Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.28094

248 (2022) 70–78
February

Coagulation–flocculation performance and floc properties of composite bioflocculant PAFC-CBF in treating the surface water

Lixin Li[a,b,*], Cheng Peng[a], Fang Ma[b,*]

[a]*School of Environment and Chemical Engineering, Heilongjiang University of Science and Technology, Harbin 150022, China, emails: lilixin1980@163.com (L. Li), pengchengdeuxiang@126.com (C. Peng)*
[b]*State Key Lab of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China, email: mafang@hit.edu.cn (F. Ma)*

Received 3 July 2021; Accepted 24 December 2021

ABSTRACT

This study mainly studied the coagulation–flocculation behavior and floc properties of composite bioflocculant (PAFC-CBF) to treat low turbidity surface water. Results showed that compared with PAFC alone, PAFC-CBF could improve turbidity removal efficiency from 87.50% up to 92.14%, and effectively enhanced the removal effect of UV_{254} and TOC. Moreover, the distribution of [Al + Fe] species in PAFC-CBF showed that the content of $[Al + Fe]_b$ was the best when mass ratios of m(PAFC):m(CBF) = 20 and pH was 7. In addition, CBF contributed to the increased growth rate of flocs and flocs size. Moreover, PAFC-CBF formed denser and more porous flocs with higher recovery factor, which was easy to recovery and re-growth after breakage. And the coagulation–flocculation synergistic effect of PAFC-CBF was achieved by combining adsorption charge neutralization and adsorption bridging.

Keywords: Coagulation–flocculation performance; Floc properties; [Al + Fe] species; Surface water

1. Introduction

Coagulation–flocculation is the most widely used unit process to remove particles and organic matter in water and wastewater treatment because of its high efficiency and low cost [1]. In the coagulation–flocculation process, the choice of coagulants plays an essential role in the removal of target pollutants. So far, various categories of coagulation have been offered in the market. Such aluminum salts [2], iron salts, and polyacrylamide [3] are still widely applied in water treatment due to their outstanding coagulation performance and low cost. As an efficient and stable inorganic polymeric coagulant, polyaluminum ferric chloride (PAFC) possesses better coagulation performance [4]. Nevertheless, its use has resulted in some health and environmental problems. For instance, high concentrations of remaining aluminum are suspected of inducing Alzheimer's disease [5]. Furthermore, synthetic polymers are difficult to be biodegraded, and some residual monomers are considered carcinogenic [6]. Therefore, the demand for environment-friendly coagulants is increasing.

In recent years, bioflocculant has attracted wide attention of researchers because of its advantages of biodegradability, non-toxicity, no secondary pollution, vast sources, and rich variety [7,8]. Bioflocculant is a variety of extracellular biopolymers secreted by algae, bacteria, and fungi, such as glycoprotein, protein, polysaccharide, and nucleic acid [7,9,10]. And the chemical structure, flocculation mechanism and culture conditions of the bioflocculants have also well studied [11–13]. Nevertheless, so far,

---

* Corresponding authors.

the bioflocculants has not been put into practical industrial production and water treatment industry due to the low flocculating capacity, low yields and high production cost [3,14]. In order to overcome these limitations, researchers have done a lot of work in screening efficient strains and optimizing culture conditions [13,15]. Meanwhile, composite bioflocculant (bioflocculant used in combination with inorganic coagulant) is another cost reduction method, which can not only reduce the dosage of bioflocculant, but also enhance the flocculating activity. In addition, the secondary pollution and harm to human body by chemical flocculants were reduced duo to their dosage has been cut down. Yang et al. [16] found that composite bioflocculant (MBFGA1 and PAC) obtained a favorable flocculating effect and reduced flocculent costs. Bo et al. [17] reported that the dual coagulants (CBF and AS) were more effective in removing humic acid and could increase the size and growth rate of flocs. Wang et al. [18] studied the physicochemical properties and flocculation performance of CBF (CBF produced by mixed culture of *Rhizobium radiobacter* F2 and *Bacillus sphaeicus* F6), and the results showed that CBF was a polysaccharide bioflocculant with an average molecular weight of 4.79×10^5 Da and high flocculation activity. However, the coagulation–flocculation performance and mechanism of bioflocculant combined with inorganic flocculant are rarely reported.

Based on previous research, the PAFC was selected to be combination with CBF. Due to the combination of two advantages, coagulation–flocculation efficiency could be enhanced significantly and reduce the dosage of both [4], so as to save the cost and reduce the secondary harm to the environment due to the presence of heavy metals in PAFC [10]. In this paper, composite bioflocculant PAFC-CBF was prepared, and the distribution of [Al + Fe] hydrolytic species of PAFC-CBF in the coagulation–flocculation process was studied. Furthermore, a detailed investigation was also conducted to understand the growth, breakage, and re-growth of flocs formed by PAFC-CBF coagulant. Finally, the relationship between floc properties and coagulation–flocculation mechanism was also discussed.

2. Materials and methods

2.1. Raw water

Raw water in this study was collected from the Harbin section of Songhua River (located in Heilongjiang, China). The characteristics of the raw water were as follows: temperature 13.22°C, turbidity 25.20 NTU, pH 6.9.

2.2. Preparation of composite bioflocculant

CBF produced by mixed culture of *Rhizobium radiobacter* F2 and *Bacillus sphaeicus* F6, which was primarily composed of polysaccharide (90.6%) and protein (9.3%) [8,10]. The PAFC (containing 30.4% Al_2O_3 and 1.5% Fe_2O_3) solid (0.5, 1.0, and 1.5 g) was added to the beaker, and added about 75 mL of distilled water, used the magnetic stirrer to stir until it was completely dissolved, slowly added 25 mL of CBF, and stirred the polymerization 1 h at 50°C–60°C. Finally, the composite bioflocculant with different weight ratios of PAFC-CBF (n = 10, 20, and 30) was prepared [19]. The PAFC-CBF was preserved in a refrigerator at 4°C.

2.3. Determination of distribution of [Al + Fe] species

The distribution of aluminum and iron in PAFC-CBF was determined by Ferron-complexation timed spectrophotometry. The species that can react with Ferron reagent rapidly within 1 min were free ion monomer or hydroxyl oligomer compound, which was expressed by $[Al + Fe]_a$; The reaction with Ferron reagent within the range of 240 min was medium polymer hydroxyl complex, which was represented by $[Al + Fe]_b$; The species of the third type of hydrolysis was high polymer and colloidal or solid species, which was basically no longer reacted after 240 min, which was represented by $[Al + Fe]_c$ [20].

2.4. Jar test

Coagulation–flocculation experiments were performed in 1.0 L beakers using conventional Jar-test apparatus (TA6, Wuhan Hengling Technology Co. Ltd., China) at room temperature. Each experiment was repeated three times. First, the solution was quickly mixed (200 rpm) for 0.5 min and then slowly mixed (60 rpm) for 2 min. And finally, settle down to precipitate the aggregated flocs for 20 min [21,22]. The supernatant water sample about 3 cm below the water surface was taken for measurement. Turbidity and zeta potential were measured by turbidimeter (SGZ, Shanghai Shiheng Instruments, China) and a Zetasizer Nano-Z (Malvern Instruments, UK), respectively. Total organic carbon (TOC) and UV_{254} were measured by total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan) and ultraviolet spectrophotometer (T6, Puxi General Instrument Co., Ltd., Beijing) respectively.

2.5. Floc size, breakage, and re-growth

Coagulation–flocculation tests were performed on a jar tester as mentioned above. However, after the slow stir phase, the shear rate was increased to 200 rpm for 0.5 min to break the flocs and then back to 60 rpm for 14.5 min for flocs to re-grow. Dynamic floc size was monitored using a laser diffraction instrument Mastersizer 2000 (Malvern Instruments, UK) as the coagulation–flocculation process.

Floc strength and recovery ability after breakage were evaluated by strength factor, breakage factor, and recovery factor, respectively [23,24], as shown in Eqs. (1)–(3):

$$\text{Strength factor} = \frac{d_2}{d_1} \times 100 \tag{1}$$

$$\text{Breakage factor} = \frac{d_1 - d_2}{d_1} \times 100 \tag{2}$$

$$\text{Recovery factor} = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \tag{3}$$

where d_1 is the size before floc breakage, d_2 is the size after floc breakage, d_3 is the size after floc recovery. Thus, flocs with an enormous value of strength factor are better to resist rupture. Likewise, flocs with more prominent recovery factors have better recovery capacity after breakage [25].

2.6. SEM analysis

Morphological properties of flocs were characterized using Scanning Electron Microscopy (SEM) (S-4700, Japan).

3. Results and discussion

3.1. [Al + Fe] species distribution in enhanced coagulation–flocculation process

3.1.1. Effect of CBF on blank absorbance of Ferron chromogenic reagent system

Distilled water was taken as the reference solution and measured the absorbance at the wavelength of 362 nm.

It can be seen from table 1 that CBF had little effect on the blank absorption of the Ferron chromogenic agent system. After CBF and Ferron were mixed, the absorbance was relatively stable, and it can be judged that there was no chemical reaction between CBF and Ferron [26]. Therefore, the interaction between CBF and Ferron can be ignored in the determination of [Al + Fe] species distribution in PAFC-CBF by Ferron-complexation timed spectrophotometry.

3.1.2. Effect of different mass ratio of PAFC and CBF on the species distribution of [Al + Fe]

The effect of different composite mass ratios m(PAFC):m(CBF) on the distribution of species of [Al + Fe] was investigated. The dosage of PAFC-CBF was 20 mg/L, and pH = 7 of the solution.

It is generally considered that $[Al + Fe]_b$ with a moderate degree of polymerization are the best flocculating components of inorganic flocculants such as polyaluminum and polymerized iron contents can reflect the coagulation–flocculation performance of the products [27]. Fig. 1 showed no noticeable change in the species distribution of [Al + Fe] between the different mass ratios of PAFC-CBF and PAFC alone. In comparison, the different mass ratios of m(PAFC):m(CBF) had some influence on the distribution of [Al + Fe] species. Among them, as the mass ratio of m(PAFC):m(CBF) increased, the content of $[Al + Fe]_a$ in the composite system was basically stable, the content of $[Al + Fe]_b$ initially increased and then decreased, and the content of $[Al + Fe]_c$ decreased first and then increased slightly. The content of $[Al + Fe]_b$ was maximum for 65.1% at $n = 20$, whereas the content of $[Al + Fe]_b$ with PAFC alone was the minimum, only 59.2%, indicating that the introduction of CBF promoted the production of more $[Al + Fe]_b$ species.

Table 1
Effect of CBF on the absorbance of Ferron chromogenic reagent

CBF dosage (mL)	Absorbance
0.00	0.305
0.50	0.310
1.00	0.307
1.50	0.299
2.00	0.301
2.50	0.305

From the above results, it can be seen that the appropriate composite mass ratio was a contribution to the formation of the affective component $[Al + Fe]_b$. It was speculated that due to the oxygen atom functional group on the microbial flocculant complexes with the hydrogen atom on the monomer or oligomer in water, reducing the content of $[Al + Fe]_a$, while the content of $[Al + Fe]_b$ increased correspondingly, and the coagulation–flocculation effect was further enhanced. Therefore, it was an effective measure to control the hydrolytic components to improve the coagulation–flocculation effect. Therefore, the hydrolysis components can be controlled by catalytic hydrolysis to improve the coagulation–flocculation efficiency and reduce residual aluminum concentration [28].

3.1.3. Effect of pH on [Al + Fe] species distribution

pH value has a great influence on Al, Fe, and their hydrolytic species. If the pH value was low, it would lead to the acidolysis of Al and Fe polymers. If the pH value was high, it will further hydrolyze and polymerize, which will affect the instantaneous species changes of the measured results [29]. Fixed dosage was selected in experiment, the species distribution of [Al+ Fe] during coagulation–flocculation at pH 5–9 was investigated, as shown in Fig. 2.

The content of $[Al + Fe]_b$ and $[Al + Fe]_c$ in the composite system increased gradually with the increased pH value, while the content of $[Al + Fe]_a$ in the composite system decreased significantly, and a minimum of 0.5% of mole fraction of $[Al + Fe]_a$ was obtained under the condition of pH value 9. As pH was from 5 to 9, the OH^- in the system

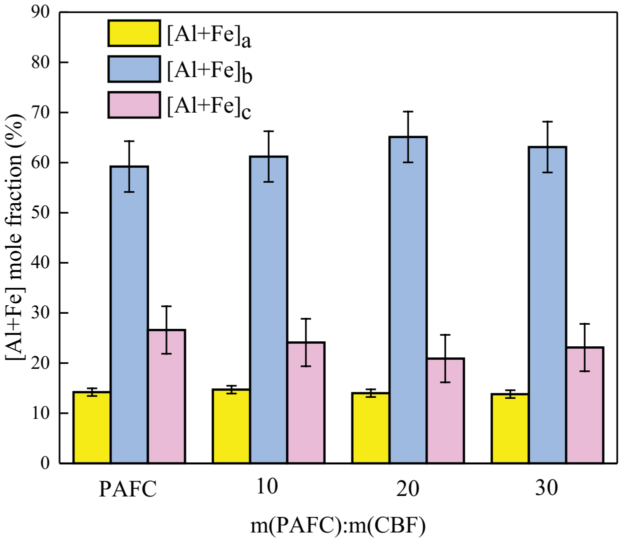

Fig. 1. Effect of m(PAFC):m(CBF) on [Al + Fe] species distribution.

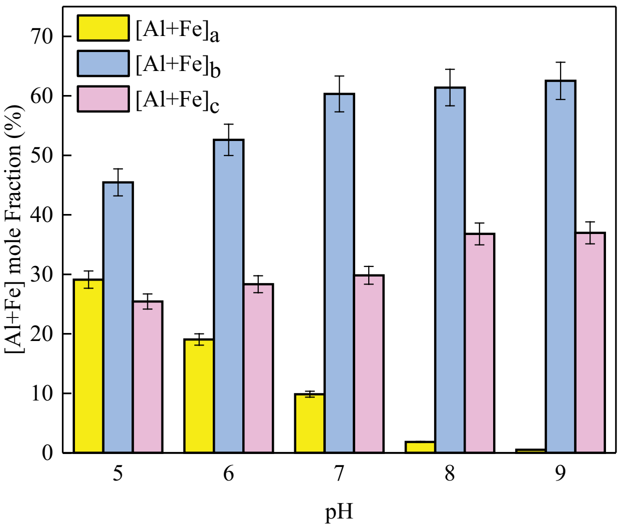

Fig. 2. Effect of pH on [Al + Fe] species distribution of PAFC-CBF.

increased, resulting in the decrease of free ions and mononuclear hydroxyl complexes.

Therefore, the number of intermediate polynuclear hydroxyl complexes and polymers increased correspondingly, and the number of complexes $[Al + Fe]_a$ that was easy to react with Ferron reagent decreases, while the number of complex $[Al + Fe]_c$ that was difficult to react with Ferron reagent increases [4,30]. However, when pH > 7, the increasing trend of $[Al + Fe]_b$ content was not evident. Therefore, the raw water was neutral or weak alkaline, which contributed to removing pollutants in the water by PAFC-CBF.

3.1.4. Effect of temperature on [Al + Fe] species distribution

It can be seen from Fig. 3 that the reaction temperature has little influence on the species distribution of [Al + Fe] in the PAFC-CBF at pH = 7.

As the reaction temperature has gone up, the content of the affective component $[Al + Fe]_b$ was basically stable, while the content of $[Al + Fe]_a$ was slightly reduced, and the content of the component $[Al + Fe]_c$ was slightly increased. Under specific pH conditions, the higher the system's temperature, the ion product of water increased continuously. Because the concentration of H^+ in the solution was constant, the concentration of OH^- in the solution also showed an upward trend [30,31]; moreover, the hydrolysis rate of Al^{3+} and Fe^{3+} was accelerated with the increased of reaction temperature, and it was easy to combine with OH^- in the system to form polynuclear hydroxyl complex and polymer.

Therefore, the complex which was easy to react with Ferron reagent in the composite system was reduced, while the complex that was difficult to react with Ferron reagent increases [31]. Hence, from low temperature to high temperature, the effect of temperature on the species distribution of [Al + Fe] was relatively small, proving that the PAFC-CBF can still obtain a better coagulation–flocculation effect at low temperature.

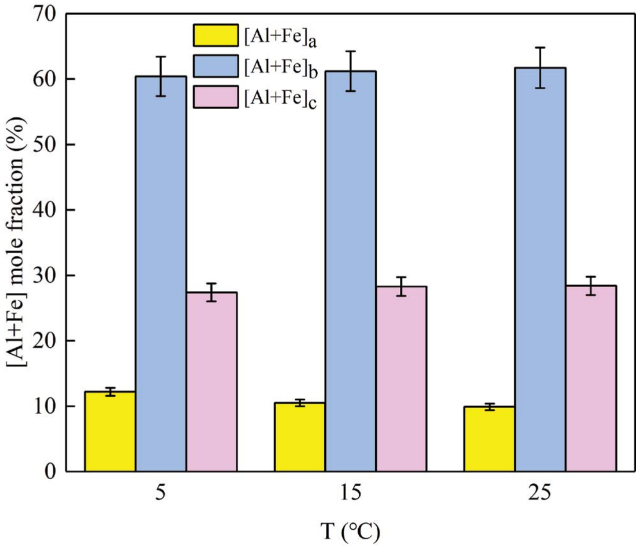

Fig. 3. Effect of temperature on [Al + Fe] species distribution of PAFC-CBF.

3.2. Flocs surface morphology of PAFC-CBF

As observed in Fig. 4a, it was evident that PAFC showed loose structure, and the boundaries between individual flocs were not very obvious.

As shown in Fig. 4b, PAFC-CBF displayed a different surface morphology from that of PAFC. The flocs of PAFC-CBF have become further dense, and the boundary between them was apparent. In addition, there were traces of extracellular polymer (EPS) wrapped on the flocs surface, which showed that it increased its adsorption bridging effect and enhanced its adsorption capacity for pollutants [32]. Meanwhile, it can be seen on the surface of PAFC-CBF flocs that there were many micropores due to the role of CBF, which increased the adsorption property and significantly improved the settlement performance of flocs so as to achieve the purpose of strengthening the flocculation of CBF [33].

3.3. Floc size, breakage, and re-growth

3.3.1. Floc growth, breakage and re-growth

The floc size has a significant influence on the solid-liquid separation effect and ultimately affects the treatment efficiency of the whole process [34]. Therefore, the effect of four dosage ratios of PAFC, PAFC-CBF (n = 10), PAFC-CBF (n = 20), and PAFC-CBF (n = 30) on the formation, breakage, re-growth of flocs was investigated, and the corresponding results are shown in Fig. 5.

There were three stages in the curves: the floc rapid growth stage, steady floc stage, and floc re-growth stage [35]. And the coagulation–flocculation time was prolonged from 30 s to 5 min, and the flocs particle size increased rapidly, resulting in the flocs particle size increased from 2 μm to 108–184 μm. In this period, the surface charge of flocs was neutralized by PAFC, and the particles collide with each other to form a larger floc. At the same time, the adsorption bridging effect of the system strengthened by

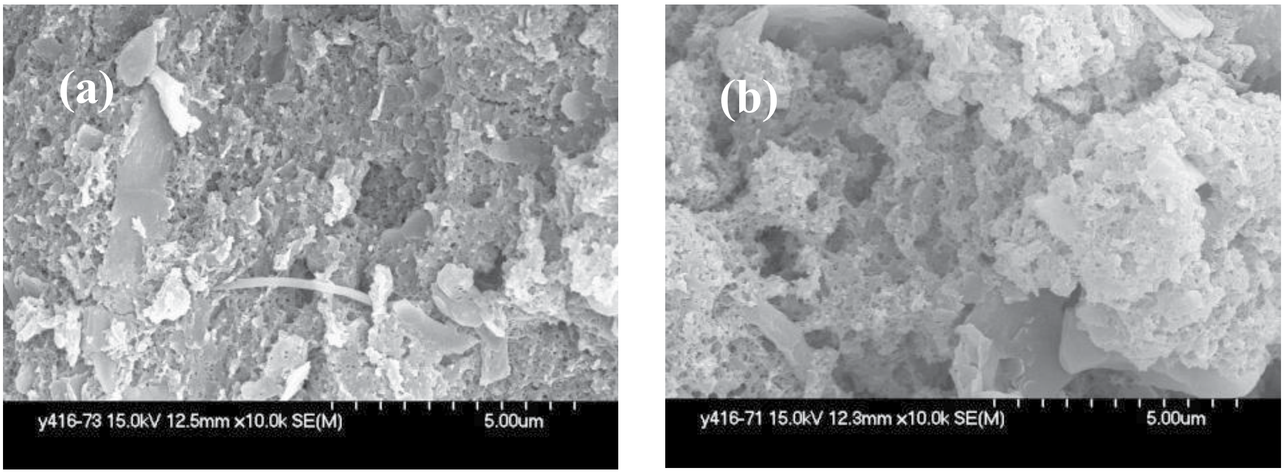

Fig. 4. SEM of flocs: (a) PAFC and (b) PAFC-CBF.

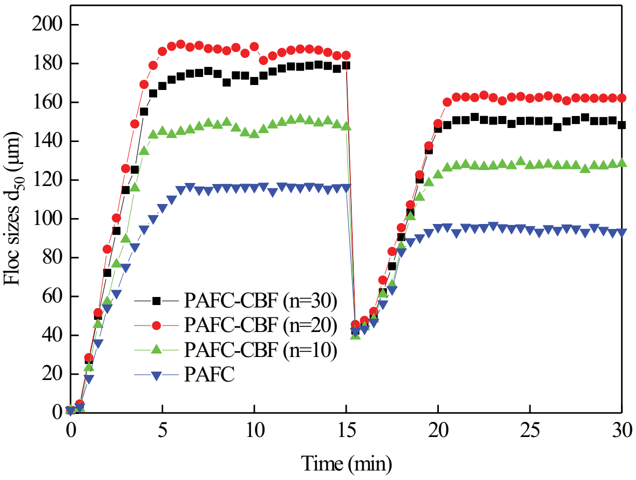

Fig. 5. Effect of proportion on floc formation, breakage, and re-growth.

CBF flocculant, the smaller particles can be adsorbed on the larger particles, thus increasing the size of the flocs [36]. In a steady period (5–15 min), and the size of the flocs will hardly change, which coagulation–flocculation process was a dynamic equilibrium process of flocs growth and breakage. Compared with the PAFC group, size of flocs increased by 40–80 μm, which indicated that CBF played a role in adsorption bridging, and accelerated the growth of flocs and increased the particle size, which was consistent with Bo et al. [17]. In the floc breakage and re-growth period (15–30 min), along with the shear increased to 200 rpm and entered the breakage period, the particle size of the flocs became sharply smaller. At 15 min, the size of the flocs decreased from 184 μm to 39 μm. As the shear dropped to 60 rpm, the breakage flocs re-growth and the particle size continued to increase and eventually remained steady. The growth and particle size change of breakage and re-growth flocs were consistent with that before breakage, but the size of recovered flocs was smaller than before breakage.

Meanwhile, the dosing ratio has a particular impact on the growth process of flocs. PAFC-CBF with a certain proportion produced more effective hydrolytic species $[Al + Fe]_b$ in the coagulation–flocculation process, so it has a decisive role in charge neutralization and bridging, which were a contribution to the aggregation of micro flocs into larger flocs. PAFC-CBF with a mass ratio of 20 has the fastest growth rate, the largest particle size, and the most substantial recovery ability. While the mass ratio was 30, due to the low content of CBF, and the effect of net catching and sweeping was not fully exerted, so the coagulation–flocculation effect was worse. And the mass ratio was 10, which was not conducive to the growth of flocs due to CBF being overdosed. Overdose of CBF was combined with the particles, which hinders the formation of micro flocs. Because the particles have like charge, the electrostatic repulsion force between them was enormous, so the flocs structure was loose, and the size of the flocs was small [36,37]. The results showed that the appropriate amount of CBF could accelerate the flocs growth and significantly increase the floc size.

3.3.2. Strength and recovery capability of PAFC-CBF flocs

Table 2 indicated the floc strength factor, breakage factor, and recovery factor. Floc strength factor decreased gradually with the increased dosage of PAFC, and breakage factor increased gradually, while recovery factor increased first and then decreased. The results showed that the floc strength of PAFC-CBF was slightly lower than that of PAFC alone, but the breakage flocs were accessible to recovery, which was beneficial to re-flocculation.

The maximum recovery factor was 86.21%, while the recovery factor with PAFC alone was 67.91%. For the flocs produced by adding PAFC alone, although its strength factor was more extensive, which was 56.25%, it was difficult to recover after breakage, which was not conducive to re-flocculation. Moreover, the previous experiment found that after adding PAFC alone, the residual turbidity of flocs was large and high. In contrast, the residual turbidity of PAFC-CBF was slight, which was consistent with the research of Bo et al [17] and Zhao et al [25].

Table 2
Breakage factor, strength factor, and recovery factor of different proportion of PAFC-CBF

	Proportion	Breakage factor	Strength factor	Recovery factor
PAFC	–	48.75%	56.25%	67.91%
PAFC-CBF	10	53.20%	46.80%	82.51%
PAFC-CBF	20	55.27%	44.73%	86.21%
PAFC-CBF	30	56.32%	43.68%	77.51%

As a biomacromolecule, bioflocculant has the characteristics of large charge, high molecular weight, and contains more active functional groups [38]. Therefore, it will further accumulate breakage micro flocs and form larger particles through the adsorption bridging effect. Because the adsorption sites of colloidal particles were partially damaged or covered by other materials, the size of the flocs will be affected to return to the size of the original flocs before the damage. The results showed that the whole process of flocs growth, breakage, and re-growth was as follows: The colloidal particles in the water were destabilized and aggregated under the substantial adsorption neutralization of PAFC, and then the micro flocs grow up under the adsorption bridging of CBF [39]. Flocs breaking under high shear force, simultaneously, the long chain of microbial flocculant may break, molecule adsorbed on the particle surface will be rearranged, the adsorption sites will be exposed again, and the flocs will be newly re-adsorbed and re-flocculated, so the recovery ability of PAFC-CBF flocs was more potent than that of PAFC flocs alone [34].

3.4. Effect of PAFC-CBF dosage on removal efficiency

3.4.1. Effect of PAFC-CBF on Zeta potential and turbidity

Zeta potential is an important index to reflect the stability of suspension and colloid, which can measure the strength of the interaction between particles [40]. Zeta potential and turbidity change with different proportions (dosage was 20 mg/L) and dosage of PAFC-CBF were studied, and the results are shown in Fig. 6.

As the increase of PAFC-CBF mass ratio, the zeta potential value of flocs formed by PAFC-CBF increased gradually. Adding PAFC alone, the zeta potential of flocs was –9.64 mV, which was the largest in all treatment groups, indicating that the introduction of CBF reduced the zeta potential of flocs. Due to CBF itself has a high negative charge, and the addition of CBF can reduce the zeta potential of flocs [41]. In addition to the charge neutralization, adsorption bridging plays a significant role in the coagulation–flocculation of PAFC-CBF [42].

The proportion of PAFC-CBF was $n = 30$, the zeta potential was the largest among PAFC-CBF experimental groups, but the coagulation–flocculation effect was not the best, which showed that CBF could enhance the coagulation–flocculation effect when it was correctly added. However, excessive CBF will reduce the neutralization effect, making it difficult for microparticles to form micro flocs, and increase the use cost from the practical application, resulting in the synergistic adsorption bridging effect of CBF was small, and the enhanced flocculation function was weak. Besides, the turbidity of adding PAFC-CBF was lower than that of adding PAFC alone, and the turbidity was the lowest when the mass ratio of PAFC-CBF was 20. This may be due to the introduction of an appropriate amount of CBF to produce more $[Al + Fe]_b$ and larger floc size, contributing to coagulation–flocculation strengthening, which was consistent with the results of Zhang et al. [4].

Zeta potential of flocs and turbidity removal rate increased gradually as the PAFC dose increased. The dosage of PAFC was 30 mg/L, the zeta potential was –0.31 mV, close to the isoelectric point. And the turbidity removal rate was the highest, reaching 87.50%. It can be concluded that the neutralization of adsorption plays a major role in PAFC coagulation. The effect of PAFC-CBF on turbidity and zeta potential was similar to that of PAFC. As the dosage was 30 mg/L, the zeta potential was -1.92 mV, and the turbidity removal rate reached the maximum, which was 92.14%, but there was no significant difference in 20–30 mg/L. By comparison PAFC, the introduction of CBF with a large number of negative charges in PAFC-CBF reduced the zeta potential value of flocs, and the turbidity removal rate was higher than that of PAFC alone, which was similar to the conclusion of Huang et al. [35].

3.4.2. Effect of PAFC-CBF dosage on UV_{254} and TOC

As shown in Fig. 7, with the increase of PAFC and AFC-CBF dosage, the removal of UV_{254} and TOC increased gradually. At the dosage was greater than 10 mg/L, the UV_{254} removal of PAFC-CBF was higher than that of PAFC alone, and TOC results were similar. These results shown that the introduction of CBF into PAFC can effectively enhance the removal effect of UV_{254} and TOC. It could be concluded that PAFC has more capability on changing the potential of colloid and CBF was good at absorption and bridge effect. It could be concluded that PAFC has more ability to change colloidal potential, and CBF has good adsorption and bridge effect. The combination of these two advantages and the increase of $[Al + Fe]_b$ species were conducive to improve the coagulation–flocculation effect, reducing the flocculation cost and decreasing the secondary pollution. Yang et al. [16] research also shown that composite bioflocculant has more advantages than single flocculant in enhancing flocculating rate, reducing flocculent costs and decreasing secondary pollution.

3.5. Summary of coagulation–flocculation mechanism of PAFC-CBF

In summary, the coagulation–flocculation mechanism of PAFC-CBF was as follows: firstly, the adsorption charge

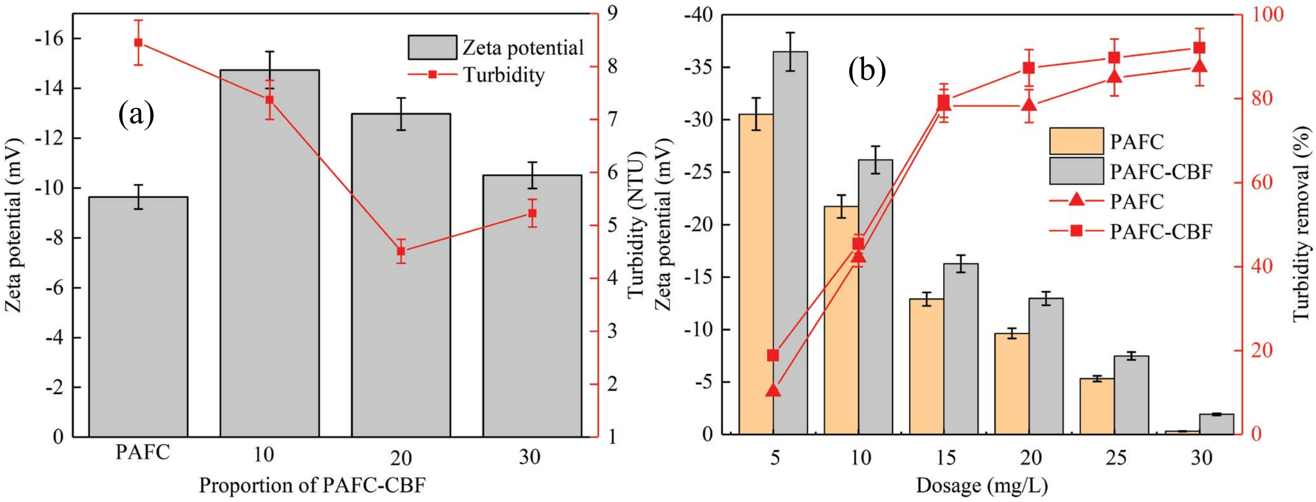

Fig. 6. Effect of proportion (a) and dosage (b, and $n = 20$) of PAFC-CBF on zeta potential and turbidity of flocs.

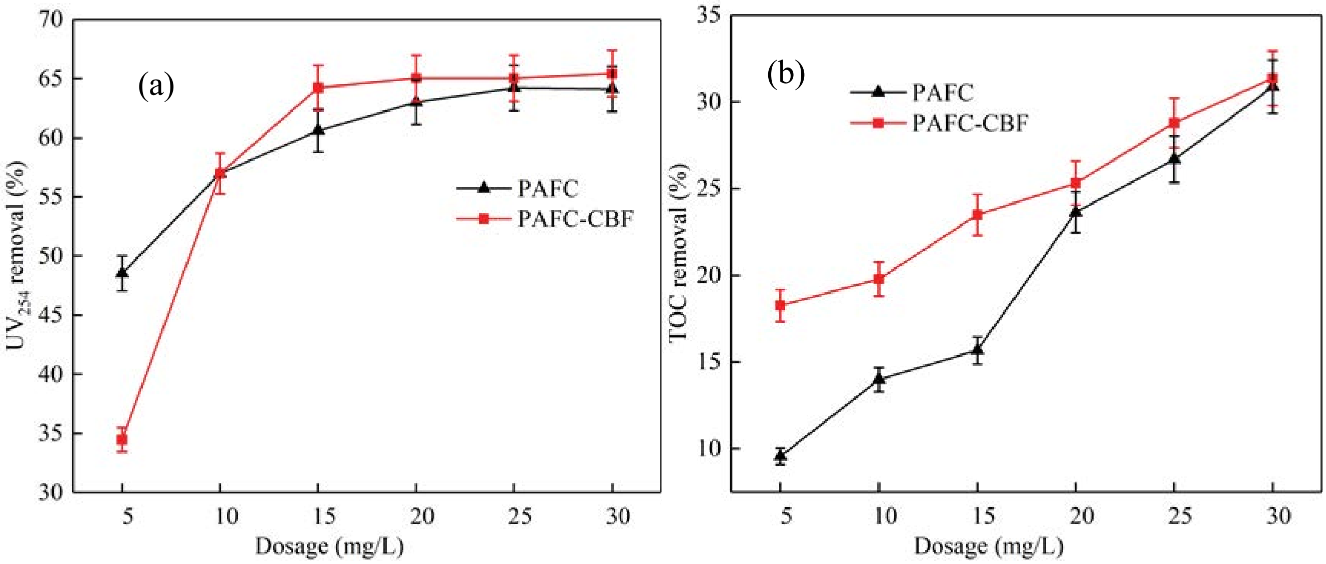

Fig. 7. Effect of PAFC-CBF ($n = 20$) dosage on UV_{254} (a) and TOC (b) removal.

neutralization of PAFC made colloidal particles in water destabilize and agglomerate, and some of them formed micro flocs [43,44]; Secondly, CBF has a variety of active functional groups such as $–NH_2$, –OH, –COOH, which can be adsorbed and combined with destabilized colloidal particles through hydrogen bond and covalent bond [45]. Because CBF was amphoteric flocculant, it has a variety of hostile charge groups, which can be combined with PAFC through ionic bond and van der Waals forces to form larger flocs [46]; Finally, because there were a lot of the same charge groups on the CBF molecular chain, the repulsive force was formed between them, so that the macromolecular substances were fully expanded, the bridging effect was fully exerted, and finally, the large flocs with larger size and good sedimentation performance were formed [47]. From the above results, it can be inferred that the coagulation–flocculation mechanism of PAFC-CBF was mainly adsorption charge neutralization, supplemented by adsorption bridging, and various coagulation–flocculation mechanisms gave full play to their individual characteristics to achieve a synergistic effect.

4. Conclusion

Compared to adding PAFC alone, PAFC-CBF with bioflocculant CBF hydrolyzed to produce more $[Al + Fe]_b$ species during the coagulation–flocculation process, and the content of $[Al + Fe]_b$ was the highest when the ratio was 20. The results showed that the flocs with the composite mass ratio of 20 had the fastest growth rate, the largest particle size, and the most robust recovery ability. The maximum recovery rate was 86.21%, while the recovery rate of PAFC alone was only 67.91%. Then, PAFC-CBF could improve turbidity removal efficiency, and effectively enhanced the removal effect of UV_{254} and TOC. Finally, it can be concluded that the coagulation–flocculation with PAFC-CBF was achieved by a combination of precipitate adsorption charge neutralization and adsorption bridging, and various coagulation–flocculation mechanisms give full play to their individual characteristics to achieve a synergistic effect.

Acknowledgments

The research is funded by grants from the National Natural Science Foundation of China (No 51408200), Open Project of State Key Laboratory of Urban Water Resource and Environment (No ES201803), and The China Postdoctoral Science Foundation (No 2018M641888).

References

[1] N.D.L. Beluci, G.A.P. Mateus, C.S. Miyashiro, N.C. Homem, R.G. Gomes, M.R. Fagundes-Klen, R. Bergamasco, A.M.S. Vieira, Hybrid treatment of coagulation/flocculation process followed by ultrafiltration in TiO_2-modified membranes to improve the removal of reactive black 5 dye, Sci. Total Environ., 664 (2019) 222–229.

[2] A.K. Tolkou, M. Mitrakas, I.A. Katsoyiannis, M. Ernst, A.I. Zouboulis, Fluoride removal from water by composite Al/Fe/Si/Mg pre-polymerized coagulants: characterization and application, Chemosphere, 231 (2019) 528–537.

[3] Z. Li, S. Zhong, H.Y. Lei, R.W. Chen, Q.H.L. Yu, Production of a novel bioflocculant by *Bacillus licheniformis* X14 and its application to low temperature drinking water treatment, Bioresour. Technol., 100 (2009) 3650–3656.

[4] Y.L. Zhang, S.P. Li, X.G. Wang, X.L. Ma, W.R. Wang, X.M. Li, Synthesis, purification and characterization of polyaluminum ferric chloride (PAFC) with high $(Al + Fe)_b$ content, Sep. Purif. Technol., 146 (2015) 311–316.

[5] L. Lévesque, C.A. Mizzen, D.R. Mclachlan, P.E. Fraser, Ligand specific effects on aluminum incorporation and toxicity in neurons and astrocytes, Brain Res., 877 (2000) 191–202.

[6] T. Lou, G.P. Cui, J.J. Xun, X.J. Wang, N.Y. Feng, J. Zhang, Synthesis of a terpolymer based on chitosan and lignin as an effective flocculant for dye removal, Colloids Surf., A, 537 (2018) 149–154.

[7] M.F. Elkady, S. Farag, S. Zaki, G. Abu-Elreesh, D. Abd-El-Haleem, *Bacillus mojavensis* strain 32A, a bioflocculant-producing bacterium isolated from an Egyptian salt production pond, Bioresour. Technol., 102 (2011) 8143–8151.

[8] L.X. Li, F. Ma, H.M. Zuo, Production of a novel bioflocculant and its flocculation performance in aluminum removal, Bioengineered, 7 (2016) 98–105.

[9] X.W. Bo, B.Y. Gao, N.N. Peng, Y. Wang, Q.Y. Yue, Y.C. Zhao, Effect of dosing sequence and solution pH on floc properties of the compound bioflocculant aluminum sulfate dual-coagulant in kaolin-humic acid solution treatment, Bioresour. Technol., 113 (2012) 89–96.

[10] L.X. Li, J. Xing, F. Ma, T. Pan, Introduction of compound bioflocculant and its application in water treatment, Adv. J. Food Sci. Technol., 9 (2015) 695–700.

[11] M. Fujita, M. Ike, S. Tachibana, G. Kitada, S.M. Kim, Z. Inoue, Characterization of a bioflocculant produced by *Citrobacter* sp. TKF04 from acetic and propionic acids, J. Biosci. Bioeng., 89 (2000) 40–46.

[12] W.J. Liu, K. Wang, B.Z. Li, H.L. Yuan, J.S. Yang, Production and characterization of an intracellular bioflocculant by *Chryseobacterium daeguense* W6 cultured in low nutrition medium, Bioresour. Technol., 101 (2010) 1044–1048.

[13] N. He, Y. Li, J. Chen, S.Y. Lun, Identification of a novel bioflocculant from a newly isolated *Corynebacterium glutamicum*, Biochem. Eng. J., 11 (2002) 137–148.

[14] N. He, Y. Li, J. Chen, Production of a novel polygalacturonic acid bioflocculant REA-11 by *Corynebacterium glutamicum*, Bioresour. Technol., 94 (2004) 99–105.

[15] S.G. Wang, W.X. Gong, X.W. Liu, L. Tian, Q.Y. Yue, B.Y. Gao, Production of a novel bioflocculant by culture of *Klebsiella* mobilis using dairy wastewater, Biochem. Eng. J., 36 (2007) 81–86.

[16] Z.H. Yang, J. Huang, G.M. Zeng, M. Ruan, C.S. Zhou, L. Li, Z.G. Rong, Optimization of flocculation conditions for kaolin suspension using the composite flocculant of MBFGA1 and PAC by response surface methodology, Bioresour. Technol., 99 (2009) 4233–4239.

[17] X.W. Bo, B.Y. Gao, N.N. Peng, Y. Wang, Q.Y. Yue, Y.C. Zhao, Coagulation performance and floc properties of compound bioflocculant-aluminum sulfate dual-coagulant in treating kaolin-humic acid solution, Chem. Eng. J., 173 (2011) 400–406.

[18] L.L. Wang, F. Ma, Y.Y. Qu, D.Z. Sun, A. Li, J.B. Guo, B. Yu, Characterization of a compound bioflocculant produced by mixed culture of *Rhizobium radiobacter* F2 and *Bacillus sphaeicus* F6, World J. Microbiol. Biotechnol., 27 (2011) 2559–2565.

[19] L.X. Li, Y.J. Piao, F. Ma, T. Sheng, C.Y. Sun, W.M. Liu, Preparation of a novel inorganic-biological composite flocculant for the removal of turbidity and organic matter in the surface water, Desal. Water Treat., 180 (2020) 219–226.

[20] J. Zhang, F. Chang, Y.J. Ren, Q.Y. Shi, An important improvement in Ferron-timed spectrophotometry, Appl. Spectrosc., 67 (2013) 985–992.

[21] Y. Chen, M. Zhang, L. Xie, Z. Wang, Q. Zhou, Molecular-weight-fractionation characteristics and coagulation behaviors of biorecalcitrant dissolved organic matter and colorants in cassava distillery wastewater, Ind. Eng. Chem. Res., 57 (2018) 4442–4451.

[22] Y.X. Zhao, B.Y. Gao, H.K. Shon, B.C. Cao, J.H. Kim, Coagulation characteristics of titanium (Ti) salt coagulant compared with aluminum (Al) and iron (Fe) salts, J. Hazard. Mater., 185 (2011) 1536–1542.

[23] X. Huang, B.Y. Gao, Q.Y. Yue, Y. Wang, Q. Li, S. Zhao, S.L. Sun, Effect of dosing sequence and raw water pH on coagulation performance and flocs properties using dual-coagulation of polyaluminum chloride and compound bioflocculant in low temperature surface water treatment, Chem. Eng. J., 229 (2013) 477–483.

[24] Y.X. Zhao, B.Y. Gao, H.K. Shon, Y. Wang, J.H. Kim, Q.Y. Yue, X.W. Bo, Anionic polymer compound bioflocculant as a coagulant aid with aluminum sulfate and titanium tetrachloride, Bioresour. Technol., 108 (2012) 45–54.

[25] S. Zhao, B.Y. Gao, X.Z. Li, M. Dong, Influence of using Enteromorpha extract as a coagulant aid on coagulation behavior and floc characteristics of traditional coagulant in Yellow River water treatment, Chem. Eng. J., 200 (2012) 569–576.

[26] Y.Y. Hu, C.Q. Tu, H.H. Wu, Species distribution of polymeric aluminium ferrum timed complexation colorimetric analysis method of Al-Fe-Ferron, J. Environ. Sci., 13 (2001) 418–418.

[27] I. Krupinska, Removal of natural organic matter from groundwater by coagulation using prehydrolysed and non-prehydrolysed coagulants, Desal. Water Treat., 132 (2018) 244–252.

[28] H.Z. Zhao, C. Liu, Y. Xu, J.R. Ni, High-concentration polyaluminum chloride: preparation and effects of the Al concentration on the distribution and transformation of Al species, Chem. Eng. J., 155 (2009) 528–533.

[29] B.C. Cao, B.Y. Gao, M.W. Wang, X.M. Sun, J. Wang, Floc properties of polyaluminum ferric chloride in water treatment: the effect of Al/Fe molar ratio and basicity, J. Colloid Interface Sci., 458 (2015) 247–254.

[30] M.Q. Yan, D.S. Wang, J.H. Qu, W.J. He, C.W.K. Chow, Relative importance of hydrolyzed Al(III) species (Al_a, Al_b, and Al_c) during coagulation with polyaluminum chloride: a case study with the typical micro-polluted source waters, J. Colloid Interface Sci., 316 (2007) 482–489.

[31] S.X. Duan, H. Hu, F. Xiao, D.S. Wang, C.Q. Ye, R.Y. Jiao, Y.J. Liu, Effects of Al species on coagulation efficiency, residual Al

and floc properties in surface water treatment, Colloids Surf., A, 459 (2014) 14–21.

[32] B.Y. Gao, B. Liu, T. Chen, Q.Y. Yue, Effect of aging period on the characteristics and coagulation behavior of polyferric chloride and polyferric chloride-polyamine composite coagulant for synthetic dying wastewater treatment, J. Hazard. Mater., 187 (2011) 413–420.

[33] X. Huang, X.W. Bo, Y.X. Zhao, B.Y. Gao, Y. Wang, S.L. Sun, Y.Q. Yue, Q. Li, Effects of compound bioflocculant on coagulation performance and floc properties for dye removal, Bioresour. Technol., 165 (2014) 116–121.

[34] J.C. Wei, B.Y. Gao, Q.Y. Yue, Y. Wang, Strength and re-growth properties of polyferric-polymer dual-coagulant flocs in surface water treatment, J. Hazard. Mater., 175 (2010) 949–954.

[35] X. Huang, S.L. Sun, B.Y. Gao, Q.Y. Yue, Y. Wang, Q. Li, Coagulation behavior and floc properties of compound bioflocculant polyaluminum chloride dual-coagulants and polymeric aluminum in low temperature surface water treatment, J. Environ. Sci., 30 (2015) 215–222.

[36] C.Z. Sun, Q.Y. Yue, B.Y. Gao, B.C. Cao, R.M. Mu, Z.B. Zhang, Synthesis and floc properties of polymeric ferric aluminum chloride-polydimethyl diallylammonium chloride coagulant in coagulating humic acid-kaolin synthetic water, Chem. Eng. J., 185 (2012) 29–34.

[37] W.Z. Yu, J. Gregory, L. Campos, G. Li, The role of mixing conditions on floc growth, breakage and re-growth, Chem. Eng. J., 171 (2011) 425–430.

[38] C.L. Pang, A. Li, D. Cui, J.X. Yang, F. Ma, H.J. Guo, Complete genome sequence of *Klebsiella pneumoniae* J1, a protein-based microbial flocculant-producing bacterium, J. Biotechnol., 220 (2016) 90–91.

[39] C.Z. Sun, J.W. Qiu, Z.B. Zhang, T.F. Marhaba, Y.H. Zhang, Coagulation behavior and floc characteristics of a novel composite poly-ferric aluminum chloride- polydimethyl diallylammonium chloride coagulant with different OH^-/(Fe^{3+}+Al^{3+}) molar ratios, Water Sci. Technol., 74 (2016) 1636–1643.

[40] H.Y. Rong, B.Y. Gao, M. Dong, Y.X. Zhao, S.L. Sun, Y. Wang, Q.Y. Yue, Q. Li, Characterization of size, strength and structure of aluminum-polymer dual-coagulant flocs under different pH and hydraulic conditions, J. Hazard. Mater., 252 (2013) 330–337.

[41] E.L. Sharp, P. Jarvis, S.A. Parsons, B. Jefferson, The impact of zeta potential on the physical properties of ferric-NOM flocs, Environ. Sci. Technol., 40 (2006) 3934–3940.

[42] Z.Q. Zhang, S.Q. Xia, J.A. Zhang, Enhanced dewatering of waste sludge with microbial flocculant TJ-F1 as a novel conditioner, Water Res., 44 (2010) 3087–3092.

[43] E.A. López-Maldonado, M.T. Oropeza-Guzman, J.L. Jurado-Baizaval, A. Ochoa-Terán, coagulation–flocculation mechanisms in wastewater treatment plants through zeta potential measurements, J. Hazard. Mater., 279 (2014) 1–10.

[44] P. Yang, D.D. Li, W.J. Zhang, N. Wang, Z.Y. Yang, D.S. Wang, T. Ma, Flocculation-dewatering behavior of waste activated sludge particles under chemical conditioning with inorganic polymer flocculant: effects of typical sludge properties, Chemosphere, 218 (2019) 930–940.

[45] Y.M. Li, Q. Li, D.K. Hao, Z.H. Hu, D.X. Song, M. Yang, Characterization and flocculation mechanism of an alkali-activated polysaccharide flocculant from *Arthrobacter* sp. B4, Bioresour. Technol., 170 (2014) 574–577.

[46] Z.C. Zhang, The flocculation mechanism and treatment of oily wastewater by flocculation, Water Sci. Technol., 76 (2017) 2630–2637.

[47] C.F. Zhao, S. Shao, Y.Y. Zhou, Y.H. Yang, Y. Shao, L.P. Zhang, Y.K. Zhou, L.N. Xie, L. Luo, Optimization of flocculation conditions for soluble cadmium removal using the composite flocculant of green anion polyacrylamide and PAC by response surface methodology, Sci. Total Environ., 645 (2018) 267–276.