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Effect of organic ligands on the removal of Cr(III) from water by coagulation process

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ABSTRACT

The existence of Cr(III) complexes in water has become the key problem posed for the standard discharge of Cr-containing wastewater. Coagulation is the most common method for the treatment of chromium wastewater. However, little information has been collected regarding the effect of organic matters on Cr(III) removal by the coagulation process. In this study, the removal of Cr(III)-acetate (Cr-ace) complexes with the molar ratio of 1:1, 1:2 and 1:3 by coagulation were systematically investigated. Fe(III) salts were more efficient than Al(III) in Cr(III) removal. Approximately 95% removal rate of Cr-ace (1:1) was obtained with Fe(III) dosage of 0.8 mM, while about 70% and 35% removal efficiency of Cr(III)-ace (1:2 and 1:3) were achieved, respectively. With the increase of carboxyl contents, Cr removal efficiencies were decreased due to the enhanced stable structure of the Cr(III) complex. When Fe(III) concentration was 0.8 mM, the removal rate of Cr-ace (1:1, 1:2, 1:3) by Fe(III) flocs were 61.5%, 61.47%, 48.15%, respectively. Under the same condition, the removal efficiency of Cr-ace with Al(III) adsorption were 74.99%, 53.67%, 36.85%, respectively. Such results indicated adsorption played an important role in Cr removal, especially at high dosage coagulants. The growth of flocs was inhibited accompanied by acetate in high concentration. Furthermore, Ca^{2+} has limited influence on Cr removal, while short complexation time was beneficial to Cr removal. This paper provided some theoretical support for the influence parameters of Cr(III) removal from wastewater through coagulation.

Keywords: Chromium; Organic ligands; Coagulation; Adsorption; Floc size

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1. Introduction

Chromium (Cr) has been widely employed in industrial processes, such as leather tanning, electroplating, dyeing, etc [1]. A large amount of Cr was discharged into the wastewater due to limited utilization of raw materials [2]. The main species of Cr in wastewater include Cr(III) and Cr(VI). Cr(VI) is carcinogenic and highly mobile in the environment, therefore listed as the top 20 toxic pollutants by Environment Protection Agency (EPA) [3]. The main strategy for removing Cr(VI) is to convert Cr(VI) into Cr(III), then further eliminate Cr in water through physical-chemical methods like precipitation and coagulation [4–6]. Although Cr(III) is less toxic than Cr(VI), it will oxidize to Cr(VI) in the presence of manganese oxide or chlorine, which causes further damages for human beings [7–9]. Moreover, Cr(III) will also cause damages to plants and animals [10,11]. Owing to such adverse aspects to the ecosystem, the maximum contaminant level of total Cr has been limited by countries. For instance, the maximum

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concentration limitation was set as 1.5 mg/L by Chinese EPA [12]. European Commission Directive restricted that the Cr emission from industries should be reduced to zero by 2020 [13]. Therefore, the control of chromium pollution in wastewater is the key issue for industrial wastewater treatment.

In industrial wastewater, organic ligands containing carboxyl groups are largely existed, hindering the removal of total Cr [14,15]. The low efficiency of Cr(III) removal is maintained since stable metal complexes can be formed through the coordination between metal ions and the carboxyl groups [16,17]. For instance, Wang et al. [12] treated authentic tannery wastewater through precipitation, results indicated that approximately 10–20 mg/L Cr was left in the wastewater even with 400 mg/L $Ca(OH)_2$, and the main species of Cr(III) in treated water were in the form of complex state. In the further study, the researchers compared the removal efficiency of Cr(III)-acetate and Cr(III)-citrate by alkaline precipitation. The results showed that the complex structure of Cr(III)-citrate was more stable than Cr(III)-acetate and had good alkaline resistance [18]. Ma et al. found carboxyl and hydroxyl groups in organic ligands may cause the re-complexation of Cr(III), thus affected removal efficiency in the next step [16]. Zhao et al. compared different kinds of azo dyes removal by coagulation, they found more benzene rings and $–NO_2$ groups lead to reduction of Cr removal efficiency [14]. In general, the highly stable and soluble Cr(III) complexes have become the obstacles to chromium wastewater treatment.

Coagulation is a reliable and convenient treatment method for industrial wastewater in large-scale applications [19–22]. Up to now, there are few studies related to the effect of organic matters on pollutants removal by coagulation. Zhou et al. conducted experiments to investigate the effect of tannic acid on phosphorus removal through Fe coagulation [23]. The results showed that tannic acid could accelerate the settling speed of forming flocs with large size, and slightly increased the phosphorus removal efficiency. Another study related to the effect of organic ligands on arsenic removal proposed that nearly 100% removal efficiency could be achieved for As(V), while only 95% and 57% were obtained for monomethyl arsenate and dimethyl arsenate, respectively [24]. Jia et al. [25] found that tetracycline could coordinate with Cu(II) and enhance Cu(II) removal efficiency. According to the above studies, there are many possibilities for the influence of organic ligands on the removal of heavy metals. The effects of organic matters on removal performance, mechanisms of Cr(III) are not fully investigated. Although Ca^{2+} has been proved to have a significant effect on the removal of NOM and Cr(VI), the effect on Cr(III) complexes removal was still unclear [26,27]. The lack of knowledge in coagulation mechanism restricted the application of this method in organic-rich chromium wastewater.

Based on the above discussion, the objects of this study were as follows: (1) to elucidate the effect of organic ligands on Cr(III) removal by coagulation in terms of coagulant dosage and initial pHs; (2) to explore the role of adsorption in coagulation of Cr(III) complexes; (3) to compare the different floc sizes by coagulation; (4) to investigate the effect of Ca^{2+} and complexation time on coagulation efficiency. Acetic acid, which is the main organic acid used in tanning, electroplating and other typical industrial production, is selected as the representative ligand. The effect of ligand number, coagulant concentration and pH were quantified for the coagulation process. Experiments were also designed to confirm the possible coagulation mechanisms, especially the role of adsorption between flocs and Cr(III) complexes. The sizes of flocs generated in the coagulation process were analyzed in detail. Moreover, the influencing factors, such as concentration of Ca^{2+} and complexation time, on Cr(III) removal were systematically investigated.

2. Experimental

2.1. Chemicals

$FeCl_3$ and $Al_2(SO_4)_3$ were selected as the source of Fe and Al coagulant. All the reagents were in analytical purity (≥99.0%), and purchased from the Sinopharm Chemical Reagent Co., Ltd., China. Cr(III) complexes were prepared according to previous studies [28–30]. Briefly, sodium acetate was added into Cr(III) solution with the molar ratio in 1:1, 1:2 or 1:3. Then the solution pH was adjusted to 5.0, and heated to a water bath of 60°C for 2 h. Finally, the solution was left in the dark for 24 h.

2.2. Coagulation experiment

Coagulation experiments were conducted in 500 mL beakers with a program-controlled jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co., Ltd., China). Coagulant stock solutions were obtained by directly dissolving iron or aluminum salts at the concentration of 1 M, followed by direct dilution to obtain coagulants with different concentrations. The whole process was divided into three steps: 1 min rapid mixing (200 rpm), followed by 15 min slow mixing (40 rpm) and 30 min sedimentation. Cr(III) complexes and coagulants were added to the solution, then the solution pHs were adjusted to the desired value before rapid mixing started. After the experiment, the mixture was filtered through a 0.45 μm filter membrane, then the solution was collected for further analysis. The removal efficiency of Cr(III)-ace was calculated by detecting the concentration of total Cr (mg/L) in the solution.

Adsorption experiments were conducted to evaluate the uptake of Cr on the flocs. Firstly, in the water sample without Cr, the pH of the solution was adjusted to 7.0, which was a benefit for Fe/Al flocs formation during the slow mixing stage. Secondly, a certain amount of Cr(III) complex was added to the suspension. The total Cr concentration was set as 0.2 mM. Finally, extra slow mixing and settling stages were initiated to make sure the conditions were the same with the coagulation experiment.

Considering Ca^{2+} was the common cation found in water, thus the effect of Ca^{2+} on Cr(III) complexes removal was evaluated. 0–40 mg/L Ca^{2+} was added into the solution before the coagulation experiment. The structures of Cr(III) complexes are greatly affected by the complexation time. Therefore, investigating reaction time was necessary for further understanding the coagulation behavior of coagulants toward Cr(III) complexes. In the complexation experiment, a certain amount of Cr(III) and acetate was mixed in the beaker, then a coagulation test was conducted immediately. Other experiment conditions were the same as the coagulation experiment.

2.3. Analysis

The concentration of metals in the solution was measured by ICP-OES (ICAP-7000, Thermo Co., USA). The particle size of flocs was analyzed by Malvern 3000 (Mastersizer-3000, Malvern Co., UK). The morphology of flocs was characterized by scanning electron microscopy (SEM, Zeiss Sigma 300, Germany). The zeta potential of flocs under different pH was detected by Nano Zetasizer (Nano ZS-90, Malvern Co., UK).

3. Results and discussion

3.1. Effect of coagulant dosage on Cr removal by coagulation

The removal of Cr(III)-ace with different molar ratios were explored with various dosage of coagulant at pH 7.0. As shown in Fig. 1a, the residual concentration of Cr decreased with increasing dosage of Fe(III) salts, and it remained stable when the concentration of Fe(III) exceeded 0.6 mM. The concentration of total chromium increased with the increase of acetate concentration. When the dosage of Fe(III) was 0.8 mM, initial pH was 7.0, the residual concentration of Cr(III)-ace with molar ratio 1:1, 1:2, 1:3 were 0.3, 1.8 and 3.4 mg/L, respectively. It was observed that the trend of removing Cr by Al(III) was consistent with that by Fe(III) salts. As displayed in Fig. 1b, when Al(III) dosage was 0.8 mM, solution pH adjusted to 7.0, the concentration of Cr-ace with molar ratio of 1:1, 1:2, and 1:3 were 0.8, 3.0 and 4.8 mg/L, respectively. All the results indicated low molecular ligands had an inhibitory effect on the coagulation removal of Cr(III), which may be due to the formation of more stable complex structure [18,24].

The concentration of Cr decreased gradually with the increase of coagulant dosage, which was ascribed to enhancement of coagulation performance brought by more Fe(III) flocs. For Cr-ace (1:1), the residual Cr was 0.3 mg/L at Fe dosage of more than 0.6 mM, while minimum concentration of Cr was about 1.0 mg/L at Al concentration of 0.2 mM. The removal efficiency of Cr-ace with the molar ratio of 1:2 and 1:3 by Fe(III) was also higher than Al(III). The experimental results from Fig. 1 also indicated that Fe salts were more effective than Al salts for Cr(III) complex removal.

3.2. Effect of pH on Cr removal

In the coagulation process, the removal of Cr from wastewater depends on the coagulant performance, the amount of flocs produced and the affinity between flocs and Cr(III) ions [31]. The performance of coagulant is affected by the pH value, and the performance of Al(III) or Fe(III) coagulants were quite different. Accordingly, the effect of initial pH on the Cr(III) removal by coagulation was explored in this section. As shown in Fig. 2a, when the pH of the solution was 4.0–5.0, the Cr(III) complexes in solution remained at 10 mg Cr/L, which indicated that Fe(III) salts had poor Cr(III) removal performance under low pH. As the pH increased, the concentration of Cr was gradually decreased. When the pH was 7.0–8.0, the residual Cr concentration was the lowest, which may be ascribed to the formation of stable iron hydroxide [32]. By comparing the removal performance of different Cr(III) complexes, it was found that Fe(III) coagulation had the higher removal rate for Cr(III)-ace with a molar ratio of 1:1. Poor treatment performance was obtained for Cr(III)-ace with a molar ratio of 1:2 or 1:3, which was because Cr(III) complexes were more stable with the increase of carboxyl contents [33,34].

As displayed in Fig. 2b, the removal rule of Cr(III) complex by Al(III) salts was similar to that of Fe(III) salt. The concentration of total Cr decreased at first and then increased with the pH enhancement. When the ratio was 1:1, pH was 6.0–8.0, the Cr concentration was decreased to 1.0 mg/L. The coagulation performance brought by Fe(III) was superior to that of Al(III) at the same coagulant concentration. This may be due to the open and looser structure of Fe(III) hydroxide, thus providing a large specific surface area available for complexation or adsorption of Cr(III) [35,36].

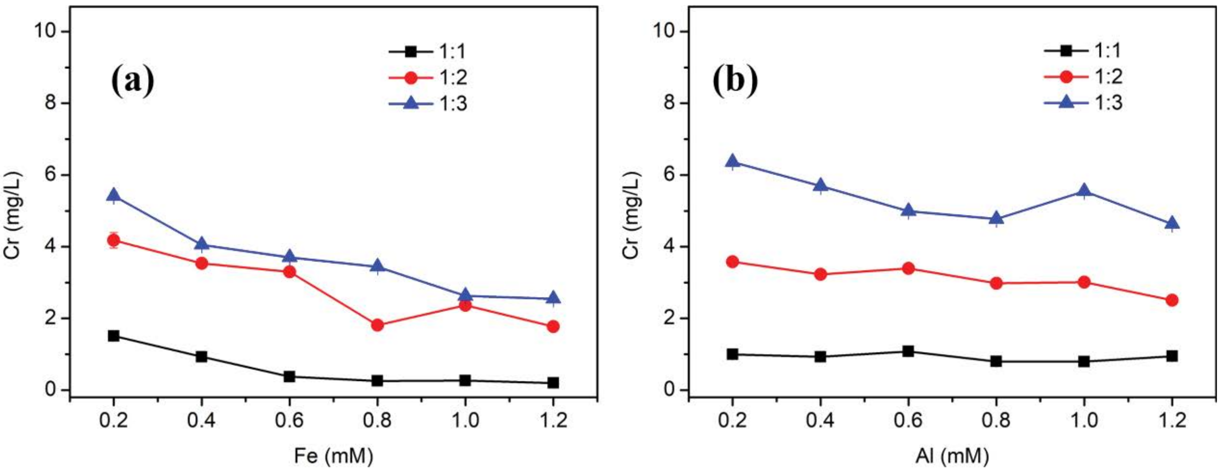

Fig. 1. Effect of coagulant dosage on Cr(III) complex removal (a) Fe coagulation and (b) Al coagulation (initial Cr: 0.2 mM; pH: 7.0).

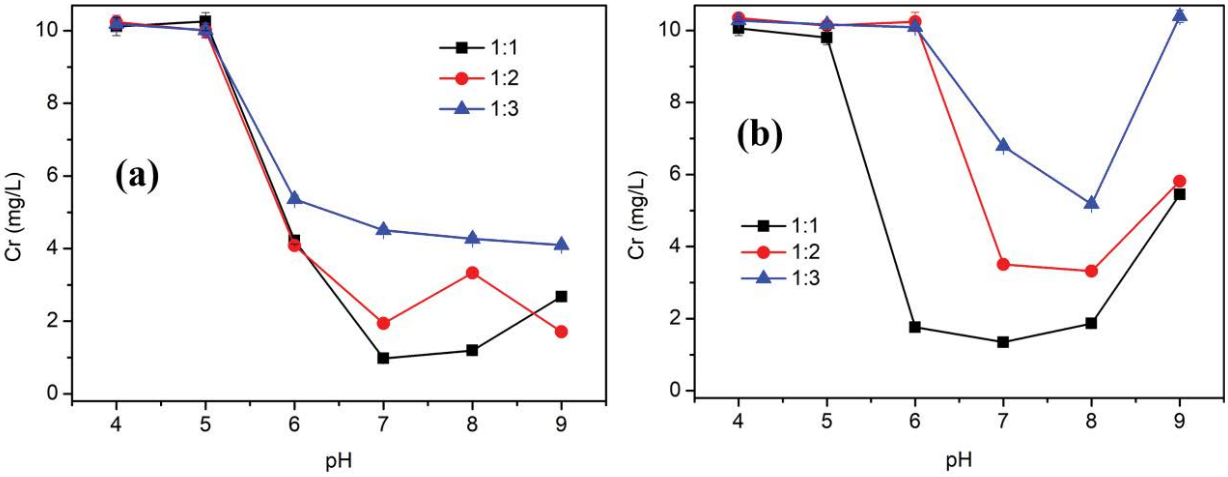

Fig. 2. Effect of initial pH on Cr(III) complex removal (a) Fe coagulation and (b) Al coagulation (initial Cr: 0.2 mM; Fe(III) or Al(III) dosage: 0.8 mM).

3.3. Mechanism of complexed Cr(III) removal by coagulation

The possible coagulation mechanisms of Cr(III) include precipitation, co-precipitation and adsorption [30]. In order to explore which mechanism was predominant for the removal of Cr(III) complexes, experiments were designed to compare the performance of coagulation directly and adsorption by preformed Fe/Al hydroxides. As displayed in Fig. 3, the removal efficiency of the Cr(III) complex by coagulation was higher than that by adsorption. For Cr-ace (1:1), there was a big difference between coagulation and adsorption, which indicated precipitation and co-precipitation played an important role. As the concentration of organic ligands increased, the gap between coagulation and adsorption was limited, implying adsorption was the main mechanism under such circumstances. Moreover, the difference was more distinct at low coagulant dosage than that at high dosage. The results showed that adsorption on flocs was the most important mechanism for Cr(III) complex removal, while precipitation and co-precipitation also played a certain role. According to the literature, few hydroxide flocs will be produced at low dosage coagulant, then affecting incorporation of Cr(III) complexes into the growing hydroxides via inclusion or occlusion, which was similar to the removal mechanisms of other pollutants like As, Se [37,38].

In order to better understanding the mechanisms, pH variation and zeta potential of flocs under different initial pH were conducted. As shown in Fig. 4, pH value decreased ascribed to the consumption of hydroxide by coagulants hydrolysis. With the function of Fe(III), solution pH decreased more sharply than that of Al(III) (Fig. 4a). This phenomenon indicated ferric salts hydrolyzed strongly than aluminum salts, thus the coagulation effects brought by Fe(III) were better, in consistent with previous results. Electrical property was an important factor to evaluate coagulation performance, therefore the zeta potentials of flocs at pH 6.0–8.0 were determined. As displayed in Fig. 4b, when the pH value was around 7.0, zeta potentials of flocs tended to zero. This indicated the flocs were easier to aggregate under this condition, further suggesting the good performance at such conditions. In summary, adsorption and sweep effect played important roles in Cr(III) complexes removal by coagulation.

3.4. Characterization of flocs

Fig. 5 presents the growth, breakage and regrowth profiles of flocs during coagulation processes. In all cases for Fe(III), the floc size exhibited a significant increase during the slow mixing stage, indicating a balance between aggregation and breakage. With the introduction of rapid mixing at 200 rpm, an apparent drop of floc size was observed, followed by gradual floc reformation as the slow mixing went on. A similar change in floc size with coagulation time was also seen for Al(III), however, the particle size of broken floc was so close to that the floc generated during rapid mixing. These results indicated that the Al(III) flocs had stronger resistance to breakage than Fe(III) flocs.

It was observed that organic ligand contents had a significant influence on the floc sizes. When no ligand existed, flocs generated through Fe(III) coagulation were about 500 μm. When Cr(III) and ligands molar ratio were 1:1, 1:2 and 1:3, the floc sizes were about 270, 260 and 250 μm, respectively. This indicated that the production of flocs was inhibited in the presence of organic ligands, and then influence the subsequent separation performance. However, the particle sizes of Al(III) flocs were approximately 120 μm when organic ligands were 0–3 times to Cr(III), which indicated that the Al(III) flocs growth were not affected significantly in the presence of organic ligands. This may be because the Al(III) flocs were more stable than Fe(III) flocs.

SEM spectra of flocs in coagulation are displayed in Fig. 6. It could be clearly found that bulk Fe(III) floc was observed during coagulation process, and the surface was rough. In comparison, the generated flocs during Al(III) coagulation exhibited as small pieces of aggregates, which

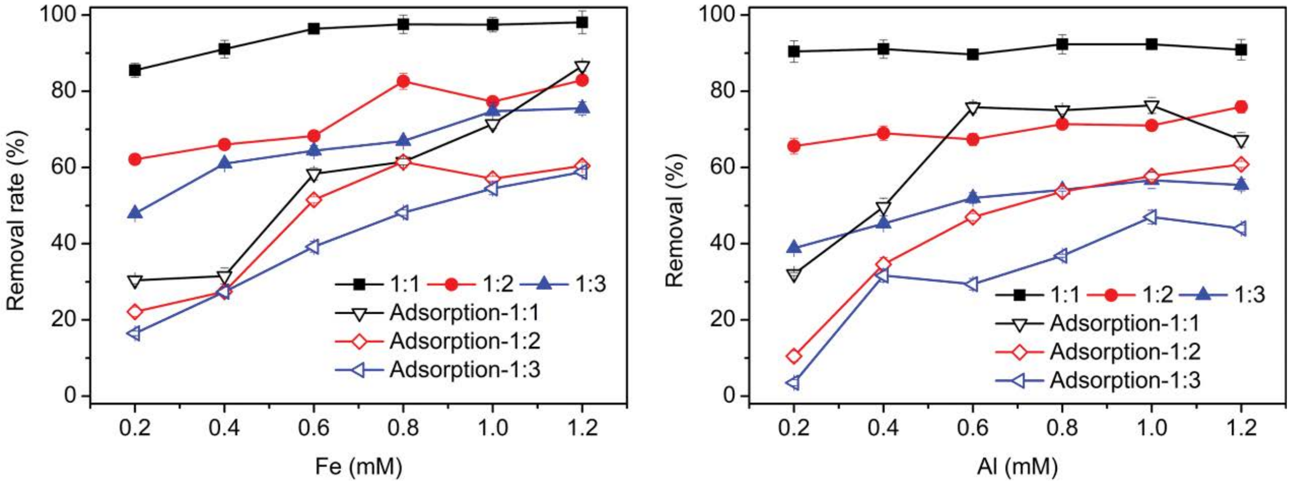

Fig. 3. Comparison of floc adsorption and coagulation performance of Cr(III) complexes: (a) Fe(III) coagulation and (b) Al(III) coagulation (initial Cr concentration: 0.2 mM; $pH_0 = 7.0$).

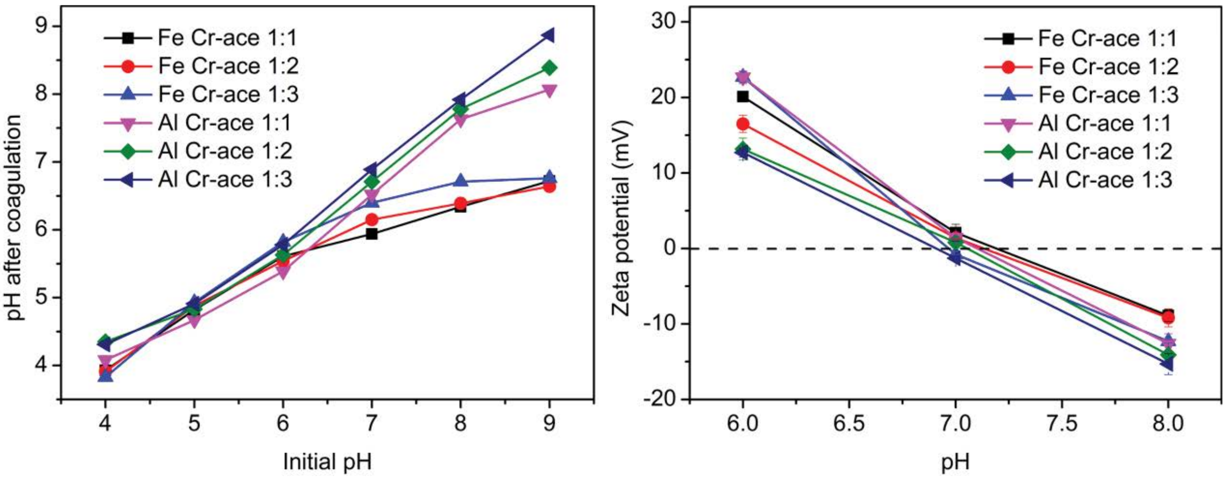

Fig. 4. (a) pH changes with different initial pH and (b) zeta potential of flocs under different conditions (initial Cr concentration: 0.2 mM; Fe(III) or Al(III) dosage: 0.8 mM).

was smaller than that in Fe(III) coagulation. The above results further proved that the performance of iron salts toward Cr(III) complexes was better than that of aluminum salts.

3.5. *Effect of Ca^{2+} and complexation time on Cr removal by coagulation*

According to the results above, Fe(III) salts showed better removal performance on Cr(III) complexes than Al(III), therefore the influence of factors on iron coagulation was discussed only in this part. As displayed in Fig. 7a, with the increase of calcium ion concentration, the total Cr concentration enhanced at first and then decreased. This is because the existence of Ca^{2+} will change the electrical properties of Fe flocs, which will affect the adsorption performance of Cr(III) complexes. Further enhancement of Cr removal may be ascribed to sweep properties brought by calcium hydroxide [26]. Calcium ions had little effect on Cr(III)-ace with the molar ratio of 1:3, which was due to stable structure of such Cr(III) complex.

Effect of complexation time on the removal of Cr(III) is displayed in Fig. 7b. When Cr(III) and organic ligands coexisted for a short time, the removal rate of total Cr could be achieved by more than 95%. Moreover, the removal efficiency of Cr(III) was not affected by the ligand concentration, which may be caused by the slow complexation rate of Cr(III) and organic ligands. Once Cr(III) and organic ligands stayed for a long time, the stable complex structure will be formed, and then the properties of Cr(III) removal by coagulation were largely affected [17,31]. Therefore, the reduction of coexisting time between Cr(III) and organic ligands will be beneficial to total Cr removal.

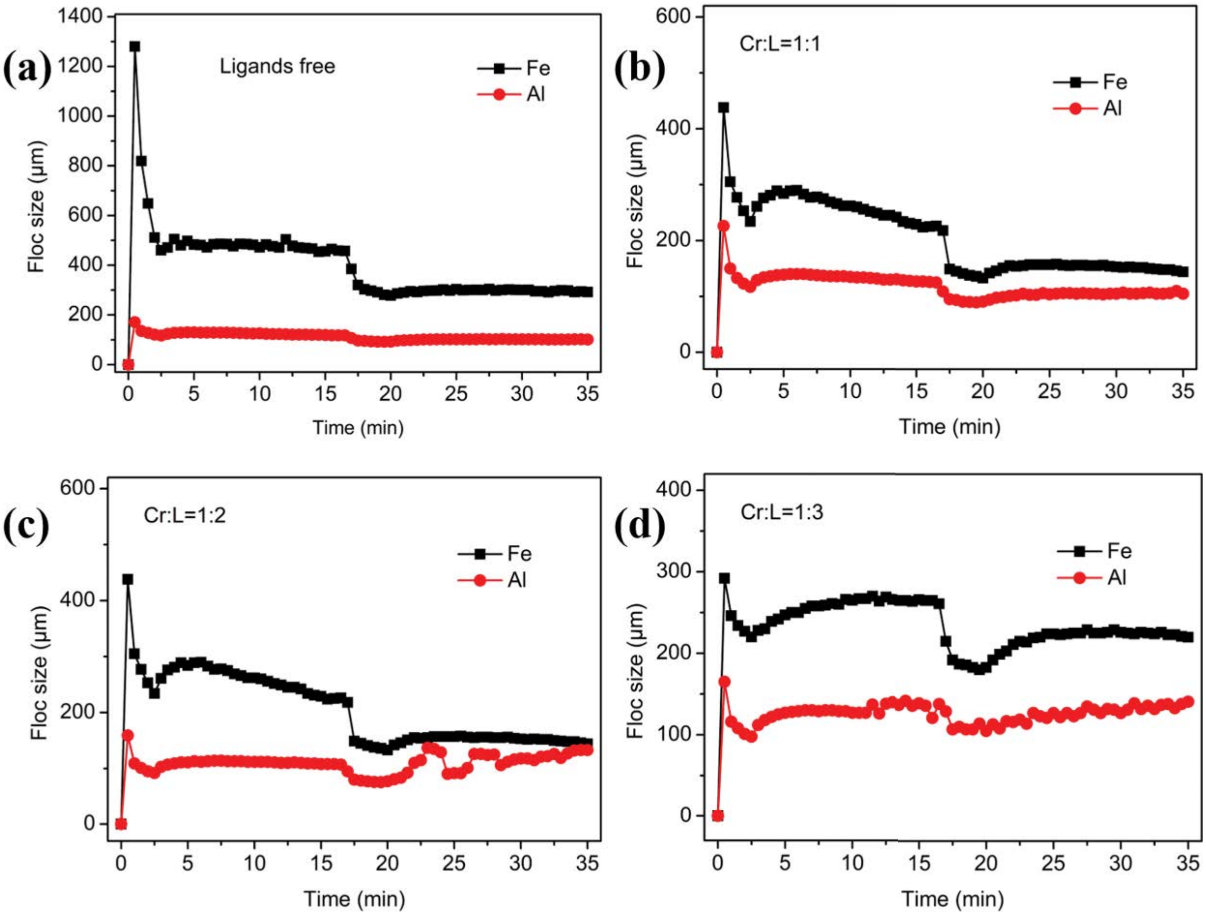

Fig. 5. Characteristics of flocs formed during coagulation process (initial Cr concentration: 0.2 mM; Fe(III) or Al(III) dosage: 0.8 mM; $pH_0 = 7.0$).

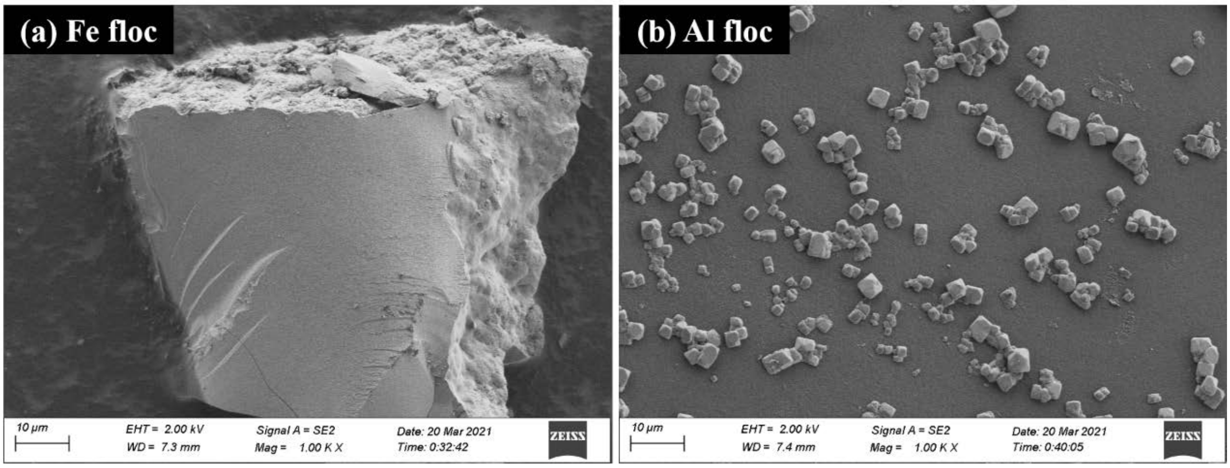

Fig. 6. SEM images of flocs after coagulation process for Cr-ace removal (initial Cr concentration: 0.2 mM; Cr/acetate molar ratio: 1:1; Fe(III) or Al(III) dosage: 0.8 mM; $pH_0 = 7.0$).

4. Conclusions

In this study, coagulation process was successfully applied for Cr(III) complexes removal. Some influence factors on the removal performance and floc size properties were investigated. It was found that Fe(III) showed better Cr removal efficiency than that brought by Al(III). As the increase of organic ligands, the optimum dosage of coagulant increased, and the pH range became narrow.

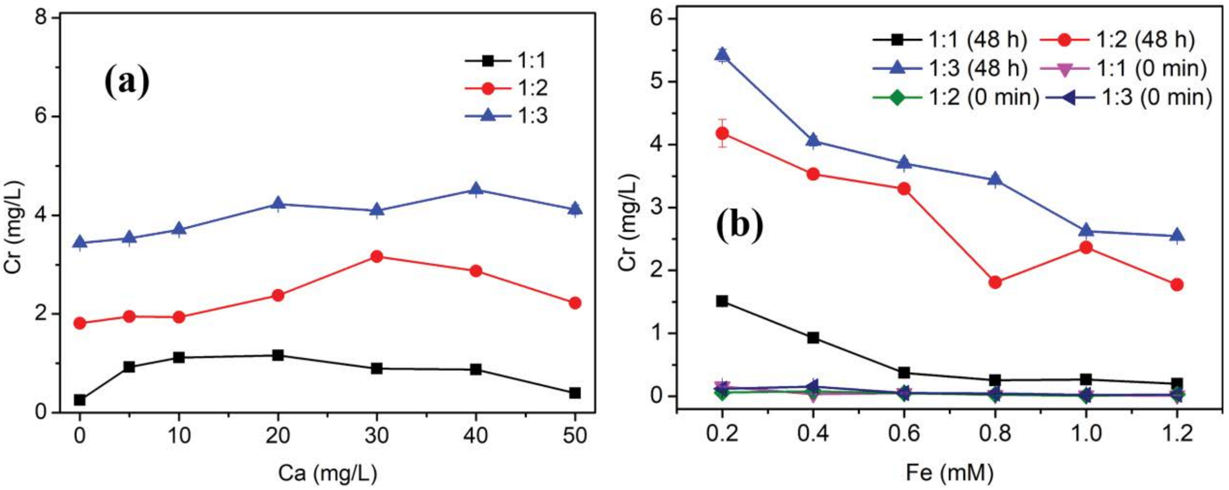

Fig. 7. Effect of (a) Ca^{2+} and (b) complexation time on the removal of Cr(III) complexes by coagulation (initial Cr concentration: 0.2 mM; $pH_0 = 7.0$; Fe(III) dosage: 0.8 mM).

During the coagulation process, when the coagulant was in high concentration, the main mechanism was adsorption, while sweep effect played an important role in low dosage. The particle size of Fe floc was larger than that of Al flocs. Meanwhile, the particle size of floc decreased with the increase of organic ligands concentration. The presence of Ca^{2+} had a limited effect on coagulation, and the short complexation time was beneficial to the removal of total Cr.

Some conclusions could be used for guiding wastewater treatment. For instance, the organic contents in water should be considered before adopting of coagulation process in chromium wastewater. If possible, avoid long-term storage of chromium-containing wastewater, so as to decrease treatment difficulties. We believe that this paper will provide technical guidance for the removal of Cr(III) compounds in wastewater by coagulation.

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