Magnetic polymeric ferric magnesium chloride: Fe species distribution, characterization and coagulation removal of microplastics in water†

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A novel composite coagulant, magnetic polymerized ferric magnesium chloride (MPFMC), was prepared based on traditional inorganic coagulants of polymeric ferric chloride (PFC). It was used to remove polystyrene (PS), a major component of microplastics that is easily suspended in water. The distribution of Fe species under different preparation conditions was investigated, and the physical and chemical properties of MPFMC were characterized using FTIR, XRD, SEM, and VSM. The effects of dosage, pH and temperature on the removal of PS by MPFMC and the floc structures were also investigated. PS removal was maximized when \( n(\text{Fe}) : n(\text{Mg}) = 4 : 1 \), \( \frac{n(\text{OH})}{n(\text{Fe} + \text{Mg})} = 0.4 \) and \( M_{\text{Fe}_2\text{O}_3} : M_{\text{Fe}} = 2 : 1 \). The content of Fe(b), the most critical component of the iron salt coagulant, increased compared with that of PFC after the introduction of appropriate amounts of magnesium salt and \( \text{Fe}_3\text{O}_4 \). In addition, MPFMC has a wide adaptability to pH and temperature. When the dosage of MPFMC was 0.12 mmol L\(^{-1}\) (pH of 4.5–9.5, temperature of 19–34 \(^\circ\)C, rapid stirring at 300 rpm for 2 min, slow stirring at 100 rpm for 10 min, and external magnetic field settling for 10 min), the coagulation performance was excellent, and the removal of PS was greater than 85%. The fractal dimension peak value of the flocs formed reached 1.87, and the floc structure was dense. In conclusion, the modification of introducing magnetic particles and magnesium salt into PFC has proven to be an effective strategy for improving the removal efficiency of microplastics by iron salt coagulants.

1. Introduction

Since their large-scale production in the 1950s, plastics have had a wide range of applications in industry and consumer products due to their lightness, durability, low cost, as well as outstanding mechanical, thermal, and tensile properties.\(^ {1,2} \) The exponential growth of plastic production globally has increased the amount of plastic waste released into the environment to the point that it poses potential risks and significant challenges to water environmental safety.\(^ {3–5} \) World plastic production increased alarmingly to 367 million tons per year in 2020, with approximately 20 million tons of plastics entering the water environment each year due to improper management. It is estimated that the cumulative quantity of plastics will reach 250 million tons by 2025.\(^ {6} \) Plastic wastes entering the water environment produce smaller plastic particles, via decomposition by abrasion,\(^ {7,8} \) UV radiation,\(^ {9} \) oxidation,\(^ {10} \) and microorganisms.\(^ {11} \) Plastic particles < 5 mm in size are internationally defined as microplastics (MPs).\(^ {12} \) Microplastics have long-lived, nondegradable properties and can persist in the natural environment for decades or centuries.\(^ {13–15} \) These small plastic particles are widely distributed in water environments and are easily ingested by various organisms, thus entering food webs. The extensive surface area and hydrophobicity of microplastics increase their ability to absorb trace amounts of pollutants.\(^ {16} \) In particular, the oxidized parts of microplastics adsorb to other surfaces and interact with other contaminants or chemicals.\(^ {17} \) Therefore, microplastics carry toxic and harmful contaminants (heavy metals, organic pollutants, pathogenic bacteria, etc.) that are likely to be released after ingestion, causing incalculable consequences.\(^ {18} \) Sun et al.\(^ {19} \) reported that the presence of microplastics exacerbated the toxicity of co-contaminants by 18%, as manifested by increased cytotoxicity, endocrine disruption, immunotoxicity and oxidative stress. Therefore, there is an urgent need for an efficient water treatment technology to remove microplastics.

In recent years, several methods have been developed for the treatment of water containing microplastics, including coagulation,\(^ {20} \) membrane separation,\(^ {21} \) adsorption,\(^ {22} \) advanced oxidation,\(^ {23} \) and biodegradation.\(^ {24} \) Among them, coagulation is
the most widely used treatment, due to its simple operation, low cost and high efficiency. In a previous study, Zhou et al.\textsuperscript{25} used 90 mg L\textsuperscript{-1} polymerized aluminum chloride (PAC) to remove microplastics, and obtained 77.83% and 29.70% removal rates of polystyrene (PS) and polyethylene (PE), respectively. Although traditional coagulants are significantly effective at removing microplastics, the natural settling of flocs is a time-consuming process that takes 30 minutes or more.\textsuperscript{26} Magnetic composite coagulants are thought to have advantages over traditional coagulants, because the former can not only optimize coagulation performance but can accelerate floc settling rate. For instance, Jiang et al.\textsuperscript{27} and Zhang et al.\textsuperscript{28} compounded magnetic particles with a traditional coagulant, and revealed that the magnetic composite coagulant removed pollutants better than the conventional coagulant. Increasing the dosage of the coagulant is an effective way to improve the efficiency of microplastic removal in conventional coagulation processes. However, excessive use of aluminum salt can adversely affect human health, because of the neurotoxic effects of residual aluminum in water;\textsuperscript{29} iron salt has a high floe density and better settling performance than aluminum salt, but the effluent often carries a certain degree of chromaticity.\textsuperscript{30} In contrast, magnesium salt is an environmentally friendly water treatment agent with the advantages of fast floc formation, good stability, safety and nontoxicity.\textsuperscript{31} Therefore, we chose to use iron salt, which has a good settling performance, as the base, and introduced appropriate amounts of magnesium salt and Fe\textsubscript{3}O\textsubscript{4} to optimize the coagulation performance and accelerate the floc settling rate.

In the present work, a novel composite coagulant for microplastics removal was prepared by Fe\textsubscript{3}O\textsubscript{4} and PFMC (polymerized ferric magnetite chloride). The Ferron method\textsuperscript{32} was used to determine the distribution of Fe species, which is closely related to coagulation performance. FTIR, XRD, SEM, and VSM were used to characterize the chemical structure, morphology and typical properties of Fe\textsubscript{3}O\textsubscript{4} and coagulants. The removal of microplastics in water was further investigated using the method of MPFMC (magnetic polymerized ferric magnetite chloride). Comparing MPFMC in removing microplastics at different dosages, pH values and temperatures, the possible coagulation mechanism was analyzed by measuring the zeta potential and floc fractal dimension.

2. Materials and methods

2.1. Materials

All reagents used were analytical reagents (ARs). Ferric chloride (FeCl\textsubscript{3}\cdot6H\textsubscript{2}O), magnesium chloride (MgCl\textsubscript{2}\cdot6H\textsubscript{2}O), sodium dihydrogen phosphate (Na\textsubscript{2}HPO\textsubscript{4}), sodium hydroxide (NaOH), sodium bicarbonate (NaHCO\textsubscript{3}) and hydrochloric acid (HCl) were purchased from Kemiu Chemical Reagent Co., Ltd (Tianjin, China). Ferroferric oxide (Fe\textsubscript{3}O\textsubscript{4}) magnetic powder was obtained from Macklin Chemical Reagent Co., Ltd (Shanghai, China) with a particle size of 200 nm. PS microplastics (≤1 μm) were supplied by Tesulang Chemical Raw Material Co., Ltd (Guangdong, China). Deionized ultrapure water used in all experiments was purified with Millipore offered by Purkinje General Co. (Beijing, China).

The primary instruments used in this study included a constant temperature water bath (HH-12468, China), a cantilever electromagnetic mixer (JB70-70s, China), a peristaltic pump (YZ15, China), a water bath constant temperature oscillator (SHZ-82B, China), an ultrasonic cleaner (KQ2200E, China), and a pH meter (PH-100B, China).

2.2. Preparation of MPFMC

MPFMC was prepared using the following steps: FeCl\textsubscript{3}\cdot6H\textsubscript{2}O and MgCl\textsubscript{2}\cdot6H\textsubscript{2}O at a Fe/Mg molar ratio (n(Fe)/n(Mg)) in the range of 0.5 : 1–8 : 1 were fully dissolved, and an NaOH solution (1 mol L\textsuperscript{-1}) was added drop-wise (0.15 mL min\textsuperscript{-1}) according to a predetermined basicity (n(OH)/n(Fe + Mg)), in the range of 0.2–1.2. The water bath was kept at 60 °C and the stirring speed was 350 rpm. Then, a certain amount of Na\textsubscript{2}HPO\textsubscript{4} ([Na\textsubscript{2}HPO\textsubscript{4}] / [Fe + Mg] = 0.05) was added as a stabilizer, and the resulting solution was continuously oscillated on a shaking table (60 °C, 160 rpm) for 2 h. PFMC was obtained after standing and curing for 24 h, and pure water was added to 500 mL (0.02 mol L\textsuperscript{-1}). Next, a certain mass of Fe\textsubscript{3}O\textsubscript{4} according to the mass ratio of Fe\textsubscript{3}O\textsubscript{4} to Fe in PFMC (MFe\textsubscript{3}O\textsubscript{4} : MFe, in the range of 0.5 : 1–3.0 : 1), was added to the PFMC solution, which was ultrasonicated for 30 min, and subsequently ripened to obtain MPFMC.

2.3. Fe species distribution

The modified Ferron method has been widely used to study the distribution of Fe species in iron salt coagulants. The absorbance capabilities of each Fe species were measured using a UV-visible spectrophotometer (TU-1900, China) at a wavelength of 600 nm, where Fe(a) represents free iron ions and non-nuclear hydroxyl complexes of iron; Fe(b) represents the polymeric form, which is the most effective form of iron salt coagulants; and Fe(c) represents the colloidal and precipitated species.\textsuperscript{33,34} Due to the spontaneous hydrolysis of iron-based coagulants in water, Ferron reagent (7-iodo-8-hydroxyquinoline-5-sulphonic acid) can react with the hydrolyzed form of iron ions to produce various green complexes. Since these complexes react at different rates, the solutions change color at different rates. Thus, different absorbances can be used to determine the iron content of different forms of iron salt coagulants.

2.4. Characterization

The surface morphology of MPFMC was obtained by scanning electron microscopy (SEM, Hitachi SU8010, Japan), the composition of MPFMC was determined by Fourier transform infrared spectroscopy (FTIR, Bruker Tensor II, Germany) and X-ray diffractometry (XRD, Bruker D8 Advance, Germany), and the hysteresis line of MPFMC was measured using a vibrating sample magnetometer (VSM, LakeShore 7404, America).

2.5. Coagulation test

The coagulation comparison test was carried out using a 1 L beaker. Lake water (Taihu, 5.66 ± 0.05 NTU) was used to a
prepare microplastics (PS) stock solution with a concentration of 25.00 mg L\(^{-1}\). The initial pH was 7.5, and the pH value was adjusted using NaOH (0.1 mol L\(^{-1}\)), HCl (0.1 mol L\(^{-1}\)) and buffer NaHCO\(_3\) (0.1 mol L\(^{-1}\)). The coagulant dosage (liquid infusion) was measured by the effective Fe composition. The coagulant was rapidly stirred at 300 rpm for 2 min, then slowly stirred at 100 rpm for 10 min, and finally allowed to stand (natural settlement for 30 min, external magnetic field settlement for 10 min). And then measured by sampling the supernatant at 3 cm for further measurements. All tests were conducted three times to ensure the credibility of the data.

2.6. Analysis methods

Turbidity was measured using a turbidimeter (Hach 2100Q, America), and microplastics removal rates were estimated through the linear relationship between turbidity and particle concentration;\(^{35,36}\) the residual iron in each water sample was determined using \(o\)-diazepine spectrophotometry, and each sample’s absorbance was determined using a UV-visible spectrophotometer (TU-1900, China) at a wavelength of 510 nm;\(^{37}\) the potential values of the coagulation tests were measured using a Malvern potential/particle size analyzer (Zetasizer Nano ZS, Britain); and two-dimensional photographs of the flocs were obtained by electron microscopy (LLX 4800-B, China), after which ImageJ software was used to measure the projected areas and maximum lengths of the flocs.

Chakraborti et al.\(^{38}\) proposed calculating the fractal dimension of flocs using the functional relationship between the projected area and the maximum length. The functional relationship between the projected area and the maximum length is given by eqn (1):

\[
A = zL^{D_h}
\]

\[
\ln A = D_h \ln L + \ln z
\]

where \(A\) is the projected area of the flocs, \(L\) is the maximum length of the floc projection, \(z\) is a constant of proportionality, and \(D_h\) is the fractal dimension of the flocs in two dimensions. Taking the natural logarithm of eqn (1), we get eqn (2). Then, the slope of the line is calculated, and a confidence test (\(R^2\)) is performed according to the linear relationship between \(\ln A\) and \(\ln L\). The slope is \(D_h\).

3. Results and discussion

3.1. Influence of preparation conditions on coagulation effect and Fe species

3.1.1. \(n(\text{Fe}):n(\text{Mg})\). To study the influence of \(n(\text{Fe}):n(\text{Mg})\) on coagulant performance and Fe species distribution, \(n(\text{OH}):n(\text{Fe} + \text{Mg})\) was fixed at 0.4. The coagulation effect was analyzed with the PS removal rate as the index of investigation. As shown in Fig. 1a, different \(n(\text{Fe}):n(\text{Mg})\) exhibited a substantial influence on the removal of PS. When \(n(\text{Fe}):n(\text{Mg})\) is relatively small, the PS removal effect is poor. The reason may be that \(\text{Mg}^{2+}\) or \(\text{Mg(OH)}^+\) is dominant, and restricts the formation of high molecular weight polymers.\(^{39}\) The amount of polymeric iron is insufficient to allow the suspended PS to achieve significant sedimentation and removal. Although the settling of flocs increases with increasing Fe content, the removal effect of PS is the greatest when \(n(\text{Fe}):n(\text{Mg}) = 4:1\). On the other hand, Fig. 1b represents the influence of different \(n(\text{Fe}):n(\text{Mg})\) on the distribution of Fe species. The performance of polymeric iron coagulants was proven to be positively related to the distribution of Fe(b).\(^{40,41}\) With increasing \(n(\text{Fe}):n(\text{Mg})\), Fe(a) gradually increased from 23.20% to 52.21%. The remaining Fe(b) and Fe(c) both increased initially and then decreased. Thus when \(n(\text{Fe}):n(\text{Mg})\) is relatively small or large, the bridging capacity is relatively weak, and the PS removal effect decreases. When \(n(\text{Fe}):n(\text{Mg}) = 4:1\), Fe(b) accounted for up to 44.56%, and the coagulation performance of PFMC was optimal.

3.1.2. \(n(\text{OH})/n(\text{Fe} + \text{Mg})\). To study the influence of \(n(\text{OH})/n(\text{Fe} + \text{Mg})\) on coagulant performance and Fe species distribution, \(n(\text{Fe}):n(\text{Mg})\) was fixed at 4:1. Previous studies have shown that the OH content influences the existing forms of metal ions in coagulants.\(^{42}\) As shown in Fig. 1c, different \(n(\text{OH})/n(\text{Fe} + \text{Mg})\) result in different PS removal capabilities. When \(n(\text{OH})/n(\text{Fe} + \text{Mg})\) is lower, its electric neutralization ability is strong, but the bridging ability is weak, and the PS removal effect is relatively weakened. Gradually increasing \(n(\text{OH})/n(\text{Fe} + \text{Mg})\) causes excessive OH\(^{-}\) leading to excessive hydrolysis of metal salts.\(^{43}\) Fe\(^{3+}\) easily forms polymers and copolymers with Mg\(^{2+}\). Because the stabilization of intermediate multinuclear complexes cannot be maintained, the coagulation effect is reduced. Fig. 1d represents the influence of different \(n(\text{OH})/n(\text{Fe} + \text{Mg})\) on the distribution of Fe species. With increasing \(n(\text{OH})/n(\text{Fe} + \text{Mg})\), Fe(a) gradually decreases from 47.29% to 29.14%, Fe(b) increases from 24.01% to 32.74%. The reasons for these distributions are as follows, when the OH\(^{-}\) concentration is low, Fe\(^{3+}\) complexes with OH\(^{-}\) to generate mononuclear hydroxyl complexes, at which time the distribution of Fe(a) is relatively high. With increasing OH\(^{-}\) concentration, Fe\(^{3+}\) further polymerizes with hydroxyl groups to generate multinuclear hydroxyl complexes, and gradually shifts from oligomers to polymers, causing the distribution of Fe(b) and Fe(c) contents to gradually increase. It is worth noting that the best PS removal effect is achieved when \(n(\text{OH})/n(\text{Fe} + \text{Mg}) = 0.4\). This may be because when \(n(\text{OH})/n(\text{Fe} + \text{Mg}) > 0.4\), the stability of the polymers formed by Fe hydrolyzed compounds decreases, the polymers easily decompose, and the coagulation effect decreases.\(^{39}\) Therefore, \(n(\text{OH})/n(\text{Fe} + \text{Mg}) = 0.4\) was selected as the optimized preparation condition.

3.1.3. \(\text{M}_{\text{Fe,O}_x} : \text{M}_{\text{Fe}}\). To study the influence of \(\text{M}_{\text{Fe,O}_x} : \text{M}_{\text{Fe}}\) on coagulant performance and Fe species distribution, \(n(\text{Fe}):n(\text{Mg})\) was fixed at 4:1 and \(n(\text{OH})/n(\text{Fe} + \text{Mg})\) was fixed at 0.4. As shown in Fig. 1e, different \(\text{M}_{\text{Fe,O}_x} : \text{M}_{\text{Fe}}\) directly affect the PS removal effect. The best coagulation effect is achieved when \(\text{M}_{\text{Fe,O}_x} : \text{M}_{\text{Fe}} = 2:1\). On the other hand, Fig. 1f represents the influence of different \(\text{M}_{\text{Fe,O}_x} : \text{M}_{\text{Fe}}\) on the distributions of Fe species. Both Fe(a) and Fe(c) tend to increase, then decrease, and then increase again, while Fe(b) shows the opposite trend. The percentage of Fe(b) can reach 47.40% when \(\text{M}_{\text{Fe,O}_x} : \text{M}_{\text{Fe}}\) is
Fig. 1 Influence of $n$($\text{Fe}$):$n$($\text{Mg}$) (a) and (b), $n$(OH)/$n$(Fe + Mg) (c) and (d), and $M_{\text{Fe}_3\text{O}_4}$:$M_{\text{Fe}}$ (e) and (f) on the coagulation effect and Fe species distribution. (The coagulation operation conditions were solution pH = 7.5 ± 0.1, room temperature = 22 °C, and natural settlement = 30 min).

2:1, at which point MPFMC is more stable and demonstrates the best coagulation performance. Therefore, $n$($\text{Fe}$):$n$($\text{Mg}$) of 4:1, $n$(OH)/$n$(Fe + Mg) of 0.4, and $M_{\text{Fe}_3\text{O}_4}$:$M_{\text{Fe}}$ of 2:1 were chosen to obtain MPFMC. In addition, Fig. S1 (ESI†) shows that after the introduction of an appropriate amount of magnesium salt and $\text{Fe}_3\text{O}_4$, the amount of Fe(b) in PFMC was greater than that in PFC, and the amount of Fe(b) in MPFMC was greater than that in PFMC. Overall, the coagulation performance...
gradually improved. Here, the introduction of Fe$_3$O$_4$ destroys the equilibrium of H$^+$ and OH$^-$/C$_0$ in the solution because the pH of Fe$_3$O$_4$ is higher than that of PFMC, such that the equilibrium is shifted toward the polymer. This indicates that the addition of Fe$_3$O$_4$ increases the amount of coagulant in the solute state, which improves the ability of coagulation to remove PS.

3.2. Characteristics of MPFMC

3.2.1. Fourier transform infrared spectroscopy and X-ray diffractometry. The intrinsic mechanism of Fe$_3$O$_4$ binding to PFMC was further analyzed using FTIR and XRD. Fig. 2a shows that the peaks of the three coagulants in the wavenumber range of 3200–3500 cm$^{-1}$ and at 1630 cm$^{-1}$ were attributed to the stretching vibration of O–H and the vibration of adsorbed or bound water in the coagulant. However, the copolymers formed by Fe and Mg are mainly bonded through hydroxyl groups, so the absorption peaks of MPFMC, PFMC and PFC are basically the same. Among them, the peaks of MPFMC and PFMC at 690 cm$^{-1}$ may be caused by the bending vibration coupling of O in O–H by the asymmetric attraction of differently electronegative Fe and Mg. The peaks at 1080 cm$^{-1}$ imply that there are hydroxy-linked iron and magnesium polymers and Fe–O and Mg–O bonds. The peak at 580 cm$^{-1}$, corresponding to Fe$_3$O$_4$, represents the vibration of the Fe–O bond. These results indicate a linkage between iron and magnesium via –OH or –O–, confirming that MPFMC is a composite coagulant of iron and magnesium. As shown in Fig. 2b, Fe$_3$O$_4$ has a typical spinel structure, and the diffraction peaks of PFC and PFMC, which are amorphous structural materials, are similar. The main characteristic diffraction peaks of MPFMC contain Fe$_3$O$_4$, PFMC and PFC diffraction peaks. $2\theta = 30.3^\circ$ (220), 35.7$^\circ$ (311), 43.3$^\circ$ (400), 53.8$^\circ$ (422), 57.2$^\circ$ (511), and 62.8$^\circ$ (440) and $2\theta = 27.3^\circ$ (111), 31.6$^\circ$ (200), 45.4$^\circ$ (220), 56.4$^\circ$ (222), and 66.1$^\circ$ (400) represent the presence of Fe$_3$O$_4$ and PFC, respectively. It was also found that the intensity of the MPFMC diffraction peaks decreased significantly. The surface layer was wrapped with polymers, which changed the surface shape of the Fe$_3$O$_4$ crystals, resulting in weakening of the peaks. Finally, the peaks of Fe$_3$O$_4$ and PFMC matched well; thus, MPFMC was a combination of Fe$_3$O$_4$ and PFMC, which did not undergo phase changes or structural changes.

3.2.2. Scanning electron microscopy. Fig. 3 shows the morphologies of three coagulants at 15000 multiples, as analyzed by SEM. The dashed boxes in the figure indicate the sizes of PFC, PFMC, and MPFMC in the selected area. Fig. 3a represents PFC. The surface is not smooth, and some irregular massive particles are distributed. The average size of PFC was approximately 1.10 μm. Fig. 3b represents PFMC. After the introduction of magnesium salt, the surface of the coagulant showed a vesicular particle structure, and the pores between clusters were clear and compact. And the average size of PFMC was reduced to 0.29 μm compared to that of PFC. This may be due to the introduction of magnesium salt, and the hydrolysis products formed by metal ions in solution occur. So due to the
bridging effect of the O–H group, a vesicular structure with spatial stereo is formed. While this vesicular structure may increase the collision between the coagulant and pollutant during the coagulation process to obtain a better removal effect.48 As shown in Fig. 3c, MPFMC surface morphology did not change significantly compared to that of PFMC. Due to the encapsulation of Fe₃O₄ particles in the polymer, the average size of MPFMC increased to 0.45 μm. This indicates that PFMC was successfully loaded onto Fe₃O₄ particles.

3.2.3. Vibrating sample magnetometer. The hysteresis loops of Fe₃O₄ and MPFMC exhibit superparamagnetism in Fig. 4. Among them, the magnetic property of Fe₃O₄ is very high, and the specific saturation magnetization strength (Ms) can reach 79.16 emu g⁻¹. MPFMC has extremely low remanence (1.73 emu g⁻¹) and coercivity (63.57 Oe), and its specific saturation magnetization strength (Ms) is 28.74 emu g⁻¹. Due to the manner in which PFMC wraps Fe₃O₄, the specific saturation magnetization strength (Ms) of MPFMC decreased. Although the magnetic properties are further weakened, MPFMC still has a high response to the applied magnetic field, so it can be separated by magnetic separation technology.

3.3. Factors impacting the coagulation effect

3.3.1. Dosage. As mentioned above, MPFMC was selected as the coagulant, and the removal effect of different dosages of MPFMC on PS were investigated. Fig. 5a shows that removing PS under an applied magnetic field can significantly reduce the amount of MPFMC and save time. For example, when the dosage was 0.12 mmol L⁻¹, 30 min of natural settling was required to achieve 85.06% PS removal (Fig. 1e). At the same dosage, after the external magnetic field had settled for 10 min, a PS removal rate of 95.28% was reached. In the latter case, the residual iron concentration was lower than 0.3 mg L⁻¹ (Fig. S2, ESI†), satisfying the drinking water standard (GB5749-2022, China). Second, the removal rate of PS first increased and then decreased with increasing dosage. The reason for this decrease may be that increasing the dosage increases the amount of Fe₃O₄ contained in the coagulant. Under an applied magnetic field, the flocs settled too fast to capture enough PS, resulting in a decrease in PS removal. In addition, Fig. 5b shows that the pollutants were negatively charged, and the zeta potential increased from 32.40 mV to 53.30 mV after coagulant modification. The zeta potential increased with increasing dosage and the potential increased from −12.50 mV to −5.46 mV. This denies that an excessive dosage of the coagulant will produce colloidal protection and affect the removal rate of PS.49,50 The results indicate that the introduction of an appropriate amount of Fe₃O₄ enhances bridging adsorption and sweeping and the charge neutralization mechanism.

The generation of flocs during coagulation is a random process with nonlinear characteristics. From the initial irregular small particles into small flocs, small flocs gathered into large flocs, and the formation of this process is self-similar, indicating that the flocs have fractal characteristics. Fractal theory was proposed by the French mathematician Mandelbrot

Fig. 4 Magnetic hysteresis loop of MPFMC and Fe₃O₄.

Fig. 5 Influence of dosage on the coagulation effect: coagulation effect and fractal dimension (a); zeta potential of different samples (raw water, PFC, PFMC, and MPFMC) and different dosages of MPFMC (b). (The coagulation operation conditions were solution pH = 7.5 ± 0.1, room temperature = 22 °C, and external magnetic field settlement = 10 min).
Fractal dimension \( (D_f) \) can be used to represent the density of the floc structure. With respect to the efficiency of organizing small particles to complete space, a larger \( D_f \) indicates denser flocs and a better coagulation effect.\(^{52,53}\) The scatter plot in Fig. S3 (ESI†) shows that there is a good linear relationship between \( \ln A \) and \( \ln L \) after fitting. With a fitting coefficient \( R^2 > 0.90 \), that of a typical fractal system, the slope of the line is the fractal dimension of the flocs. First, the floc fractal dimension increases with increasing coagulant dosage, such that the same results as in Fig. 5a were obtained, with a decreasing trend at dosages greater than 0.12 mmol L\(^{-1}\). These results demonstrate good correlation between the dosage, PS removal rate and floc fractal dimension, maintaining a consistent trend and indicating that the density of flocs directly determines the removal rate of PS.

### 3.3.2. pH

Previous studies have shown that the solution pH has an important impact on coagulation performance.\(^{54,55}\) On the basis of exploring the experimental reagent dosage, the optimum coagulant dosage of 0.12 mmol L\(^{-1}\) was taken to investigate the removal of PS by MPFMC at different pH values. As shown in Fig. 6a, the removal of PS by MPFMC reached more than 85% when the pH was in the range of 4.5–9.5. Overall, the fluctuation of PS removal rate was not more than 10%, indicating that MPFMC has stable performance and good applicability to pH. Second, the pH directly affects the charge of colloidal particles in water. In order to better explore the coagulation mechanism, the zeta potential of the mixing solution with different pH values before and after coagulation were measured. Fig. 6b shows that the zeta potential of the solution before coagulation decreased from \(-10.21\) mV to \(-14.89\) mV with increasing pH. This may be due to the increase of OH\(^-\), and then makes the zeta potential decrease. After coagulation, the zeta potential decreased from \(-3.09\) mV to \(-9.29\) mV due to electrical neutralization during coagulation. This implies that positively charged MPFMC and negatively charged pollutants interact with each other to form flocs through electrostatic adsorption.\(^{48}\)

Similarly, the scattering points in Fig. S4 (ESI†) demonstrate that there is a good linear relationship between \( \ln A \) and \( \ln L \), with a fitting coefficient \( R^2 > 0.90 \). The fractal dimension of flocs and the effect of removing PS showed the same trend, increasing initially and then decreasing (Fig. 6a). At pH = 7.5, the floc fractal dimension is 1.78, which is the best effect. Previous studies have shown that flocs formed by adsorption bridging are denser than those formed by charge neutralization, while flocs formed by sweeping are fragile and loose.\(^{43}\) Changes in pH are usually associated with a sweep effect during the coagulation process.\(^{56}\) Under acidic conditions, the hydrolyzed products of iron coagulant mainly exist as the monomer \( \text{Fe}^{3+} \), which cannot easily destabilize the colloid in water to form flocs.\(^{56}\) This results in the generation of looser flocs, thus reducing the wrapping effect on PS. At this time, charge neutralization and sweeping effect play a large role. Under alkaline conditions, the iron coagulant easily hydrolyzes to \( \text{Fe(OH)}_3 \), and the negatively charged \( \text{[Fe(OH)}_4]^- \) reduces the role of electric neutralization, adsorption bridging and net trapping and sweeping.\(^{57,58}\) The result is a decrease in the removal effect of PS. In general, it showed that the change in floc densities at different pH also applies to the change in PS removal rate.

### 3.3.3. Temperature

Temperature is an important technological condition in the coagulation process, and directly affects the coagulation effect. An appropriate increase in temperature can promote the hydrolysis reaction and accelerate the formation of \( \text{Fe}^{3+} \) mononuclear complexes and polynuclear complexes.\(^{59}\) For example, Dayarathne et al.\(^{60}\) investigated the effect of temperature on the removal of turbidity by coagulation, and found that the dominant species \( (\text{Fe}^{3+}, \text{Fe(OH)}^{2+}, \text{Fe(OH)}_2^+, \text{Fe(OH)}_3\text{ and Fe(OH)}_4^-) \) changed at different temperatures. Here, the optimum dosage of coagulant was 0.12 mmol L\(^{-1}\), and the removal effect of MPFMC on PS at different temperatures was investigated. As shown in Fig. 7, in the temperature range of 19–25 °C, the PS removal rate increased slowly to 96.31% with increasing temperature.

![Fig. 6 Influence of pH on the coagulation effect: coagulation effect and fractal dimension (a); zeta potential before and after coagulation (b).](image-url)
However, when the temperature exceeded 25 °C, the PS removal rate decreased. This may be because when the temperature rises, the hydrolysis rate is too fast, which causes insufficient PS to be captured and floc settling to occur.

Similarly, the scattering points in Fig. S5 (ESI†) demonstrate that there is a good linear relationship between lnA and lnL, with a fitting coefficient R² > 0.90. With increasing temperature, the fractal dimension of flocs first increased and then decreased, consistent with the trend of PS removal (Fig. 7). And the maximum fractal dimension of flocs reached 1.87 at 25 °C. Because the hydrolysis of inorganic salt coagulants is endothermic, the hydrolysis reaction is inhibited when the water temperature is lower than the required value. If the hydrolysis rate accelerates when the water temperature is higher than the required value, the movement of colloidal particles intensifies with increased collisions. This leads to loose flocs, which are not conducive to the adsorption and settlement of pollutants, thus affecting the coagulation effect. Therefore, an appropriate temperature rise will be conducive to the formation of denser flocs, thereby enhancing the coagulation effect.

3.3.4. Comparing the coagulation effects of MPFMC and other coagulants. To better understand the removal of PS by MPFMC. The novel coagulant (MPFMC) was used to remove PS compared with traditional coagulant, such as PFC. Fig. 8 shows that under an applied magnetic field, the removal rate of PS by MPFMC is significantly higher than that of PFC. Table 1 summarizes the comparison of traditional coagulation removal of microplastics in different studies.

<table>
<thead>
<tr>
<th>Traditional coagulants</th>
<th>Microplastics</th>
<th>Maximum removal efficiency (%)</th>
<th>Sedimentation time</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl₃·6H₂O</td>
<td>Polyethylene (PE)</td>
<td>12.65</td>
<td>30 min</td>
<td>61</td>
</tr>
<tr>
<td>AlCl₃·6H₂O</td>
<td>Polystyrene (PS)</td>
<td>36.89</td>
<td>30 min</td>
<td>62</td>
</tr>
<tr>
<td>PAC</td>
<td></td>
<td>99.4</td>
<td>30 min</td>
<td>63</td>
</tr>
<tr>
<td>Al₂(SO₄)₃·18H₂O</td>
<td>Polystyrene (PS)</td>
<td>98.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂(SO₄)₃·9H₂O</td>
<td>Polystyrene (PS)</td>
<td>98.9</td>
<td>30 min</td>
<td></td>
</tr>
<tr>
<td>Al₂(SO₄)₃·18H₂O</td>
<td>Polystyrene (PS)</td>
<td>85.2</td>
<td>15 min</td>
<td>65</td>
</tr>
<tr>
<td>Al₂(SO₄)₃·18H₂O</td>
<td>Polystyrene (PS)</td>
<td>85.2</td>
<td>15 min</td>
<td>65</td>
</tr>
<tr>
<td>PAC + Polyacrylamide (PAM)</td>
<td></td>
<td>Polystyrene (PS)</td>
<td>85.2</td>
<td>15 min</td>
</tr>
<tr>
<td>FeCl₃·6H₂O + PAM</td>
<td>Polystyrene (PS)</td>
<td>95.13</td>
<td>10 min</td>
<td></td>
</tr>
<tr>
<td>MPFMC</td>
<td>Polystyrene (PS)</td>
<td>95.13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
MPFMC in the early stage of sedimentation increases rapidly with time, and the removal efficiency of PS reaches 95.13% at 10 min. As a traditional coagulant, PFC can reach the removal rate of 92.84% after only 30 min of natural sedimentation. In addition, comparison of two coagulants (including the other conventional coagulants listed in Table 1) indicated that MPFMC can not only greatly accelerate the settling speed of flocs but that it can also increase the removal rate of PS. This may also be due to the fact that the flocs cover the pollutants, and then the magnetic field causes the flocs to settle in time. However, compared to traditional coagulation methods, some pollutants may fall off during the natural settling period, influencing the final removal of PS. Therefore, the comparison reveals that the magnetic composite coagulant’s ability to remove microplastics was better than that of traditional coagulant, especially in accelerating the settling rate.

4. Conclusions

In this study, the magnetic coagulant of PFMC and Fe$_3$O$_4$ was successfully prepared. The Ferron method was used to analyze the distribution of Fe species, and it was found that the distribution changes of Fe(a), Fe(b) and Fe(c) were similar to the removal changes of PS. As the percentage of Fe(b) increases, the coagulation performance and removal rate of PS also increase. The PS removal efficiency was the greatest when \( n(\text{Fe})/n(\text{Mg}) = 4:1 \), \( n(\text{OH})/n(\text{Fe} + \text{Mg}) = 0.4 \), and \( M_{\text{Fe}_3\text{O}_4}:M_{\text{Fe}} = 2:1 \). The percentages of Fe(a), Fe(b) and Fe(c) in the coagulant were 27.99%, 48.14% and 24.20%, respectively; and the percentage of Fe(b) was higher than that of PAC and PFMC. Therefore, \( n(\text{Fe})/n(\text{Mg}) = 4:1 \), \( n(\text{OH})/n(\text{Fe} + \text{Mg}) = 0.4 \), and \( M_{\text{Fe}_3\text{O}_4}:M_{\text{Fe}} = 2:1 \) were selected as the target coagulants for PS removal.

FTIR and XRD analyses showed that iron and magnesium ions in PFMC were connected by –OH or –O–, confirming that MPFMC was a combination of Fe$_3$O$_4$ and PFMC without phase and structural changes. SEM showed that the introduction of magnesium salt formed a tight vesicular structure, which enhanced the ability to sweep and net trap particles in water. VSM analyses showed that MPFMC can be separated by magnetic separation technology.

The best PS removal effect was achieved when the MPFMC dosage was 0.12 mmol L$^{-1}$. After considering the pH, the removal rate of PS by MPFMC reached more than 85% at pH = 4.5–9.5, indicating that MPFMC had a wide applicability to pH. Second, an appropriate temperature increase can promote hydrolysis of coagulant, thereby improving PS removal. Moreover, the removal effect of MPFMC (with an external magnetic field settlement of 10 min) was better than that of PFC (with a natural settlement of 30 min). Finally, the fractal dimensions of flocs are closely related to coagulation conditions and PS removal rates. The change of fractal dimension can well reflect the degree of flocculation of the coagulation process, indicating that the compactness of the flocs directly determines the efficiency of PS removal.

Author contributions

Haicheng Liu: resources, supervision, writing – review & editing. Jiahui Yang: conceptualization, methodology, investigation, formal analysis, writing – original draft.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

Conflicts of interest

There are no conflicts to declare.

References
