Application of PAFC/CPAM for the removal of ZnO nanoparticles by enhanced coagulation

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ABSTRACT

To cope with the increasingly severe challenges of zinc oxide nanoparticles (ZnO-NPs) in the field of the aquatic environment, this paper uses poly-aluminum ferric chloride (PAFC) and cationic polyacrylamide (CPAM) as coagulants to enhance the removal of ZnO-NPs from water. In two environments (pure-water environment and kaolin environment) that simulate suspended solids, we studied the dosage, pH, precipitation time, and hydraulic power of ZnO-NPs at three different initial concentrations (1, 2, and 30 mg/L). The effects of various conditions on the performance of PAFC, CPAM, and PAFC/CPAM to remove ZnO-NPs were examined. Results showed that the overall removal rate of ZnO-NPs in the kaolin environment was slightly higher than that in the pure-water environment. In contrast the removal rate of ZnO-NPs in the PAFC/CPAM was significantly higher than that of PAFC or CPAM alone. The coagulation removal conditions of ZnO-NPs were optimized using a response-surface model. Under the best conditions, the removal rate of ZnO-NPs with an initial mass concentration of 30 mg/L in the PAFC/CPAM combination in pure-water and kaolin environments was 98.54% and 99.17%, respectively. Finally, by studying the changes in floc size during coagulation, enhanced coagulation was an efficient method of removing ZnO-NPs from water.

Key words: coagulation, floc size, nanoparticles, response-surface optimization

HIGHLIGHTS

- The combination of PAFC and CPAM can efficiently remove ZnO-NPs.
- Kaolin can promote the removal efficiency of ZnO-NPs.
- The RSM model can reflect the optimal removal conditions for coagulation to remove ZnO-NPs.
- CPAM can further increase the particle size and compactness of ZnO-NPs flocs after coagulation.

GRAPHICAL ABSTRACT

INTRODUCTION

The use of nanomaterials in industries and daily life increases, so their negative impact and potential harm to the environment is gaining increased attention (Yang et al. 2019). Zinc oxide nanoparticles (ZnO-NPs), as a typical nanomaterial, are extensively used in cosmetics, paints, plastics, and packaging (Sharma et al. 2011). In the end, ZnO-NPs inevitably enter the ecological environment and interact with the surrounding environment, posing a severe threat to the animal, plant, and human health (Rajput et al. 2019). Through existing research, it is found
that due to the extensive use of ZnO-NPs, the concentration of ZnO-NPs in urban wastewater can reach 4.2 mg/L (Hou et al. 2013). Gottschalk et al. (2009) used probabilistic modeling methods to detect the concentration of ZnO-NPs in the water environment of a sampling area. They found that the concentration of ZnO-NPs in the sampling areas in Europe and the United States can reach 0.432 and 0.3 mg/L, respectively. However, when the concentration of ZnO-NPs in the aquatic environment comes 0.18 mg/L, it will cause many deaths of microalgae (Heinlaan et al. 2008). Not only that, in experiments on the acute toxicity of nanoparticles and their incubation rate, it was found that ZnO-NP is highly toxic to Artemia (Rohit et al. 2019). Moreover, research on the effect of different concentrations of ZnO-NPs on soybeans has shown that ZnO-NPs synthesized from olive extracts in soybean plants may be poisoned by the production of reactive oxygen species (Shahla et al. 2019). These values indicate a sufficient threat to microorganisms and plants in bodies of water.

The activated-sludge method is currently used in sewage-treatment plants to remove NPs from water bodies. However, the removal capacity is average and the process may have a toxic effect on microorganisms. Majerová et al. found that the degradation rate of carbamazepine in sewage-treatment plants is only 10% (Majerová et al. 2017). The treated wastewater still contains carbamazepine and its toxic by-products, which have a specific resistance to the purification system. Research on the removal of Ag-NPs in domestic sewage using a new type of permeable membrane bioreactor combined with a microfiltration membrane (MF-OMBR) has also shown that using Ag-NPs leads to a decrease in species richness in the MF-OMBR (Wang et al. 2017). As an essential process of traditional water treatment, coagulation is significant to the research on removing NPs (Gedda et al. 2021). Some studies have confirmed that NPs can be removed from water by coagulation. Serrão et al. (2017) used a common polyaluminum-based coagulant to treat TiO2 NPs through traditional coagulation/flocculation/sedimentation (C/F/S). They found that the removal ability is strongly affected by water characteristics. Hydrophobic water requires a higher coagulant dosage than hydrophilic water to achieve the same removal of TiO2 NPs. Another study has reported removing different initial sizes of TiO2, ZnO, and cerium oxide NP aqueous suspensions with coagulants. The ability to remove TiO2 is only about 68.8%, whereas the removal of ZnO-NPs is affected by a more significant pH, and the removal rate is only 61.8% under low pH (Sarawanvijit et al. 2014). In addition, through the use of poly-ferric chloride to conduct coagulation experiments on 3–4 mg/L ZnO-NPs, it was found that even at the highest dosage of coagulant, there were still 25% ZnO-NPs in the solution (Khan et al. 2019). Thus, although the current coagulation method has achieved certain results in removing ZnO-NPs, the removal rate is relatively low, the removal result is unstable, and the amount of coagulant required is large. These findings may be due to using a single iron-based or a single aluminum-based coagulant for NP removal.

The polyaluminum ferric chloride (PAFC) used in this study combines aluminum salt coagulant and iron salt coagulant advantages. Meanwhile, cationic polyacrylamide (CPAM) remove flocculated negatively charged colloids (Xu et al. 2015). In addition, it enhances the adsorption bridging effect, and significantly improves the flocculation capacity of a coagulant (Sun et al. 2014; Wang et al. 2018). Most current studies focus only on removing single-target pollutants (e.g., ZnO-NPs), and other suspended solids remain in natural water bodies. Thus, the coagulation of suspended solids in water to remove ZnO is necessary to perform. Kaolin is a widespread mineral in aquatic systems, and NPs are likely to interact with these clay minerals. pH, ionic strength, and humic acid all affect the aggregation of NPs in the kaolin system (Wang et al. 2015). Accordingly, the complex interaction of coagulant dosage, pH, kaolin, and NPs determines the colloidal stability of NPs, and systematic analysis and research are necessary. This interaction can enable further understanding of the removal and transformation law of NPs in water and help identify an efficient and low-cost method for removing NPs from water.

In the present work, the use of PAFC and CPAM coagulation was proposed to enhance the removal of ZnO-NPs from water. First, the interaction between kaolin and ZnO-NPs was macro-characterized by ultraviolet-visible spectroscopy to understand the ability and mechanism of coagulation to treat kaolin and ZnO-NPs. ZnO-NPs were then characterized by their turbidity and removal rate. Three different initial concentrations (1, 2, and 30 mg/L) in two environments (pure-water environment and kaolin environment) simulated suspended solids were studied. Under the condition of ZnO-NPs, the effects of dosage, pH, precipitation time, and hydraulic conditions on the removal performance of PAFC, CPAM and PAFC/CPAM to remove ZnO-NPs were explored through single-factor analysis and determine PAFC, CPAM, and PAFC/ The optimum condition interval for CPAM to remove ZnO-NPs. Moreover, through the response-surface method (Box–Behnken model) design principle, the dosages of the inorganic coagulant PAFC and the organic flocculant CPAM and the hydraulic
conditions were taken as the inspection objects, and the ZnO-NP removal rate was the response value. The coagulation removal conditions were optimized, the influence of the interaction between various factors was analyzed, and the optimal removal conditions were determined. Finally, a laser particle-size analyzer was used to measure the flocs’ particle size changes during coagulation.

METHODOLOGY

Materials

The ZnO-NPs used in the experiments were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd PAFC with 26% iron and aluminum content from Gongyi Tenglong Water Treatment Materials Co., Ltd was selected as the inorganic coagulant. The CPAM was produced by Tianjin Zhishuang Chemical Reagent Co., Ltd with a molecular weight of 12 million and analytical purity. The suspended solids in the water used chemically pure kaolin purchased from Shanghai Sinopharm Group.

Methods and process

The water samples needed for the experiment were prepared by adding different mass concentrations of ZnO-NPs to pure water. First, a ZnO-NP stock solution with a mass concentration of 50 mg/L was prepared, and the pH was adjusted to 7 with HCl and NaOH (concentration = 1.0 mol/L). The ZnO-NP stock solution was sonicated under 250 W power for 30 min to obtain a stable ZnO-NP suspension. After weighing 50 g of kaolin with an electronic balance (FA2204, Shanghai Liangping Instrument Co., Ltd, China), it was placed in a 500 mL volumetric flask and then pure water was used to make a 100 g/L kaolin suspension. The ZnO-NP and kaolin suspension were subjected to ultrasonic cleaning (KQ-500DB, Kunshan Ultrasonic Instrument Co., Ltd, China) for 30 min before each use. About 500 mg/L CPAM solution was prepared, and a dual-digital thermostat magnetic stirrer (85-2A, Jintan Chengdong Xinrui Instrument Factory, China) was used at 50 °C and 250 r/min rotating speed for 1 h to fully dissolve the solids. In the coagulation process, PAFC was used as the inorganic coagulant, and CPAM was used as the organic coagulant. A six-unit electric mixer (JJ-4, Guohua Electric Co., Ltd, China) was used to rapidly stir the solution at 200 r/min for 2 min and then to stir it at 80 r/min for 10 min slowly. After coagulation, the solution was allowed to stand for 30 min, and the sample at 2 cm below the liquid surface was collected. The turbidity of the water sample was measured with a HACH2100Q turbidity meter. Because ZnO-NPs have an obvious absorption peak at 365 nm (Figure S1), kaolin will not affect the peak generation. Therefore, an ultraviolet-visible spectrophotometer (UV-5500, Shanghai Yuanxi Instrument Co., Ltd, China) was used to measure the absorbance of ZnO-NPs at a wavelength of 365 nm. We repeated each experiment three times, and the relative error was less than 5%.

The laser particle-size analyzer (Winner 2018, Jinan Micronano Particle Instrument Co., Ltd, China), a peristaltic pump (BT2100-2 J, Longer pump, China), and coagulation stirrer were connected using a silicone tube with an inner diameter of 8 mm. The test device is shown in Figure S2. The coagulation water sample containing flocs was circulated from the mixing cup through the laser particle-size analyzer by using a peristaltic pump and then returned to the coagulation mixer. The flow rate was controlled at 2 L·h⁻¹. The average particle size (d0.5) was automatically recorded with a computer every 30 s to characterize the floc size.

RESULTS AND DISCUSSION

Effect of dosage on the removal of ZnO-NPs

As shown in Figure 1, the optimal dosage of PAFC for removing three different mass concentrations of ZnO-NPs under the two systems was 80 mg/L, and the optimal dosage of CPAM was 3 mg/L. At the same time, we compounded 1–6 mg/L CPAM based on the optimal dosage of PAFC 80 mg/L and found that the combination with the best removal effect was 80 mg/L PAFC and 5 mg/L CPAM. The turbidity of PAFC, CPAM, and PAFC/CPAM and the removal rate of ZnO-NPs, increased with increased coagulant dosage. After the dosage exceeded the optimal critical point, the CPAM removal performance was significantly reduced. In terms of the removal performance and stability of the two systems, PAFC/CPAM > PAFC > CPAM, and the removal rate of high ZnO initial mass concentration was better than that of low ZnO initial mass concentration. In the pure-water system, the maximum removal rate of ZnO-NPs at the initial mass concentrations of 1, 2, and 30 mg/L by PAFC was 71.43%, 87.63%, and 95.90%, respectively. In contrast, the removal rate of three concentrations of ZnO-NPs by PAFC/CPAM increased to 83.53%, 92.78%, and 98.54%, respectively. This is consistent with the
result that Sun et al. (Sun et al. 2017) found that the coagulant pairing has improved the removal effect of ZnO-NPs. The removal capacity of the kaolin system was better than that of the ZnO system alone. The maximum removal rate of ZnO-NPs with an initial mass concentration of 30 mg/L under the ZnO system and the kaolin system by PAFC increased from 95.90% to 97.14%.

First, a coagulation to remove ZnO-NPs, optimal dosage of the three flocculants was required. After reaching the critical point of the optimal dosage, the removal rate of turbidity and ZnO-NPs by CPAM decreased by nearly
40% with increased dosage, whereas the removal ability of PAFC and PAFC/CPAM tended to stabilize. This finding was primarily due to the ability of PAFC to ionize iron ions and aluminum ions in water because of the action of water molecules, and these ions were present in the ZnO-NPs water sample in the form of positive charges. Under neutral and alkaline conditions, the surface of ZnO-NPs was negatively charged (Emilie et al. 2019), so PAFC can neutralize the negative charge on the surface ZnO-NPs, thereby stably removing NPs. However, CPAM can ionize a large number of cations in water. After neutralizing ZnO-NPs, the remaining cations increased the steric hindrance effect among ZnO-NPs, resulting in the stability of the colloid and hindering the aggregation (Sang et al. 2019). Second, for the higher removal rate of high ZnO initial mass concentration than that of low ZnO initial mass concentration, the increase in the initial mass concentration may have increased the chances of collision among ZnO-NPs and the formation of floc cores (Sun et al. 2021). With the addition of PAFC and CPAM, the adsorption and co-precipitation efficiency between the flocculant and ZnO-NPs was better, so the water sample turbidity removal rate and ZnO-NP removal rate increased with increased initial mass concentration of ZnO-NPs. Moreover, PAFC/CPAM had higher removal stability than PAFC because the CPAM molecular chain can be fixed on the surface of NPs in ZnO-NPs water samples. The bridging effect of linear polymers was enhanced and passed through the adsorption frame (Sun et al. 2020). The bridging effect induced PAFC/CPAM and ZnO-NPs to quickly form flocs, which gradually enlarged and caused the removal capacity to stabilize. The removal rate of the kaolin system was better than that of the pure-water system because the addition of kaolin exerted net trapping and sweeping. The negative charge of kaolin in water under alkaline conditions enabled it to co-adsorb with ZnO-NPs, and the positively charged flocculant increased the flocs' density.

**Effect of pH on the removal of ZnO-NPs**

By combining 80 mg/L, PAFC with the best coagulation effect and 3 mg/L CPAM, pH on the coagulation removal of ZnO-NPs and solution turbidity was studied. As shown in Figure 2, the ZnO-NP removal rate and turbidity removal rate curves of the three initial mass concentrations (1, 2, 30 mg/L) in the pure-water and kaolin systems increased rapidly with increased pH before remaining unchanged. Obviously, The removal performance of CPAM was the most affected by pH. Under the condition of the initial concentration of 30 mg/L ZnO-NPs, with increased pH, the removal rate differed by nearly 60%, whereas the removal rate of PAFC and PAFC/CPAM remained stable. By comparison, under the conditions of low initial concentration of ZnO-NPs of 1 and 2 mg/L, PAFC, CPAM, and PAFC/CPAM were all affected to varying degrees with changes in pH. Under acidic conditions, the removal rate of turbidity and ZnO-NPs by CPAM in the pure-water system was only about 10%–20%, whereas for the kaolin system, the removal rate of CPAM on turbidity and ZnO-NPs reached nearly 60%. However, the kaolin system had little effect on removing ZnO-NPs by PAFC and PAFC/CPAM. When the pH of the initial water sample increased to 9, the removal rate of the three initial concentrations of ZnO-NPs increased rapidly and reached the maximum. In the kaolin system, the removal rate of ZnO-NPs removed by PAFC/CPAM coagulation all achieved more than 90%. This is about 30% higher than in the previous study, using conventional coagulants to remove ZnO-NPs (Surawanvijit et al. 2014). Conversely, under alkaline conditions, the removal efficiency of PAFC, CPAM, and PAFC/CPAM remained almost unchanged, indicating that high pH almost did not affect removing turbidity and ZnO-NP removal rate of ZnO-NPs from water by the three flocculants. In general, the turbidity and removal rate of ZnO-NPs under alkaline conditions were better than those under acidic conditions and were more stable. This discrepancy was pronounced in the pure-water system.

The above experimental phenomena indicated that the ZnO-NP removal rate and turbidity removal rate curve change trends were identical, suggesting a correlation between the concentration of water samples and turbidity. That turbidity can be supplemented to some extent. The change in pH of the water sample can directly affect the change trends were identical, suggesting a correlation between the concentration of water samples and turbidity. However, neutral and alkaline conditions, the surface of ZnO-NPs was negatively charged due to the loss of protons. The cations ionized by CPAM in water neutralized the negative surface charge of ZnO-NPs, and the NPs continued to agglomerate into large particles. The flocs were thus removed from the water. However,
under high alkaline conditions, CPAM was also negatively charged, so the particle repulsion in the solution was dominant, and the flocculation and precipitation performances were reduced. For PAFC alone, its removal rate was slightly better than that of CPAM alone. On the one hand, the single function of an inorganic coagulant was better than that of a polymer organic flocculant. On the other hand, under alkaline conditions, the aluminum and

Figure 2 | Effect of PH on the removal rate and turbidity of ZnO-NPs at different concentrations: (a) 1 mg/L ZnO-NPs removal rate, (b) 2 mg/L ZnO-NPs removal rate, (c) 30 mg/L ZnO-NPs removal rate, (d) turbidity change at 1 mg/L ZnO-NPs, (e) turbidity change at 2 mg/L ZnO-NPs, and (f) turbidity change at 30 mg/L ZnO-NPs.
iron ions ionized by PAFC neutralized the negatively charged ZnO-NPs due to the loss of protons on the surface. However, with increased pH, the negative charge on the surface of the NPs increased, and the repulsive force among the particles increased. ZnO-NPs were not easily removed, and under high alkaline conditions, PAFC was prone to hydrolysis and precipitation to form hydroxides, so the removal rate dropped. For PAFC/CPAM compound, compared with the addition of PAFC or CPAM alone, the ability to remove ZnO-NPs was better and more stable. We speculated that because the network structure of PAFC/CPAM polymer significantly increased the specific surface area of the flocculant, it played a stronger role in adsorption and bridging, and its ability to adapt to changes pH was also stronger.

Effect of settling time on the removal of ZnO-NPs

By combining 80 mg/L PAFC with the best coagulation effect and 3 mg/L CPAM, the impact of sedimentation time on the coagulation removal of ZnO-NPs and solution turbidity was studied. As shown in Figure 3, the turbidity and removal rate of ZnO-NPs increased with increased precipitation time and eventually reached a stable value. First, when only the coagulant PAFC was added, the removal rate of the three initial concentrations of ZnO (1, 2, and 30 mg/L) in the pure-water and kaolin systems all became stable after 30 min of precipitation. For the flocculant CPAM and PAFC/CPAM, the precipitation time required only 15–20 min. In the pure-water and kaolin systems, the removal rate of CPAM for 1 and 2 mg/L ZnO-NPs at a precipitation time of 5 min was only about 10–20%, whereas the initial concentration of 30 mg/L ZnO-NPs at the end of coagulation. The removal rate in the last 5 min can reach 70%. As for PAFC/CPAM, the removal rate of ZnO-NPs with initial concentrations of 2 and 30 mg/L can reach almost 80% within 5 min of precipitation time. Second, the precipitation time of CPAM and PAFC/CPAM to remove ZnO-NPs was significantly shorter than that of PAFC alone. In general, the removal rate of ZnO-NPs at 30 min was the maximum removal performance among the three flocculants, i.e., the optimal removal rate. At this time, the maximum removal rates of 30 mg/L ZnO-NP for CPAM, PAFC and PAFC/CPAM in the kaolin system were 87.27%, 97.14% and 99.17%, respectively.

The combination of PAFC, CPAM, and PAFC/CPAM had roughly the same precipitation time change curve of ZnO-NP removal rate and turbidity removal rate at three different initial concentrations (1, 2, and 30 mg/L) in the pure-water and kaolin systems. With prolonged precipitation time, the removal rate of ZnO-NPs continuously increased. When PAFC alone was added, the precipitation time was 30 min, after which the removal rate hardly increased; when CPAM alone was added, the precipitation time was 15 min, after which the removal rate hardly increased. By comparison, the optimal precipitation time of the ZnO-NP water sample treated with CPAM was twice as short as that treated with PAFC mostly because the aluminum ion produced by the inorganic coagulant PAFC generated a high polymer, and the surface of the high-polymer complexes had iron ions that rendered it positively charged. At this time, only adsorption and neutralization were dominant. The organic flocculant polymer CPAM had cationic groups and active adsorption groups on the molecular chain. Its long polymer chains and small floc particles were adsorbed, i.e., ZnO-NPs were removed primarily by adsorption bridging. As a result of its action, the floc particles immediately enlarged and the precipitation rate of ZnO-NPs greatly accelerated under the action of the net trapping and sweeping. By observing the experimental process, the flocs were found to be still in the stage of coagulation of PAFC, and ZnO-NPs were small and the sedimentation speed was slow. Although the removal rate of ZnO-NPs was better than that of the organic flocculant CPAM, the sedimentation time was longer. It also greatly increased the engineering cost PAFC/CPAM can combine the advantages of inorganic and organic flocculants. The removal rate of ZnO-NPs increased, and the required precipitation time was greatly reduced. Figure 3(c) shows that the removal rates of 30 mg/L ZnO-NPs in the kaolin and pure-water systems reached 98.54% and 99.17%, respectively.

Effect of hydraulic condition on the removal of ZnO-NPs

As shown in Figure 4, we investigated that the pH value is 9, the precipitation time is 30 min, PAFC (80 mg/L) is compounded with CPAM (3 mg/L), and the slow rotation speed is 80 r/min (10 min). Rotation speed (2 min) on the removal effect of ZnO-NPs. The results show that the removal rate of ZnO-NPs at each initial concentration reached the maximum under the condition of a fast-turning speed of 200 r/min. The trend of the ZnO-NP removal curve for the two systems was consistent with the change in hydraulic conditions. First, for the flocculant CPAM, hydraulic conditions had a more significant impact on removing the three initial concentrations of ZnO-NPs. Second, for PAFC and PAFC/CPAM, hydraulic conditions had a more significant effect on the removal of ZnO at low initial concentrations of 1 and 2 mg/L. The high initial concentration of 30 mg/L ZnO had little effect
In the pure-water system, when the rotation speeds were fast, i.e., 200 and 350 r/min, the removal rates of 1 mg/L ZnO-NPs by CPAM were 47.67% and 11.90%, respectively (a difference of about 35%), and the removal rate was 30 mg/L. The rates were 78.04% and 61.84%, respectively, and the difference was about 16.2%.

**Figure 3** | Effect of sedimentation time on the removal rate and turbidity of ZnO-NPs at different concentrations: (a) 1 mg/L ZnO-NPs removal rate, (b) 2 mg/L ZnO-NPs removal rate, (c) 30 mg/L ZnO-NPs removal rate, (d) turbidity change at 1 mg/L ZnO-NPs, (e) turbidity change at 2 mg/L ZnO-NPs, and (f) turbidity change at 30 mg/L ZnO-NPs.

On removal. In the pure-water system, when the rotation speeds were fast, i.e., 200 and 350 r/min, the removal rates of 1 mg/L ZnO-NPs by CPAM were 47.67% and 11.90%, respectively (a difference of about 35%), and the removal rate was 30 mg/L. The rates were 78.04% and 61.84%, respectively, and the difference was about
15%. The removal rates of 1 mg/L ZnO-NPs by PAFC/CPAM were 83.33% and 23.81%, and the difference was about 60%. The removal rates of 30 mg/L were 97.22% and 92.59%, respectively, and the difference was only about 5%. In the kaolin system, the removal rates of 10 mg/L ZnO-NPs by PAFC/CPAM were 96.28% and 90.13% when the fast rotation speed was 200 and 350 r/min, respectively. The coagulation removal stability of

Figure 4 | Effect of hydraulic condition on the removal rate and turbidity of ZnO-NPs at different concentrations: (a) 1 mg/L ZnO-NPs removal rate, (b) 2 mg/L ZnO-NPs removal rate, (c) 30 mg/L ZnO-NPs removal rate, (d) turbidity change at 1 mg/L ZnO-NPs, (e) turbidity change at 2 mg/L ZnO-NPs, and (f) turbidity change at 30 mg/L ZnO-NPs.
ZnO-NPs with higher initial concentration and lower initial concentration of ZnO-NPs was stronger against those under hydraulic conditions. Second, the speed of fast stirring can also be obtained. The difference of fast stirring G value had a greater impact on the removal of ZnO-NPs by the three flocculants.

Hydraulic conditions include two factors: stirring speed and stirring time. These factors can be reflected by the G value, which is the speed gradient of mixing and reaction. It is an important factor affecting the removal rate of ZnO-NPs in coagulation and is particularly critical for forming and breaking flocs (Mohammadighavam et al. 2016). First, Figure 4 shows that for the removal of ZnO-NPs with low initial concentrations of 1 and 2 mg/L, the change in fast-turning speed had a greater impact on it. The main reason was that the concentration of ZnO-NPs was too low and generating large and stable ZnO-NPs was difficult. The flocs can adapt to changes in hydraulic conditions. When the initial concentration of ZnO-NPs of 30 mg/L was added to the water sample, the influence of hydraulic conditions was relatively small the system was more stable. Second, the rapid stirring speed during mixing cannot be too low because this was not conducive to the demulsification of the solution and the stability of the colloid, and a good mixing result cannot be achieved. Thus, the speed of 100 r/min during rapid mixing was too low. The G value was too small, and the collision probability between the flocculant and ZnO-NPs was small, thereby preventing a good flocculation environment. With a continuous increase from 100 r/min to 250 r/min, the chance of collision among particles increased, and flocs were continuously generated and became denser. Thus, at 250 r/min, the removal rate of ZnO-NPs reached the maximum value. However, when the stirring speed exceeded 250 r/min, it affected the aggregation of particles in the solution and destroyed the formed flocs. In particular, when the high-molecular-weight organic flocculant CPAM was added in the experiment because the rotation speed was too high, the adsorption bridging effect of this polymer was not successfully completed and its structure was destroyed. As a result, the removal rate of ZnO-NPs was greatly reduced.

Response-surface analysis
Based on the coagulation removal experiment of ZnO-NPs with an initial concentration of 30 mg/L in the kaolin system, according to the response-surface method (Box–Behnken model) design principle, we used the PAFC dosage, the CPAM dosage, and the hydraulic conditions as the object of investigation, as well as the ZnO-NP removal rate as the response value. The coagulation removal conditions of ZnO-NPs were designed for the experiment. The experimental factors and levels are shown in Table 1. A three-factor three-level experimental design was carried out for the removal conditions of ZnO-NPs, and a mathematical regression model was established, as shown in Table 2.

Response-surface model
The slope of the response surface graph reflects the influence of various factors on the removal rate of ZnO-NPs. The larger the slope, the greater the influence. The shape of the contour line reflects the influence of the interaction of the two factors on the removal rate. The closer to the ellipse, have more significant the impact. From Figure 5(a)–5(c), it can be seen that the significance of the influence of each factor on the removal rate of ZnO-NPs is hydraulic conditions, PAFC dosage, CPAM dosage, and three factors in the interaction. None of the interactions has a significant effect, and this conclusion is consistent with the conclusion obtained from the analysis of variance in Table 3.

It can be seen from Figure (a) that within the selected coagulant concentration range, the PAFC dosage and CPAM dosage have the best effect on the removal rate of ZnO-NPs, and the dosage of PAFC is 72.00–93.50 mg/L, the dosage of CPAM is 2.00–4.00 mg/L. And compared with the hydraulic conditions, the interaction between the dosage of PAFC and CPAM has no significant effect on the removal rate of ZnO-NPs.

**Table 1 | Analytical factors and levels for RSM**

| Number | Factor                      | Level   |
|--------|-----------------------------|---------|
| A      | PAFC dosage (mg/L)         | 60      | 80  | 100  |
| B      | CPAM dosage (mg/L)         | 1       | 3   | 5    |
| C      | hydraulic condition (r/min)| 100     | 200 | 300  |
Figure (b) shows that within the selected conditions, the removal rate of ZnO-NPs by PAFC increases first and then decreases; with the increase of hydraulic conditions, the removal rate of ZnO-NPs also has a peak. Among them, the optimal range of PAFC dosage is 70.00–95.00 mg/L, and the optimal range of hydraulic conditions is 175–280 r/min. It can be seen that hydraulic conditions have a greater impact on the removal rate of ZnO-NPs, which is consistent with the variance of the regression equation. The analysis results are consistent. It can be seen from Figure (c) that when the CPAM dosage and hydraulic conditions are fixed, there is a peak in the effect of another factor on the removal rate of ZnO-NPs, and the best ranges of the two are 1.80–4.40 mg/L and 175–280 r/min.

**Variance analysis**

The regression equation between PAFC dosage, CPAM dosage, hydraulic conditions, and ZnO-NP removal rate is shown in Equation (1).

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\text{ZnO-NP removal rate} = 98.73 + 0.77A + 2.27C - 2.85A^2 - 2.76B^2 - 3.70C^2
\]  

(1)

Table 3 shows the analysis of variance of the regression equation. The model was highly significant (F = 29.83, P < 0.0001). The significant effects were hydraulic conditions, PAFC dosage(C), CPAM dosage(A), and their interaction(B). The squared terms (A^2, B^2, C^2) and cross product terms (AB, AC, BC) in the model equation indicate the process variables quadratic effects, and interactive effects. The interaction of these factors had no significant influence, consistent with the results of response-surface analysis. The lack of fit of the model was not significant (P > 0.05), and the coefficient of determination R^2 was 0.9746. The coefficient of determination Radj^2 for the model correction was 0.9419, indicating that the model can explain 94.19% of the response-value change. The actual value had a good correlation with the predicted value. This model can optimize the analysis and prediction of the removal of ZnO-NPs by PAFC/CPAM.

**Model validation**

To achieve the optimization of PAFC/CPAM coagulation removal conditions for ZnO-NPs, the regression equation shown in Equation (1) was analyzed and solved, and the optimal removal conditions for ZnO-NPs were obtained as follows: PAFC dosage of 82.60 mg/L, CPAM dosage of 3.11 mg/L, and hydraulic conditions of 2 min fast rotation (231.04 r/min) and 10 min of slow rotation (80 r/min). Under these conditions, the
theoretical value of ZnO-NP removal rate was 99.14%. The accuracy of the model was verified, and the predicted removal conditions were corrected. Under the conditions of PAFC dosage of 82.00 mg/L, CPAM dosage of 3.10 mg/L, and hydraulic conditions of 2 min with a fast rotation speed of 230 r/min, the three groups were carried out. Parallel experiments showed that the removal rates of ZnO-NPs were 97.76%, 98.91%, and 99.17% (average = 98.61%). The relative error between the experimental and predicted values was 0.54%, proving that the model can better reflect the coagulation removal and the optimal removal conditions for ZnO-NPs.

Monitoring of floc particle size

As shown in Figure 6, the flocs formed at 80 mg/L PAFC + 3 mg/L CPAM (containing 2 mg/L ZnO and 30 mg/L kaolin) after flocculation had larger particle sizes than those obtained at 80 mg/L PAFC + 3 mg/L CPAM (containing 2 mg/L ZnO). Thus, the flocs formed by the kaolin NPs containing kaolin were larger in volume and denser than the flocs formed by ZnO-NPs without kaolin. In the water sample containing only ZnO-NPs, the

Figure 5 | (a) Mutual effect of PAFC dosage and CPAM dosage on ZnO-NP removal rate. (b) Mutual effect of PAFC dosage and hydraulic condition on ZnO-NP removal rate. (c) Mutual effect of CPAM dosage and hydraulic condition on ZnO-NP removal rate. (d–f) Contour map corresponding to 3D graphics.
Particle size (d0.5) of flocs formed by adding 80 mg/L PAFC was about 130 μm, and that of flocs formed by adding 80 mg/L PAFC and 3 mg/L CPAM (d0.5) was about 250 μm. In the water sample containing kaolin and ZnO-NPs, the particle size (d0.5) of the flocs formed by adding 80 mg/L PAFC was about 150 μm, whereas the flocs formed by adding 80 mg/L PAFC and 3 mg/L CPAM had a particle size (d0.5) of about 280 μm. The particle-size distribution of the flocs after flocculation showed that CPAM addition helped improve the compactness and particle size of the flocs. The calculation of particle size showed that CPAM addition could increase the particle size of the flocs by about 90%.

When PAFC alone was used in the coagulation system, the positive charge generated by the hydrolysis of aluminum salt and iron salt was less, so PAFC did not provide sufficient positive charge to neutralize the negative charge on the surface of suspended particles, leading to loose flocs and small particle size (Zhang et al. 2015). After adding CPAM, the positive charge on the CPAM polymer chain further neutralized the negative charge.

### Table 3 | Analysis of variance

| Source | Sum of Squares | df | Mean Square | F Value | p-value Prob > F |
|--------|----------------|----|-------------|---------|-----------------|
| Model  | 185.67         | 9  | 20.63       | 29.83   | <0.0001 Significant |
| A      | 4.68           | 1  | 4.68        | 6.77    | 0.0553 Significant |
| B      | 0.10           | 1  | 0.10        | 0.14    | 0.7164 Not significant |
| C      | 41.36          | 1  | 41.36       | 59.80   | 0.0001 Significant |
| AB     | 0.00           | 1  | 0.00        | 0.00    | 0.9954 Not significant |
| AC     | 0.02           | 1  | 0.02        | 0.02    | 0.8848 Not significant |
| BC     | 1.46           | 1  | 1.46        | 2.12    | 0.1890 Not significant |
| A²     | 34.22          | 1  | 34.22       | 49.49   | 0.0002 Significant |
| B²     | 32.04          | 1  | 32.04       | 46.33   | 0.0003 Significant |
| C²     | 57.60          | 1  | 57.60       | 83.28   | <0.0001 Significant |
| Residual | 4.84       | 7  | 0.69        |         |                 |
| Lack of Fit | 2.88       | 3  | 0.96        | 1.95    | 0.2633 Not significant |
| Pure Error | 1.96       | 4  | 0.49        |         |                 |
| Cor Total | 190.51      | 16 |             |         |                 |

### Figure 6
Flocc particle size of (a) 80 mg/L PAFC with 2 mg/L ZnO, (b) 80 mg/L PAFC with 2 mg/L ZnO and 30 mg/L kaolin, (c) 80 mg/L PAFC + 3 mg/L CPAM with 2 mg/L ZnO, and (d) 80 mg/L PAFC + 3 mg/L CPAM with 2 mg/L ZnO and 30 mg/L kaolin.
on the surface of ZnO-NPs, so the suspended particles were adsorbed, neutralized, and destabilized. Eventually adsorption bridging occurred during coagulation, which enabled PAFC and the flocs formed by CPAM and ZnO-NPs to effectively aggregate and grow, further increasing the degree of compaction between the flocs.

CONCLUSION
The dosage and initial water samples were studied under three different initial concentrations (1, 2, and 30 mg/L) of ZnO-NPs in two environments (pure-water and environments) simulating suspended solids in water. The effects of pH, precipitation time, and hydraulic conditions on the ZnO-NP removal performance of PAFC, CPAM, and PAFC/CPAM were explored. In the two systems of pure water and kaolin, the turbidity of the ZnO-NP water sample and the removal rate of ZnO-NPs increased with increased initial mass concentration ZnO-NPs, and the removal ability of kaolin system was greater. The removal of NPs had a promoting effect. Single-factor experimental analysis and the response-surface analysis revealed that when the initial pH of the water sample was 9, 80.00 mg/L PAFC was added for rapid stirring at 200 r/min for 2 min. Then, 3.00 mg/L CPAM was added and the solution was slowly stirred at 80 r/min for 10 min. Under these conditions, the combination of the inorganic coagulant PAFC and the organic flocculant CPAM achieved the best ZnO-NPs removal effect. For the pure-water system, the removal rates of ZnO for the three initial mass concentrations of PAFC/CPAM for 1, 2, and 30 mg/L were 83.33%, 92.78%, and 98.54%, respectively. For the kaolin system, the removal rates of ZnO at the three initial mass concentrations of 1, 2, and 30 mg/L by PAFC/CPAM were 89.51%, 93.13%, and 99.17%, respectively. Therefore, we proved that enhanced coagulation could effectively remove ZnO-NPs from water bodies and thus provided theoretical support for removing ZnO-NPs from complex water environments.

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DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.

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