023), the fraction that is not removed is discharged into the environment.

Existing uncertainties and the limited understanding of this type of pollution highlight the need for further research, the definition of clear criteria, the improvement of existing requirements, and the development of sustainable alternatives in order to reduce microplastic pollution in the environment (Belzagui et al., 2022).

Urgent and efficient methods for removing microplastics from water are needed. Microplastics enter WWTPs from multiple sources. The most significant sources are municipal wastewater, which contains residues from personal care products, as well as wastewater generated during the production and processing of plastic materials.

It is essential to develop efficient methods for removing microplastics from water and to enable monitoring of their concentrations. Although microplastic pollution has increasingly become the focus of research, a comprehensive analysis of physical, chemical, and biological methods for microplastic removal is still lacking. This indicates the necessity of improving wastewater treatment technologies to reduce their environmental impact (Ali et al., 2021; Moteallemi et al., 2024).

Coagulation is a chemical process in which a coagulant acts on wastewater to convert dissolved pollutants into particles, which are then removed by sedimentation (Li et al., 2024). Flocculation is a physical method that is typically applied after coagulation. The combination of coagulation and flocculation has become a successful physico-chemical strategy for removing microplastics from water (Peydayesh et al., 2021). The presence of microplastics in wastewater requires certain modifications in treatment processes. Conventional methods often struggle to remove these pollutants, making it necessary to adapt treatment procedures (e.g., by adding components that can enhance the process, such as activated carbon, microsand, or similar materials). The main goal of coagulation and flocculation processes is to improve the efficiency of microplastic removal by enabling particle aggregation, followed by sedimentation or flotation (Chazovachii et al., 2021). During coagulation, particle destabilization occurs through the addition of coagulants, which neutralize their electrostatic charges. Coagulants remove the surface charges of particles, and this charge neutralization allows them to approach each other, facilitating aggregation and subsequent removal.

Studies have shown that through multiple stages of water treatment, up to 88% of microplastics can be removed, with coagulation and sedimentation contributing the most to their removal (Pivokonsky et al., 2020). Various other studies also confirm that coagulation can almost completely eliminate microplastics from water (Skaf et al., 2020; Xu et al., 2022). For this reason, coagulation is considered a sustainable technology for the complete removal of microplastics from water, and in recent years it has gained attention due to its simplicity of application, cost-effectiveness, and energy efficiency. Aluminum- and iron-based salts are most commonly used, along with coagulants such as polyacrylamide (PAM), which facilitate the aggregation of fine particles into larger groups for easier removal (Ojha et al., 2024).

Based on the above, it is necessary to conduct research on the efficiency of microplastic removal from water, with a particular focus on assessing performance in the presence of factors that influence treatment efficiency. Jar tests are used to simulate the process of floc formation during water treatment by coagulation and flocculation. In addition to their use for research purposes, these tests are essential for optimizing operational parameters in existing water treatment plants and for designing new systems.

Therefore, the aim of this study was to examine the efficiency of microplastic removal from water using coagulation and flocculation, with and without the addition of microsand.

MATERIAL AND METHODS

Coagulation experiment

The materials used in the experiments were powdered polyethylene (PE, particle size 500 μm) and powdered polyvinyl chloride (PVC, particle size 171–279 μm). Their removal by coagulation was tested in Danube River water and in the effluent of municipal wastewater from a wastewater treatment plant. The materials used (PE and PVC) are shown in Fig. 1.

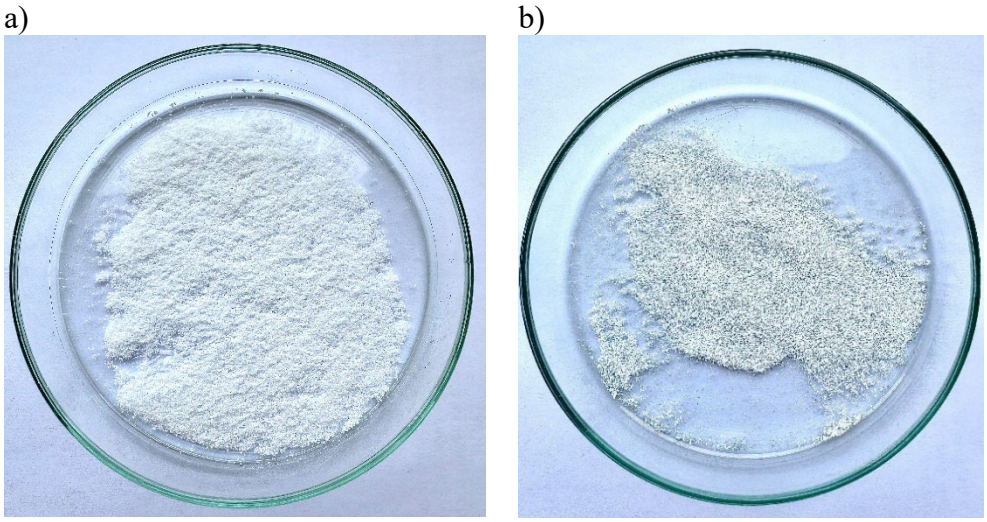


Fig. 1. *Materials used in experiment: a) PE and b) PVC*

In the experiments, ferric chloride ($FeCl_3$) and polyaluminum chloride (PACl) were applied as coagulants. Coagulation experiments were performed on a Jar test apparatus (VELP Scientifica) under laboratory conditions, at mixing speeds ranging from 10 to 300 rpm. All experiments were conducted in triplicate. Prior to the Jar test, 50 mg of plastic material was added to 0.5 L of the water matrix and left to homogenize for 24 h without mixing, before the coagulation/flocculation experiments. The coagulant concentrations used in the experiments ranged from 20 to 220 mg/L (20, 40, 60, 100, 140, 180, and 220 mg $FeCl_3$/L) for $FeCl_3$ and from 10 to 50 mg/L (10, 20, 30, 40, 50 mg Al/L) for PACl. Coagulation was performed by adding the coagulant at a mixing speed of 120 rpm for 2 min, followed by flocculant addition and continued mixing at 45 rpm for 30 min. Sedimentation was carried out for 30 min. After settling, the samples were filtered through a cellulose nitrate membrane filter with a pore size of 0.45 μm using a vacuum filtration device. The filter papers were dried in Petri dishes at room temperature for 24 h. After 24 h, the masses of the filters after coagulation, as well as the masses of the filters before filtration, were measured. Based on these data, further calculations were performed, and the microplastic removal efficiency from water was determined. Optimal coagulant doses were selected and applied in subsequent experiments.

To improve coagulation efficiency and increase the removal rate of microplastics from water matrices, treatment optimization was carried out by adding microsand as an auxiliary agent. Microsand acts as a physical support during floc formation, contributing to their stability, higher density, and faster sedimentation behavior, all of which enhance microplastic removal from solution (Su et al., 2013). In this study, microsand was used at a concentration of 10 mg/L. All experiments were performed at the previously determined optimal coagulant doses, allowing the evaluation of the effect of microsand independently from the basic coagulation parameters. This approach provided insights into the synergistic mechanisms between coagulants and microsand, as well as into the potential of this combination for application in real water treatment conditions.

RESULTS AND DISCUSSION

In this chapter, the results of the study on the effect of microsand addition on the coagulation process are presented, using the optimal doses of $FeCl_3$ and PACl coagulants. These results are discussed in more detail for each tested material in the following sections. Microsand was applied at a concentration of 10 mg/L. Fig. 2 shows the removal efficiencies of the tested materials from Danube River water by coagulation and flocculation, using the optimal doses of $FeCl_3$: 100 mg/L for PE and 20 mg/L for PVC.

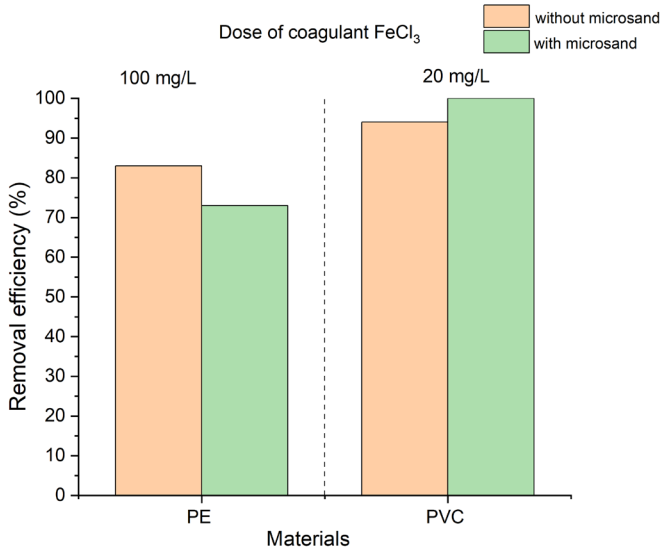


Fig. 2. *The effect of microsand addition on the efficiency of coagulation and flocculation in microplastic removal from Danube river water using $FeCl_3$ coagulant*

Fig. 2 also shows that, for effective removal of PE in the absence of microsand, a higher coagulant dose (100 mg/L) was required due to its low density and weak interaction with coagulation agents. In the presence of microsand, the removal efficiency of PE was similar (from 83% to 73%), which can be explained by possible competitive interactions between microsand and flocs, as well as the influence of interfering substances present in river water.
In contrast, the addition of microsand improved the removal of PVC from Danube river water, increasing efficiency from 94% to 100%, indicating that heavier and denser PVC particles interact more effectively with microsand in the sedimentation process. The high removal efficiency of PVC in the presence of microsand can primarily be attributed to its higher density compared to lighter polymers such as PE, which facilitates sedimentation when additional inert material is present.
The results shown in Fig. 2 confirm that under more complex conditions of a natural water matrix, the effect of microsand can be selective and dependent on the type of microplastic, as well as on the chemical composition and interfering substances in the water. The use of microsand is not always synergistic, especially when competition for interaction with flocs occurs, or when destabilization arises due to the presence of natural matter.
Fig. 3 presents the removal efficiencies of microplastics using the optimal doses of the PACl coagulant: 20 mg/L for PE and 30 mg/L for PVC.
It can be observed that the addition of microsand improved the removal of PE (82%) compared to the results without microsand (68%). In this case, a lower PACl dose (20 mg/L) was used, yet significantly higher efficiency was achieved, indicating the success of the process. In contrast, PVC showed lower removal efficiency (59%) compared to the efficiency obtained with PACl alone, without microsand addition, which was 88%.

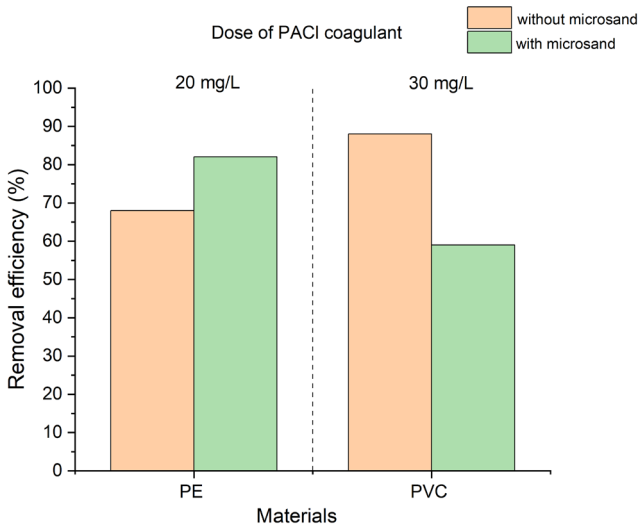


Fig. 3. *The effect of microsand addition on the efficiency of coagulation and flocculation in microplastic removal from Danube river water using PACl coagulant*

The results in Figures 2 and 3 indicate that the addition of microsand has a differentiated impact on the removal efficiency of different types of microplastics, depending on the type of coagulant and the composition of the water matrix. The best removal of PVC was achieved with $FeCl_3$ in the presence of microsand (Fig. 2), owing to its higher density, which favors sedimentation. On the other hand, PE was most effectively removed using PACl in the presence of microsand (Fig. 3), which can be attributed to its polymeric nature and greater ability to form stable flocs with this coagulant. The experimental results confirm that optimal treatment must be adapted to the specific properties of the pollutants and the chemical characteristics of the water matrix, with careful selection of coagulants and auxiliary agents.
Figures 4 and 5 show the removal efficiencies of the tested materials by coagulation from municipal wastewater effluent.

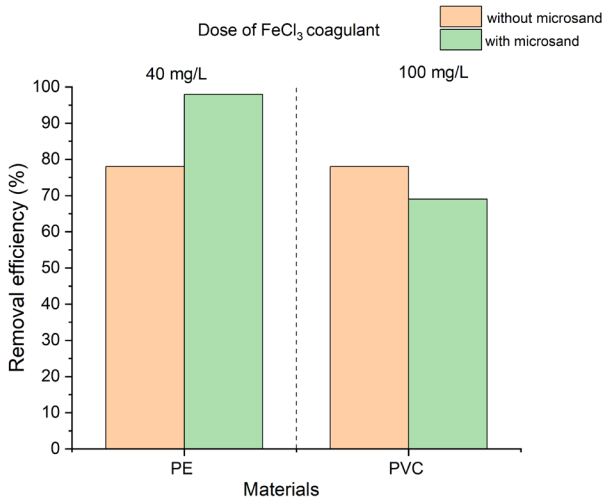


Fig. 4. *The effect of microsand addition on the efficiency of coagulation and flocculation in microplastic removal from municipal wastewater effluent using $FeCl_3$ coagulant*

Based on the results shown in Fig. 4, it can be concluded that the addition of microsand generally contributed to improving the removal efficiency of PE. Compared to the values obtained without microsand addition (78% for PE and 88% for PVC), a similar efficiency in PE removal efficiency is observed. These results indicate that microsand can play a significant role in enhancing flocculation and sedimentation of lighter materials, while for denser and less reactive materials, such as PVC, its contribution remains limited. Considering that PVC has a higher density compared to PE, it is assumed that the optimal $FeCl_3$ coagulant dose used in

this experiment (100 mg/L) was insufficient to form adequate flocs capable of incorporating PVC and microsand and promoting sedimentation. Instead, smaller or underdeveloped flocs remained suspended in the solution, reducing the efficiency of the process.
The results presented in Fig. 4 suggest that coagulation in the presence of microsand can depend on the specific properties of the microplastics, such as density and surface characteristics, as well as on the optimal coagulant dosing. Therefore, for materials like PVC, further experiments over a wider range of $FeCl_3$ doses would be necessary to determine the optimal combination for enhanced removal. These observations further emphasize the importance of fine-tuning coagulation conditions depending on the type of microplastic present in the water matrix.

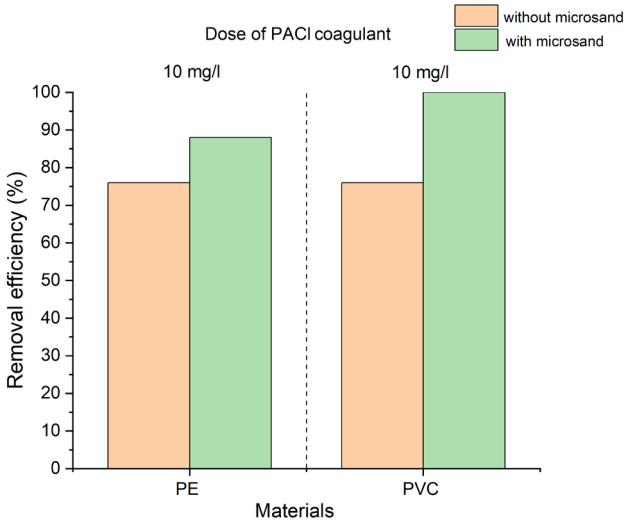


Fig. 5. *The effect of microsand addition on the efficiency of coagulation and flocculation in microplastic removal from municipal wastewater effluent using PACl coagulant*

The application of the PACl coagulant in the effluent of wastewater from a treatment plant (Fig.5) showed high microplastic removal efficiency at the applied optimal doses. Doses of 10 mg Al/L for PE and PVC proved sufficient to achieve significant particle destabilization and aggregation in the presence of organic matter typical for municipal wastewater effluent. The results presented in Figures 4 and 5 indicate that the addition of microsand can contribute to improving microplastic removal efficiency in municipal wastewater effluent, but its effect is selective and depends on the type of material, the applied coagulant, and the characteristics of the water matrix. As previously mentioned, the greatest contribution is observed for PE, whose removal is significantly enhanced due to its lower density and stronger interaction with microsand. PVC removal, due to its higher density and weaker interaction with flocs and microsand, was most effectively achieved through the application of the PACl coagulant.
The results obtained in this study confirm that the success of coagulation, with or without microsand, depends on a carefully optimized approach that considers the type of pollutants, the chemical and physical properties of microplastics and fibers, as well as the characteristics of the water matrix itself.

CONCLUSION

The results presented in this study indicate that $FeCl_3$ demonstrated broad applicability as a coagulant for microplastic removal from various water matrices, including Danube River water and municipal wastewater effluent from a treatment plant. Its efficiency under standard conditions, particularly in the presence of higher organic matter content, confirms its potential for use in real municipal wastewater treatment scenarios. Although some results showed that PACl can achieve higher efficiency at lower doses and under modified conditions (e.g., with the addition of microsand), $FeCl_3$ remains a coagulant that provides stable performance and consistent results, making it a reliable choice across different scenarios.

The addition of microsand had a selective but significant effect in certain cases. In Danube River water, microsand addition improved PE removal from 68% to 82% at a low PACl dose, while no significant changes were observed for PVC. A more pronounced effect of microsand addition was observed in municipal wastewater effluent, where PE removal reached 98%, confirming the effectiveness of coagulation in the presence of these microsand particles.
The results emphasize that coagulant selection must be based on the characteristics of the specific pollutants, the chemical properties of the water matrix, and the presence of additional agents such as microsand. An integrated approach that considers interactions between pollutants, the matrix, and coagulants is essential for optimizing treatment and developing efficient, sustainable technologies for the removal of micropollutants from water.

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