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Novel ferromagnetic nanoparticle composited PACls and their coagulation characteristics

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ABSTRACT

Effects of magnetic nanoparticles on inorganic coagulants and their coagulation performances were studied in the present work. The Fe_3O_4 – SiO_2 core-shell particle (FSCSP) and superfine iron (SI), were compounded with polyaluminium chloride of basicity 2.0 (PACl2.0), providing magnetic PACl2.0s (MPACl2.0s). The physiochemical properties of ferromagnetic nanoparticles were investigated using transmission electron microscopy (TEM), the BET method and a zeta potentiometric analyzer. The Al species distributions of the MPACl2.0s and PACl2.0 were examined by liquid ^{27}Al NMR. Jar tests were employed to evaluate the coagulation performances. Floc properties were assessed by use of the electromotive microscope (EM) and small angle laser light scattering (SALLS). The results showed that modified layers of nanoparticles mitigated agglomeration. FSCSP had a larger specific area and pore volume than SI. The addition of ferromagnetic nanoparticles obviously increased the content of Al_{un} . MPACl2.0s performed better than PACl2.0 in turbidity removal and DOC removal when dosed less than 0.06 mmol/L as Al. Generally, PACl2.0 + FSCSP (50 mg/L) performed best. Large, loose and weak flocs were produced by MPACl2.0s, which were preferred for the magnetic powder recycling. A plausible structure, Al species-nanoparticles cluster, contributing to the unique properties of MPACl2.0 flocs, was proposed.

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1. Introduction

Magnetic coagulation, the combination of magnetic materials and coagulants, has been tested for its effectiveness. The presence of ferromagnetic materials and magnetic fields makes magnetic collection and separation possible, leading to higher efficiency, larger handling capacity, easier manipulation and comparatively lower energy consumption (Ambashta and Sillanpää, 2010). Hence, investigations have been mainly focused on several aspects as follows: (I) Seeding of magnetic particles in the treating water to produce magnetic flocs that can be rapidly collected in a magnetic separator (Li et al., 2010); (II) Integration of magnetic ion exchange (MIEX®)

hybrid systems (Singer and Bilyk, 2002) to improve treatment efficiency (Zhang et al., 2007; Korbutowicz et al., 2008); (III) Development and improvement of the magnetic separation system/instrument (Svoboda and Fujita, 2003); (IV) Development of magnetic coagulants by compounding magnetic materials with traditional coagulants.

Although magnetic seeding coagulation and MIEX® resin adsorption can greatly improve removal efficiency, the expense of the magnetic powder and MIEX® resin have restricted their practical application. Nanosorbents, nanocatalysts and so on have been evaluated (Savage and Diallo, 2005). In aqueous systems, iron oxide particles are hydrated, and Fe–OH groups can completely cover their surface.

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Hydrous iron oxides have an amphoteric character. The Fe–OH sites on the surface can react with H^+ or OH^- ions from dissolved acids or bases. A positive (Fe–OH $^{2+}$) or negative (Fe–O $^-$) charges can be formed on the surface by protolytic reactions depending on the pH of the electrolyte solution (Illés and Tombácz, 2006). Magnetic nanoparticles exhibit a finite-size effect and/or high surface-to-volume ratio, resulting in a higher adsorption capacity. Additionally, the magnetic flocculants can be recovered by an external magnetic field.

Therefore, there is high interest in the application of magnetic nanomaterials to water treatment (Shen et al., 2009). Composite magnetic coagulants are considered to have advantages over traditional coagulants since their magnetic components may optimize coagulation behaviors and facilitate the magnetic separation following the coagulation process. Jiang et al. (2010) successfully synthesized magnetic polyferric chloride (MPFC) by combining Fe $_3$ O $_4$ nanoparticles with PFC. The MPFC, a physical mixture, gave a synergistic improvement in *Microcystis aeruginosa* removal efficiency compared to only PFC. Coagulated flocs showed a higher settling velocity by wrapping up Fe $_3$ O $_4$. Liu et al. (2006) developed a special flocculant to control freshwater cyanobacterial blooms. In their study, hydrochloric acid was firstly mixed with flyash in a proper ratio for modification, and the mixture and the magnetic powder were then put into the algae contaminated water; the aquatic hazardous substances (algal toxins) were thereby effectively adsorbed and removed.

Polyaluminum chloride (PACl) has been widely used and claimed to be superior to other traditional coagulants since it had the advantages of less alkalinity consumption and wider temperature and pH tolerance (Odegaard et al., 1990; Van Benschoten and Edzwald, 1990). The hydrolysis products of PACl comprise a series of Al species, especially Al $_{13}$ polycation, $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, which has been widely accepted as the critical species in particle aggregation by strong charge neutralization (Johansson, 1960). In addition, PACl can be temporarily refractory to hydrolysis before adsorption onto particle surfaces (Hu et al., 2006). Thus, combining ferromagnetic nanoparticles with PACl should produce favorable results. However, almost no research has addressed this to date, especially the magnetic coagulation mechanism and the characterizations of the formed flocs.

In the present work, ferromagnetic nanoparticles were mixed with PACl2.0 to develop a novel composite magnetic coagulant MAPCl2.0. The developed coagulant was characterized in terms of Al species distributions by a liquid ^{27}Al NMR method. In addition, jar tests were conducted to evaluate the MPACl2.0's performance by examining turbidity and DOC removal. The formation, breakage and regrowth of MPACl2.0 flocs were subsequently investigated. Finally, a model was proposed to elucidate the coagulation mechanisms of MPACl2.0s with special emphasis on the role of the ferromagnetic nanoparticles.

2. Material and methods

2.1. Chemicals

FeCl $_3 \cdot 6H_2O$, FeCl $_2 \cdot 4H_2O$, NaHCO $_3$, tetraethyl orthosilicate (TEOS) and absolute ethanol were obtained from the

National Medicines Corporation Ltd. of China. NH $_3 \cdot H_2O$, NaOH and hydrochloric acid were provided by Beijing Chemical Plant. AlCl $_3 \cdot 6H_2O$, NaNO $_3$ and Kaolin were obtained from the Xilong Chemical Corporation Ltd. of Shantou, the Jinke Fine Chemical Institute of Tianjin, and the Dongxu Chemical Plant of Beijing, China, respectively. Humic acid was produced by Sigma–Aldrich Corporation Ltd. of USA.

All reagents were of analytical grade without further purification except for being specified, and deionized water was used in preparing all solutions.

2.2. Preparation of the ferromagnetic nanoparticles

Fe $_3$ O $_4$ –SiO $_2$ core-shell particles (FSCSP) were prepared in the laboratory. Firstly, Fe $_3$ O $_4$ particles were synthesized by coprecipitation (Hong et al., 2009): FeCl $_3$ and FeCl $_2$ with a molar ratio of 1.7 were prepared in an N $_2$ atmosphere. Excess ammonia aqueous solution was then quickly added into the Fe $^{3+}$ /Fe $^{2+}$ solution with vigorous stirring until no precipitates could be seen in the solution, and then another 1 h's stirring was conducted. Finally, precipitates were collected and washed for several times with deionized water and ethanol until the pH value decreased to 7. A SiO $_2$ layer was built up by directly introducing Fe $_3$ O $_4$ particles into the primary silica particles by the Stöber process (Lu et al., 2008): a certain amount of ethanol, deionized water, aqueous ammonia and TEOS were added in a three neck flask in a 40 °C water bath. Fe $_3$ O $_4$ particles were added into the flask at different time under mechanical stirring. The final product was washed, dried at –50 °C and conserved in the dryer.

The other ferromagnetic nanoparticle used in this study is the superfine iron (SI), which was provided by the Research Center for Nano Technology of the Chinese Iron and Steel Institute. Its physiochemical properties may be found in the Master's thesis of Chunfeng Hou (2009).

2.3. Synthesis of PACl2.0 and of MPACl2.0s

The PACl2.0 was prepared by slow base titration of 0.5 mol/L AlCl $_3$ solution with 0.2 mol/L NaHCO $_3$ solution under rapid stirring to achieve the target molar OH/Al ratio (basicity value) of 2.0 (Tang, 2006).

MPACl2.0s were synthesized by blending PACl2.0 with ferromagnetic nanoparticles on a shaking table at room temperature (25 °C) for 2 h with a speed of 250 rpm. The final composited MPACl2.0s were aged for 24 h, and conserved at 4 °C. FSCSPs, two loading concentrations of 50 and 100 mg/L, were respectively added into PACl2.0 solutions. Hence the formed MPACl2.0s can be described as PACl2.0 + FSCSP (50 mg/L) and PACl2.0 + FSCSP (100 mg/L) respectively. Loading concentrations were determined by means of apparent dispersibility. It may be noted that FSCSP aggregated more easily than the SI. Therefore, in order to make the ferromagnetic nanoparticles fully distributed at the surface of PACl2.0, only 25 mg/L was chosen as the loading concentration of the SI (PACl2.0 + SI (25 mg/L)).

2.4. Characterization of the ferromagnetic nanoparticles, PACl2.0, and MPACl2.0s

The particle size and morphology of FSCSP and SI were determined by transmission electron microscopy (TEM) (S-570, Hitachi, Japan). The surface charges of the two nanoparticles were analyzed with a zeta potential meter (Zetasizer, Malvern, UK) by adjusting the pH of their suspensions from 3 to 11 with 1.0 and 0.1 mol/L NaOH and HCl solutions. Moreover, zeta potentials of MPACl2.0s and PACl2.0 were also measured. The specific surface area and pore size distribution were measured by a Brunauer, Emmett, and Teller (BET) surface area analyzer (ASAP-2000, Micromeritics, US) for nitrogen adsorption. The BET method was carried out under relatively high vacuum and measured primarily the external area of the particles and aggregates.

Al species of MPACl2.0s and PACl2.0 were characterized by 500 MHz ^{27}Al NMR, and instrumental settings and experimental conditions were addressed elsewhere (Xu et al., 2003). The internal standard was 0.05 mol/L NaAlO_2 with its chemical shift at 80 ppm downfield. The signals near 0 and 62.5 ppm represent mononuclear Al (Al_m) and Al_{13} , respectively. Al_{un} (the amount of undetectable species) was obtained by:

$$\text{Al}_{un} = \text{Al}_T - \text{Al}_m - \text{Al}_{13} \quad (1)$$

2.5. Preparation of synthetic water

A synthetic water was prepared by dissolving the HA and kaolin stock suspensions with 1 mmol/L NaNO_3 and 0.8 mmol/L NaHCO_3 so that the ionic strength and alkalinity of the solution could be kept at 1.0 mmol/L and 80 mg/L respectively. The pH was adjusted to 7.00 ± 0.02 using 0.1 mol/L, 0.01 mol/L NaOH or/and 0.1 mol/L, 0.01 mol/L HCl. The synthetic water had average measured zeta potential, turbidity, UV_{254} and DOC values of -21.4 mV, 75.6 NTU, 0.254 cm^{-1} and 2.318 mg/L, respectively. All measurements were obtained at room temperature.

2.6. Coagulation jar tests

Jar tests were performed on a programmable jar test apparatus (Daiyuan Jar Test Instruments, China) to investigate the coagulation performance of MPACl2.0s within the dosage

range of 0.02–0.20 mmol/L as Al. Before dosing, the three kinds of MPACl2.0s were shaken well in order to disperse the composited systems as uniformly as possible. The jar-test procedure consisted of a 30 s premix (250 rpm), a 1 min rapid mix (200 rpm), a 15 min slow mix (30 rpm) and a 20 min settling period.

A small amount of sample was taken immediately to measure the zeta potential (Malvern, Zetasizer 2000, UK) after a 30 s rapid mix. After settling, the supernatants were analyzed by a TOC analyzer (TOC-Vcph, Shimadzu, Japan) and UV_{254} (UV-Vis 8500, Hitachi, Japan) after filtration through a $0.45 \mu\text{m}$ membrane. The turbidity was measured by a turbidimeter (Hach 2100P Turbidimeter, USA).

2.7. Floc characterization

Flocs were immediately collected from beakers after the slow stirring phase of the jar test with great care to avoid unnecessary “breakage”. Image observation was done under a low resolution of $1 \mu\text{m}$ ($10 \times$ objective) using an electromotive microscope (Axioskop 2 mot plus, Carl Zeiss Co., Germany).

To investigate and compare the growth, breakage and regrowth of flocs produced by MPACl2.0s and PACl2.0, experiments similar to those of Zhu et al. (2009) were carried out. Briefly, coagulation tests were performed under the optimal dosage of 0.08 mmol/L as Al. After the slow stirring phase, flocs were suddenly exposed to a 1 min strong stirring of 400 rpm for breakage, and then regrowth was undertaken at 40 rpm for 15 min. Dynamic floc size was monitored in the whole procedure using SALLS (Mastersizer 2000, Malvern, UK). Size measurements were taken every 40 s.

The inter-particle bonds that hold aggregate flocs together are considered as the cohesive strength of the flocs. A size ratio method is used here with an index (strength factor) to express the strength of particle flocs, i.e.,

$$\text{Strength Factor} = \frac{d_2}{d_1} \times 100\% \quad (2)$$

where d_1 and d_2 are the mean sizes of the flocs before and after the shear breakage, respectively. A higher value of the

Fig. 1 – TEM images of two ferromagnetic nanoparticles: (a) FSCSP, (b) SI.

strength factor indicates a higher ability of the flocs to resist breakage when exposed to an elevated fluid shear.

When the shear intensity was reduced after the breakage phase, re-flocculation of the particles could take place. A reversibility factor is used here to measure the re-flocculation potential of the particles when the shear is returned to its original level. A modified size ratio approach may be applied to calculate the reversibility (Recovery Factor) by

$$\text{Recovery Factor} = \frac{d_3 - d_2}{d_3 - d_1} \times 100\% \quad (3)$$

where d_3 is the mean size of the particle flocs after re-flocculation at the original shear rate. A higher Recovery Factor suggests a greater flocculation and regrowth capability of the flocs after the shear breakage.

3. Results and discussion

3.1. Properties of ferromagnetic nanomaterials

3.1.1. Size and morphologies of FSCSP and SI

TEM images of FSCSP and SI are shown in Fig. 1. In Fig. 1(a), FSCSPs can be easily observed in the spherical shape with an average size of 20 nm. The non-uniform-sized nanospheres form submicron aggregates with a visible 10 nm shell. The agglomeration is due to the magnetic dipole–dipole attraction and the large specific surface area of the magnetic particles (Liu et al., 2004), in spite of fierce stirring during the silica coating process. Fig. 1(b) confirms the core-shell structure of SI. The passivated layer is Fe_3O_4 according to the product description.

The TEM results reveal that the sizes of the ferromagnetic nanoparticles are of nanoscale before agglomeration. It has been reported that Fe_3O_4 is superparamagnetic if its diameter is around 16 nm (Hong, 2008). Unlike ordinary ferromagnetic particles, superparamagnetic materials have no hysteresis effect – once the external magnetic field is cut off, the remnant magnetism will disappear. This characteristic is favored the magnetic separation process since the magnetic sludge or flocs may be easily scraped when the magnetic field is off (Ngomsik et al., 2005).

3.1.2. Specific surface area and pore volume

Nanoparticles have been proven to have relatively large specific surface areas, leading to greater interface reaction rates (Li et al., 2006). The specific surface areas and pore diameters were $78.76 \text{ m}^2/\text{g}$ and $153.24 \text{ \AA}$ for FSCSP and $22.51 \text{ m}^2/\text{g}$ and $63.48 \text{ \AA}$ for SI respectively. They were determined by BET surface measurement. Apparently, compared with the commercially available SI, the lab-prepared FSCSP has a larger surface area with more sites to react with Al species or water pollutants.

3.1.3. Surface electric charge

The electric charge characteristics of both nanoparticles are shown in Fig. 2. Zeta potentials of FSCSP and SI decrease with increase in pH values, changing from +18.7 mV to +26.0 mV down to –13.0 mV and –27.7 mV, respectively. The isoelectric

Fig. 2 – Variation of the zeta potentials of the ferromagnetic nanoparticles with pH.

point (IEP) of FSCSP is at pH 5.2 while that of SI is at pH 6.6. It is worth noting that magnetite can produce charges in the protonation and deprotonation reactions of $\equiv\text{Fe}-\text{OH}$ surface sites as expected for an amorphous solid (Hajdú et al., 2009). Therefore, both particles can be positively charged in composited coagulants since the pH value of PACl2.0 is around 4.02, lower than IEPs of SI and FSCSP (Table 1). Zeta potentials of the MPACl2.0s apparently rise with the addition of magnetic nanoparticles, and the pH values of PACl2.0 and MPACl2.0s are very close around 4.0. Among the three coagulants, PACl2.0 + FSCSP (100 mg/L) has a highest zeta potential of 21.5 mV. PACl2.0 + FSCSP (50 mg/L) has a lowest zeta potential. The zeta potential of PACl2.0 + SI (25 mg/L) is 20.5 mV.

3.2. Al species distributions of MPACl2.0s and PACl2.0

All the coagulants were aged for 1 week. The liquid ^{27}Al NMR method was used to characterize Al species distributions in MPACl2.0s and the original PACl2.0. The results are shown in Fig. 3. The Al_m , Al_{13} and Al_{un} contents of PACl2.0 were 12.8%, 63.0% and 24.2%, respectively. It should be noted that the Al_m and Al_{13} contents decline whereas the Al_{un} content increases after compounding with ferromagnetic nanoparticles. Such change is more obvious for the two PACl2.0 + FSCSPs. When the loading concentration is 50 mg/L, Al_m and Al_{13} contents decrease to 9.9% and 54.0%, respectively. For 100 mg/L, they further decrease to 9.3% and 52.5%, respectively.

Table 1 – Characteristics of electric charges for PACl2.0 and MPACl2.0s.

Types of coagulants	pH	Zeta potential (mV)
PACl2.0	4.02	3.6
PACl2.0 + FSCSP (50 mg/L)	3.99	15.0
PACl2.0 + FSCSP (100 mg/L)	3.96	21.5
PACl2.0 + SI (25 mg/L)	3.95	20.5

Fig. 3 – Comparison of Al species distributions.

All MPACl2.0s are in the form of solid–liquid mixture. The high surface energy, strong adsorption and magnetic attraction of nanoparticles are apt to play a significant role in their combination with PACl2.0. The high density of reactive surface sites and the great intrinsic reactivity of ferromagnetic nanoparticles will enhance the reactivity of the nanoscale particles (Li et al., 2006), and allow Al species to adsorb on their surface. In the process of compositing and aging the MPACl2.0, it seems that Al_m and Al_{13} may firstly aggregate into $[Al_{13}]_n$ or $[Al_m]_n$ on the surface of the nanoparticles, then transform to a sol or amorphous solid phase, and finally turn to other higher order aggregates. As a result, Al species-nanoparticle clusters form (shown in Fig. 7(a)), being identified as Al_{un} . They are not only large in size and easy to precipitate but also have a crucial positive effect on bridging, enmeshment and sorption flocculation capacity.

MPACl2.0s with different nanoparticles and loadings lead to different Al species distributions. According to the BET results, FSCSP has a larger surface area and pore volume, offering more adsorption sites for Al species. Therefore, the content of Al species-nanoparticle clusters in PACl2.0 + FSCSP, in the presence of Al_{un} , will rise. As for MPACl2.0 with SI, since SI was more positively charged in PACl2.0 (Table 1), the electrostatic repulsion between Al species and SI particles may hinder their approach and aggregation, resulting in an inconspicuous increase of Al_{un} .

3.3. Coagulation performances of MPACl2.0s and PACl2.0 with different dosages

The HA and Kaolin particles removal efficiencies of MPACl2.0s and PACl2.0 and the zeta potential of the coagulated suspensions were comparatively investigated, as shown in Fig. 4.

As anticipated, the addition of the MPACl2.0s and PACl2.0 effectively reduced the surface charge of the particles in the synthetic water, resulting in particle destabilization (Fig. 4). As the dosage increased, the particle zeta potentials approached zero. Further increase in flocculant dose caused a certain extent of charge reversal of the particles. The isoelectric dosage (IED) of PACl2.0 + FSCSP (50 mg/L) is close to 0.0 mmol/L as Al, slightly lower than that of the others which were higher than 0.10 mmol/L as Al. The whole dosage range can be divided into three parts according to the change of zeta potentials and turbidity removals: (I) No significant flocculation from -30 to -10 mV. Dosages of coagulants are too low for MPACl2.0s and PACl2.0 to effectively flocculate/coagulate with water pollutants. (II) Obvious flocculation from -10 to 0 mV. As the dosage increases, big flocs are formed and zeta potentials are close to the IEP. Optimal turbidity removals are achieved in this range. (III) Restability from 0 to 10 mV. In the high dosage range, the coagulation performance is ineffective.

The jar-test flocculation and sedimentation results for turbidity and DOC removals from the synthetic waters are in general agreement with the zeta potential analysis. For all four flocculants, it is obvious that the optimal dosage range for MPACl2.0s and PACl2.0 lies in Part II, and the optimal dosage is 0.08 mmol/L as Al. At the optimal dose, 90% of DOC and more than 90% of turbidity can be removed. Especially for PACl2.0 + FSCSP (50 mg/L), the DOC and turbidity removal efficiencies can reach 92% and 98%, respectively. In comparison, PACl showed a slightly worse water treatment performance.

The results indicated that the nanoscale magnetic particles did play a significant role in DOC and particle removal. Firstly, ferromagnetic nanoparticles could affect the hydrolyzed Al species by increasing Al species-nanoparticle clusters, which may increase effective collision rates. Secondly, the addition of ferromagnetic nanoparticles would enhance the adsorption capability due to their large specific surface areas and magnetic dipole–dipole attraction, resulting in a higher removal rate of water pollutants (Li et al., 2006). Therefore,

Fig. 4 – Variation of turbidity and DOC removal with coagulant dosages.

Fig. 5 – Representative images of flocs formed with (a) PACl₂.0; (b) PACl₂.0 + FSCSP (50 mg/L); (c) PACl₂.0 + FSCSP (100 mg/L) and (d) PACl₂.0 + SI (25 mg/L).

adsorption, enmeshment and sweep would have simultaneously taken place by adding MPACl₂.0. That is the primary reason why the performance of MPACl₂.0 coagulation is superior to that of PACl₂.0 coagulation.

3.4. Floc properties

3.4.1. Morphology of flocs

Microscopic examination in this study (Fig. 5) suggested the formation of large and fractal-like flocs, resulting in the removal of turbidity and DOC in the suspension. Representative images of flocs coagulated by PACl₂.0, PACl₂.0 + FSCSP (50 mg/L), PACl₂.0 + FSCSP (100 mg/L), and SI (PACl₂.0 + SI (25 mg/L) are shown in Fig. 5. It may be noted the black dots were observed in the flocs formed by MPACl, revealing that nanoscale magnetic particles were successfully composited with the PACl. This can also imply the formation of Al species-nanoparticle clusters. Those clusters influence not only the kinetics of aggregation, but also the structure and resulting fractal dimension of the aggregates.

3.4.2. Floc formation, breakage and regrowth

The coagulation kinetics of PACl₂.0 and MPACl₂.0s are demonstrated in Fig. 6. It shows the variation in the average floc size during the hydrodynamic sequencing. In the jar tests, all the four coagulants were dosed of 0.08 mmol/L as Al. After the slow mix phase, the coagulation for four suspensions achieved a steady-state with the mean sizes denoted as d_1 in Table 2. Then floc size was immediately reduced following an increase in shear. 1 min later, it can be assumed the flocs reached the size d_2 . A reversibility phenomenon in terms of

floc size was observed, as mentioned in previous studies (Yukselen and Gregory, 2002; Zhu et al., 2009). When the shear was reduced to its initial value, the broken particles could collide with each other again to form the larger ones. However, it may be noticed that the formed flocs could not regrow to anywhere near their previous size. This may be attributed to the different coagulation mechanisms. Flocs formed by charge neutralization should give total recoverability. Thus, the irreversible breakage of the flocs was considered as evidence that the flocs formed in these systems were not dominated by pure charge neutralization mechanisms and were therefore held together by chemical rather than physical bonds, such as the combination of entrapment

Fig. 6 – Comparison of the floc formation kinetics curves.

Table 2 – Strength and recovery factors of MPACl2.0s and PACl2.0.

Suspensions	d_1 (μm)	d_2 (μm)	d_3 (μm)	Strength factor (%)	Recovery factor (%)
PACl2.0	136.5	43.6	73.9	31.9	32.6
PACl2.0 + FSCSP (50 mg/L)	165.4	42.9	51.3	25.9	6.9
PACl2.0 + FSCSP (100 mg/L)	139.0	46.7	77.9	33.7	33.8
PACl2.0 + SI (25 mg/L)	173.3	46.4	61.5	26.8	11.9

bridging and complexation with coagulant metal hydrolysis species (Yukselen and Gregory, 2004).

Table 2 summarizes the values of the strength factor and recovery factor for the suspensions with different coagulants. PACl2.0 + SI (25 mg/L) and PACl2.0 + FSCSP (50 mg/L) are less able to resist the shearing condition, and their strength factor values are 26.8% and 25.9%, respectively, lower than those of 33.7% for PACl2.0 + FSCSP (100 mg/L) and 31.9% for PACl2.0. Meanwhile, recovery factors of PACl2.0 + SI (25 mg/L) and PACl2.0 + FSCSP (50 mg/L) are only as low as 6.9% and 11.9%.

Compared with PACl2.0, the small addition of ferromagnetic nanoparticles slightly reduced the floc strength but severely weakened the recovery ability of the flocs. This can be explained according to the variation of the Al species shown in Fig. 3. The floc strength is dependent upon the interparticle bonds between the components of the aggregates. As reported by Wang et al. (2009), the Al_m species can complex with HA to form large and strong flocs while the Al_{13} species react with HA to form small and unstable flocs. Those two HA-

Al flocs can be joined together by adsorption and bridging due to larger polymer and solid-phase $\text{Al}(\text{OH})_3$, resulting in larger flocs. In our study, the increase of Al_{un} in MPACl2.0s, containing the probably existing Al species-nanoparticle clusters, may have helped to form larger flocs than PACl2.0. The decrease of Al_m in MAPCl2.0s and the possible loose conformation of Al species-nanoparticle clusters may lead to weaker flocs.

Moreover, the results also indicate that flocs formed by MPACl2.0s show lower strength and reflocculating ability after breakage. As required for the magnetic particle recycling, the smash of magnetic flocs/sludge is a prerequisite, after which the separation of magnetic particles from the flocs/sludge is easier to achieve. Therefore, the incompact flocs, induced by PACl2.0 + FSCSP (50 mg/L) and PACl2.0 + SI (25 mg/L), are favored for practical purposes because of the low energy consumption for flocs/sludge breakage.

3.5. Mechanisms of nanoscale magnetic coagulants

The results of this work indicate that the ferromagnetic nanoparticles could play a significant role in coagulation. A plausible MPACl2.0 coagulation mechanism has been described schematically in Fig. 7. It can be noted that Al species-nanoparticle clusters will be formed when ferromagnetic nanoparticles are added into the PACl (as shown in Fig. 7(a)). The formed clusters would increase the proportion of Al_{un} , which has a great potential to enhance charge neutralization, enmeshment and adsorption when aggregated with the pollutants. The flocs produced by those clusters exhibited different characteristics as shown in Fig. 4.

Fig. 7 – Coagulation mechanism of MPACl2.0: (a) formation of Al species-nanoparticle clusters in MPACl2.0, (b) coagulating process of MPACl2.0.

As illustrated as Fig. 7(b), the flocs formed by PACl2.0 + FSCSP (50 mg/L) and PACl2.0 + SI (25 mg/L) are larger but weaker. As stated previously, ferromagnetic nanoparticles exhibited a preference to form Al species-nanoparticle clusters. These clusters enhance the bridge and adsorption effects, leading to a larger floc size. Moreover, the recovery factors of the flocs show marked differences. The recovery factors of PACl2.0 + FSCSP (50 mg/L) and PACl2.0 + SI (25 mg/L) are very low (6.9% and 11.9% respectively). This implies that, in a suitable range of ferromagnetic nanoparticle addition, the connections between the clusters and pollutants are unique, being based on chemical bonds rather than physical ones.

Flocs formed by PACl2.0 + FSCSP (100 mg/L) showed a different situation. They were stronger and had a comparable size with those formed by PACl. The difference is in the concentration of ferromagnetic nanoparticles. Apparently, PACl2.0 + FSCSP (100 mg/L) had the highest concentration. Aggregation of nanoparticles happened easily, and thus Al species-nanoparticle clusters were reduced. Therefore, the bridge and adsorption effects of Al_{un} were limited to some degree, and the floc size did not obviously increase. Additionally, the formed flocs were considerably porous and fractal. The excess nanoparticles could penetrate into flocs. The embodiment of those nanoparticles would increase the strength of the flocs as indicated in Table 2.

4. Conclusions

Three novel ferromagnetic nanoparticle composites MPACl2.0s (MPACl2.0s) were synthesized by compounding FSCSP and SI respectively with PACl2.0. They are described as PACl2.0 + FSCSP (50 mg/L), PACl2.0 + FSCSP (100 mg/L) and PACl2.0 + SI (25 mg/L). A series of characterizations in terms of physiochemical properties illustrated that the ferromagnetic nanoparticles used in the study were all core-shell particles with slight agglomeration and positive charge PACl2.0. FSCSP had a larger surface area and pore volume than SI did. All MPACl2.0s were in the form of solid–liquid mixing. Liquid ^{27}Al NMR measurements indicated that, compared with PACl2.0, Al_{un} content increased whereas Al_{13} and Al_m declined with increase of ferromagnetic nanoparticle loadings. Al species-nanoparticle clusters, attributed to Al_{un} , are suggested to form.

Coagulation jar tests revealed that the MPACl2.0s performed better than PACl2.0 in both turbidity removal, and DOC removal. Among the three MPACl2.0s, the coagulation behavior of PACl2.0 + FSCSP (50 mg/L) was the best. The improved coagulation efficiency of MPACl2.0s may be considered to be due to the co-effect of Al species, ferromagnetic nanoparticles and the possible Al species-nanoparticle clusters. Investigation of floc properties revealed that the key factor that influenced floc growth, re-flocculation, size and strength was the loading of ferromagnetic nanoparticles. Moderate nanoparticle loadings induced large but weak flocs that were hard to rearrange. Such flocs are favored for magnetic particle recovery.

The formation of Al species-nanoparticle clusters might have greatly contributed to the unique Al species distributions, the coagulation performance and the floc properties of

MPACl2.0. The additions of FSCSP and SI appeared to enhance the adsorption, enmeshment, and sweep abilities of MPACl2.0s, and to further strengthen the coagulated flocs by entering into the floc pores during flocculation. When the ferromagnetic nanoparticle loadings are controlled within a certain range, the connections between clusters and water pollutants were presumed to be chemical bonds since they had a considerably low recovery factors.

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