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Removal Effect of Coagulating Sedimentation Method on Polyethylene Microplastics in Water

Shasha LIU*, Qiongru ZHUANG, Hongji HUANG, Xiaodan LIN, Yue YANG, Jinghua WU

Guangdong Provincial Key Laboratory of Environmental Health and Land Resource, School of Environmental and Chemical Engineering, Zhaoqing University, Zhaoqing 526061, China

Abstract Microplastic is a new kind of pollutant. It exists widely in the aquatic environment and seriously endangers the aquatic ecosystem. In this study, the coagulating sedimentation method was used to remove microplastics in water. Polyethylene (PE) was selected as the representative of microplastics, polyferric sulfate (PFS), polyaluminum chloride (PAC) and aluminum sulfate (AS) were used as coagulant, and polyacrylamide (PAM) was used as coagulant aid to study the effects of pH, coagulant concentration and sedimentation time on the removal of PE by single and composite coagulant. The results showed that when the dosage of PFS was 0.5 g/L and pH was 5.0, the removal rate could reach 82.14%, which was better than PAC and AS, indicating that PFS had better coagulation and sedimentation performance for PE; the composite coagulant of PFS + PAC + AS (1 g/L + 0.2 g/L + 0.2 g/L, pH was 5.0) had the highest removal rate of PE, reaching 96.06%; the removal rate of PE increased with the increase in sedimentation time, but considering that the longer sedimentation time has less contribution to the improvement of removal rate, it is recommended that 4 h is appropriate.

Key words Microplastics, Coagulating sedimentation, Polyethylene (PE), Removal

1 Introduction

Because of low price, light weight and durability, plastics and their products are widely used in production and life, resulting in a large number of waste plastics into the water environment[1]. Under long-term weathering, erosion, wear, ultraviolet radiation, biological and human action, they will be broken into plastic particles with a particle size of less than 5 mm, which is called microplastics[2]. In addition, microparticles and beads in industrial raw materials, drug delivery, and personal care products are also sources of microplastics in the environment[3-4]. At present, microplastics have been detected in the global oceans[5-6], rivers[7-8], lakes[9] and other water environments, which can cause toxic effects on aquatic organisms[10] and pose a potential threat to human health through the food chain[11]. Therefore, the removal of microplastics in water environment is an urgent problem to be solved.

Coagulation has become one of the most effective methods to remove microplastics in water because of its high efficiency, simple operation and low cost[12-14]. Compared with rapid sand filtration, membrane bioreactor and disc filtration processes, the removal rate of microplastics by coagulation is higher, reaching 90%[15]. In this study, we used the coagulating sedimentation method to remove microplastics in water, selected polyethylene (PE) as the representative of microplastics, polyferric sulfate (PFS), polyaluminum chloride (PAC) and aluminum sulfate (AS) as coagulant, and polyacrylamide (PAM) as coagulant aid to study the effects of pH, coagulant concentration and sedimentation time on the removal of PE by single and composite coagulant, and determine the optimal removal conditions of PE, so as to provide a scientific basis for the remediation of micro-plastic pollution in water environment.

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* Corresponding author. Shasha LIU, PhD., research fields: remediation of microplastics pollution.

2 Materials and methods

2.1 Preparation of water sample In this experiment, microplastics polluted wastewater was artificially prepared to simulate the microplastic pollution. We weighed 50 mg of PE and put it into a beaker, added deionized water, fully mixed it, transferred it to a 1 L volumetric flask, and made the PE evenly distributed by ultrasound after constant volume, and finally obtained a PE solution with a concentration of 50 mg/L.

2.2 Coagulating sedimentation experiment First, we poured the well-mixed PE solution (400 mL) into a beaker, and added coagulant (including PAC, PFS and AS). Then, we used 0.1 mol/L HCl and 0.1 mol/L NaOH to adjust pH of the water sample, and added 250 mg/L polyacrylamide (PAM) to the water sample, and the water sample was stirred by a stirrer for coagulation experiment. The specific steps were as follows: stirred at high speed for 15 min (400 r/min), stirring at moderate speed for 10 min (200 r/min), and stirred at low speed for 5 min (100 r/min) in turn, and then placed for later use. Dried the filter paper in an oven (60 ℃) until constant weight, denoted as M_1 (g). Took the supernatant, added HCl to remove impurities, filtered and dried, and obtained the weight M_2 (g). The removal rate of PE was calculated using the following formula:

$$\text{Removal rate} = \frac{0.1-(M_2-M_1)}{0.1}\times 100\%$$

2.2.1 Single coagulant. In the PE polluted water sample, we separately added single PFS (0.5 g/L), single PAC (0.5 g/L) and single AS (0.5 g/L) to investigate the influence of different factors (pH, coagulant concentration and sedimentation time) on the PE coagulation effect, and determine the optimal conditions. Set the pH at 5.0, 6.0, 7.0, 8.0, and 9.0. The concentration of coagulant (PAC, PFS, and AS) was 0.0, 0.2, 0.5, and 1 g/L, respectively. The sedimentation time was 1, 4, and 12 h.

2.2.2 Composite coagulant. In the PE polluted water sample, PFS+PAC (0.5 g/L+0.2 g/L), PFS (0.5 g/L) + AS (0.2 g/L), PAC (0.2 g/L) + AS (0.2 g/L) and PFS (0.5 g/L) + PAC (0.2 g/L) + AS (0.2 g/L), pH was set as 5.0, 6.0, 7.0, 8.0 and 9.0, respectively. The sedimentation time was 1, 4 and 12 h, respectively, and the effects of different pH and sedimentation time on the coagulation effect of PE were investigated. PFS, PAC and AS with concentrations of 0.05, 0.1, 0.2, 0.5 and 1 g/L were combined in pairs or three combinations, and the removal rates of PE under different concentrations were analyzed.

3 Results and analysis

3.1 Effects of pH on the removal effect of PE The effects of pH (5.0, 6.0, 7.0, 8.0 and 9.0) on the removal of PE by single and composite coagulant sedimentation n are shown in Fig. 1 and 2. The change in pH would affect the charge of colloidal particles and coagulant in water samples, which would have a greater impact on the removal of PE by coagulant sedimentation. As the pH increased from 5.0 to 9.0, the removal rate of PE by PFS gradually decreased, from 80.30% to 29.85%. Al^{3+} played a major role in the coagulation process of PAC and AS, and $Al(OH)(H_2O)_5^{2+}$ and $Al(OH)_2(H_2O)_4^{+}$ were the main flocs at low pH, and the flocs produced by PAC and AS had poor adsorption performance for PE, while $Al(OH)_3$ was the main flocs at high pH, the coagulating sedimentation effect of PE was better. The coagulating sedimentation effect of PFS on PE was better than that of PAC and AS, possibly because when PFS exists in the water sample, it generates polynuclear polymers of different forms through hydrolysis reaction, which is conducive to the aggregation and sedimentation of microplastics[16]. When pH was 5.0, the removal rates of PE by PFS + PAC, PFS + AS and PFS + PAC + AS were 89.39%, 80.00% and 95.57%, respectively. With the increase in pH, the removal rate of PE by the three coagulants decreased gradually. The coagulating sedimentation effect of PAC + AS on PE increased with the increase in pH, and the highest removal rate was 64.97% at pH 8.0.

3.2 Effects of coagulant concentration on the removal effect of PE The removal effects of PFS, PAC and AS with different concentrations on PE are shown in Fig. 3. In the concentration range of 0.05 – 1.0 g/L, the removal rate of PE by PFS was significantly higher than that by PAC and AS, and the removal efficiency of PE reached the highest (82.14%) when the added concentration of PFS was 0.5 g/L, which indicated that PFS had very good coagulation and sedimentation performance for PE. When the concentration of PAC and AS was 0.02 g/L, the removal efficiency of PE was the best, which was 51.02% and 41.79%, respectively. As shown in Table 1, the coagulation and sedimentation capacity of PE can be improved by compounding a single coagulant. PFS + PAC, PFS + AS and PAC + AS had the highest removal rate of PE when the concentration ratio was 0.5 g/L + 0.2 g/L, 0.5 g/L + 0.2 g/L and 0.2 g/L + 0.5 g/L, reaching 89.50%, 80.00%, and 67.50%, respectively. The optimum concentration of PFS + PAC + AS was 1 g/L + 0.2 g/L + 0.2 g/L, and the removal rate of PE was 96.06%.

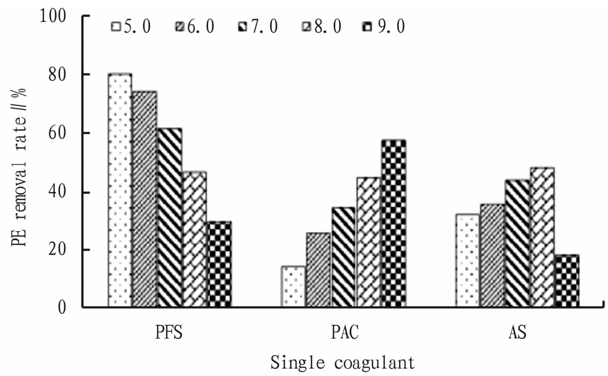

Fig. 1 **Removal effect of single coagulant on PE under different pH conditions**

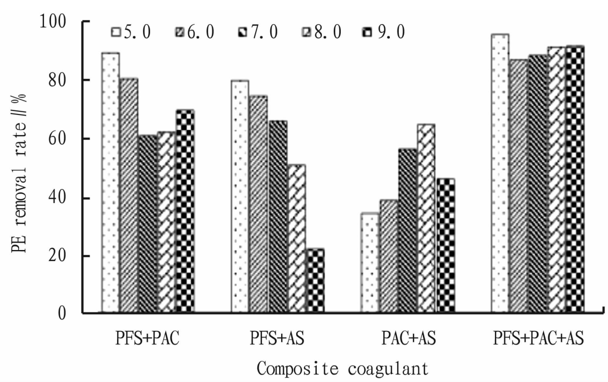

Fig. 2 **Removal effect of composite coagulant on PE under different pH conditions**

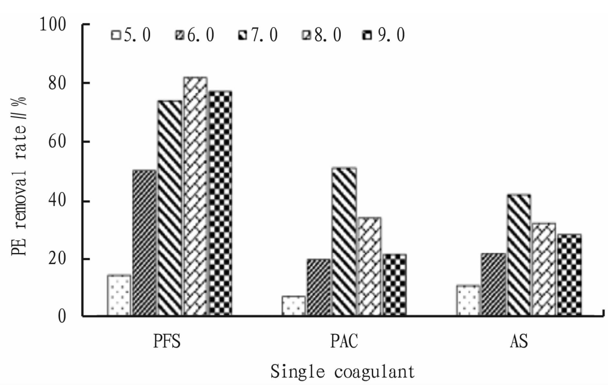

Fig. 3 **PE removal effect of single coagulant with different concentration**

Table 1 Removal effect of composite coagulant with different concentrations on PE

Concentration combination	Composite coagulant // %			
	PFS + PAC	PFS + AS	PAC + AS	PFS + PAC + AS
1 g/L + 1 g/L	62.81	50.75	21.61	–
1 g/L + 0.5 g/L	64.04	59.39	26.11	–
1 g/L + 0.2 g/L	80.10	69.90	25.37	–
1 g/L + 0.1 g/L	72.22	77.61	28.79	–
0.5 g/L + 1 g/L	55.05	44.88	32.32	–
0.5 g/L + 0.5 g/L	80.61	69.95	43.37	–
0.5 g/L + 0.2 g/L	89.50	80.00	64.53	–
0.5 g/L + 0.1 g/L	64.80	55.56	44.44	–
0.2 g/L + 1 g/L	61.42	33.99	28.64	–
0.2 g/L + 0.5 g/L	70.15	39.39	67.50	–
0.2 g/L + 0.2 g/L	74.88	60.80	64.97	–
0.2 g/L + 0.1 g/L	54.15	73.50	62.19	–
0.1 g/L + 1 g/L	27.36	27.59	24.37	–
0.1 g/L + 0.5 g/L	35.71	32.84	38.31	–
0.1 g/L + 0.2 g/L	53.30	37.56	35.03	–
1 g/L + 1 g/L + 1 g/L	–	–	–	34.67
1 g/L + 1 g/L + 0.5 g/L	–	–	–	36.95
1 g/L + 1 g/L + 0.2 g/L	–	–	–	41.29
1 g/L + 0.5 g/L + 1 g/L	–	–	–	31.50
1 g/L + 0.2 g/L + 1 g/L	–	–	–	38.89
0.5 g/L + 1 g/L + 1 g/L	–	–	–	35.71
0.2 g/L + 1 g/L + 1 g/L	–	–	–	31.03
1 g/L + 0.5 g/L + 0.5 g/L	–	–	–	46.08
1 g/L + 0.5 g/L + 0.2 g/L	–	–	–	61.11
1 g/L + 0.2 g/L + 0.5 g/L	–	–	–	51.02
1 g/L + 0.2 g/L + 0.2 g/L	–	–	–	96.06
0.5 g/L + 0.5 g/L + 1 g/L	–	–	–	47.26
0.5 g/L + 0.2 g/L + 1 g/L	–	–	–	53.77
0.2 g/L + 0.5 g/L + 1 g/L	–	–	–	23.35
0.5 g/L + 1 g/L + 0.5 g/L	–	–	–	51.72
0.5 g/L + 1 g/L + 0.2 g/L	–	–	–	74.63
0.2 g/L + 1 g/L + 0.5 g/L	–	–	–	36.00
0.5 g/L + 0.5 g/L + 0.5 g/L	–	–	–	71.21
0.5 g/L + 0.5 g/L + 0.2 g/L	–	–	–	79.40
0.5 g/L + 0.2 g/L + 0.5 g/L	–	–	–	70.00
0.2 g/L + 0.5 g/L + 0.5 g/L	–	–	–	37.56
0.5 g/L + 0.2 g/L + 0.2 g/L	–	–	–	95.57
0.2 g/L + 0.2 g/L + 0.5 g/L	–	–	–	76.38
0.2 g/L + 0.5 g/L + 0.2 g/L	–	–	–	84.39
0.2 g/L + 0.2 g/L + 0.2 g/L	–	–	–	85.07
0.2 g/L + 0.2 g/L + 0.1 g/L	–	–	–	76.57

3.3 Effects of sedimentation time on the removal rate of PE

From Fig. 4, it can be seen that with the sedimentation time increasing from 1 h to 4 h and 12 h, the removal rate of PE by single and composite coagulant increased by 2% – 4%. However, the sedimentation time of 4 h and 12 h had little effect on the removal rate of PE. If the sedimentation time is too short, there are still some flocs that have not been completely settled in the supernatant, leading to poor removal of microplastics; by contrast, if the sedimentation time is too long, the formed flocs may be broken again[17], and it has little contribution to further improve the removal rate. Therefore, the sedimentation time of 4 h is recommended.

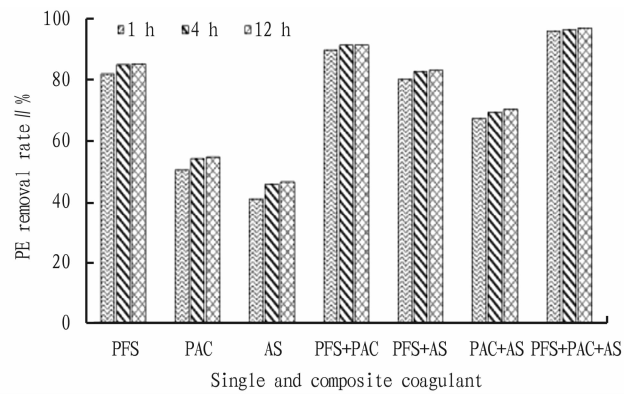

Fig. 4 Effect of sedimentation time on the removal of PE by single and composite coagulant

4 Conclusions

After adding single coagulant, the coagulating sedimentation effect of PFS on PE was the best (dosage 0.5 g/L, pH 5.0), followed by PAC (dosage 0.2 g/L, pH 9.0), and the weakest effect of AS (dosage of 0.2 g/L, pH of 8.0). After adding composite coagulant, PFS + PAC + AS (concentration combination of 1 g/L + 0.2 g/L + 0.2 g/L, pH 5.0) had the highest removal rate of PE. The order of PE removal efficiency of other combinations was PFS + PAC (0.5 g/L + 0.2 g/L, pH 5.0) > PFS + AS (0.5 g/L + 0.2 g/L, pH 5.0) > PAC + AS (0.2 g/L + 0.5 g/L, pH 8.0). The sedimentation time of both the single and composite coagulant was 4 h.

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and the tourism transportation network with G356, G105 and S221 as the backbone to form the main road traffic pattern of "three verticals and three horizontals". Three horizontals refers to the bridge to be built across Ganjiang River in the south, the east-west section of G356 in the middle, and the transverse line of provincial highway S225 and X065 in the north; Three verticals refers to national highway G105, national highway G356 and provincial highway S225. Through the construction of county-wide tourism highway network, it is able to enhance the ability of county-wide interconnection, create a traffic pattern of East – West – North – South interconnection, and enhance the complementarity of tourism development among major tourism development areas. Tourist bus, taxi and self-driving car rental are the main body in the tourism development area, and an integrated tourism transportation service network with clear hierarchy, clear structure and clear functions is constructed. Scenic spots mainly construct green corridors for leisure tourism, promote self-driving, bicycle, hiking and other modes of transportation, construct a perfect leisure greenway system, form a linear landscape service system connecting the nodes of scenic spots in series, and realize the transportation network of "point-line-plane" linkage of scenic spot-tourist line-tourist area.

6 Conclusions

There are abundant cultural tourism resources in Wan'an County, but it is necessary to rely on the characteristics and endowments of county tourism resources to reveal the spatial distribution characteristics of cultural tourism resources. The spatial relationship between the spatial distribution of tourism resources and the county transportation accessibility is analyzed to provide better reference suggestions for tourism transportation. Taking Wan'an County as an example, we made an overall analysis from the aspects of cultural tourism resources attribute structure and spatial structure, and reached the main conclusions. The cultural tourism resources of Wan'an County shows the characteristics of agglomeration distribution, and is greatly affected by the development of road construction, mainly taking national highways G356 and G105 and provincial highways S221 and S225 as the main distribution routes. The spatial pattern is characterized by "one center, two clusters, two verticals and one horizontal". The cultural tourist attractions transportation accessibility in Wan'an County shows a decreasing trend from the central city to the surrounding areas, and the accessibility of the south is worse than that of the north. The road accessibility on the west side of Ganjiang River in the northern area decreases obviously, the accessibility on the east side is better, and the southern area shows a decreasing trend from the center to both sides. The development of cultural tourism resources in Wan'an County should take the concept of "all-for-one tourism" " as the core. Combining with the spatial distribution pattern characteristics of "one center, two clusters, two verticals and one horizontal", the link function of highway traffic is strengthened, so that the network distribution of highway traffic breaks the division between administrative towns and deepens the link between towns. It is recommended to strengthen the exchange of cultural activities and form an all-for-one tourism traffic with a "point-line-plane" structure. Specifically, to solve the east-west connection of the southern area, the east-west side of the southern area can be divided into two parts by the Ganjiang River, but the necessary traffic connection should be established.

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