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The study of PAFSSB on RO pre-treatment in pulp and paper wastewater

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Abstract

Reverse osmosis approach was used to dispose pulp and paper wastewater from a papermaking company. To meet the requirements of reverse osmosis membranes for water quality, a proper pretreatment had been done before raw water into RO membranes. A new efficient composite flocculant named PAFSSB had been used in the pre-treatment of pulp and paper wastewater. In the paper, the results showed that the treatment effect of PAFSSB was better, COD content was down to 10mg/L and COD removal rate was up to 75%. The pre-treatment process was simplified and processing costs were reduced.

Keywords: RO pre-treatment; Pulp and paper wastewater; Efficient flocculation; PAFSSB; COD

1. Introduction

Papermaking industry is the traditional big polluters. At present, CODcr emission of papermaking industry is in the front row of various industrial emissions. It has important practical significance to apply new technology to control pulp and paper wastewater, turn bane into boon and promote eco-environmental protection and sustainable development of papermaking industry [1-2]. A papermaking company used reverse osmosis approach to dispose pulp and paper wastewater. But in the reverse osmosis process, the membrane itself has certain requirements to pH, temperature and certain chemicals and so on. In order to meet the requirements of reverse osmosis membranes for water quality, proper pretreatments have been done before raw water into RO membranes [3-6]. Flocculation is an important method for RO

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pretreatment, which is already used and has a mature technology. It is the most widely used, economical and important way to dispose wastewater [7]. Flocculants are the core of flocculation to dispose wastewater [8], which consists of inorganic polymer flocculants, organic polymer flocculants, microbial flocculants, natural polymer flocculants and composite flocculants [9-13]. Wastewater which needs to be disposed is often a more complex and stable decentralized system, so traditional flocculants are often unable to meet the processing requirements. Composite flocculants have been widely used because they have the advantages of broad spectrum, low toxicity, good effect and simple operation. A new efficient composite self-developed flocculant named PAFSSB was used as the main raw material, moreover flocculation and sedimentation method were used for reverse osmosis pretreatment for papermaking wastewater, which could simplify process and stabilize water quality.

2. Materials and methods

2.1Reagents and experimental instruments

- Reagents: flocculants, sulfuric acid (98%), sodium hydroxide solution(10%), hydrochloric acid solution(10%), the solution prepared with distilled water.
- Experimental instruments: JBY-Ⅱ type flocculating and stirring device, 752 spectrophotometer, portable pH meter, beaker, graduated cylinder, pipette.

2.2Raw wastewater quality analysis

Wastewater was from a papermaking company before reverse osmosis system. Water quality analysis results were shown in Table 1.

Table 1. Characteristics of raw wastewater

Parameter(Unit)	Raw wastewater
COD (mg/L)	40
pH	6.92
Turbidity (NTU)	0.2
NH_3-N(mg/L)	1.46
Electrical conductivity(us/cm)	77.4

2.3Experimental procedure

Some wastewater were taken into the 600mL beaker, and placed on the flocculating and stirring device. Then several different flocculants were added to do flocculating and stirring experiments, after that put them aside for 30min. The supernatants were analyzed after the experiments. According to the characteristics of composite flocculants, experiment conditions were changed, such as dosage, pH, kinetic factors and so on, and ultimately the optimal process parameters were determined.

3. Results and discussion

3.1Effect of flocculant type

Currently, the nature of different impurities in the water had effect on the flocculation treatment effect. So it mainly depends on experiments to determine the appropriate flocculants and the best dosage [14]. The same batch of pulp and paper wastewater was taken, which COD was of 40mg/L and pH was of 6.92.And then the same dosage of different flocculants were separately added to do flocculating and stirring experiments. The effects were shown in Figure 1.

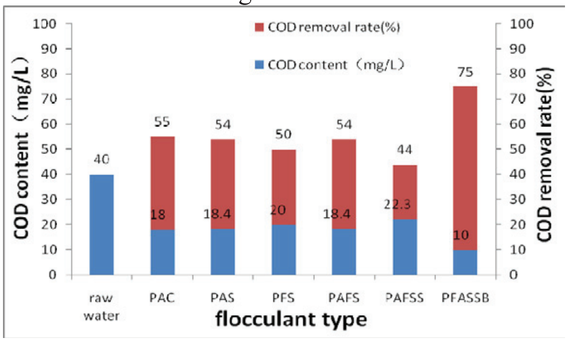


Figure 1. COD removal at different flocculant type

Figure 1 showed that, in different flocculants contrasting experiments, the efficient composite flocculant named PAFSSB had best effect, which was better than the other flocculants. COD content was from 40mg/L down to 10mg/L with the COD removal efficiency of 75%. PAFSSB had polyhydroxy complex ion Al_b and Fe_b. When it was put into the water, the pre-polymerization polyhydroxy complex ion Al_b and Fe_b immediately participated in the flocculating process, through adsorption and bridging agglomerating suspended solids, organic molecules, small molecules and particles, so that the flocculating ability doubled.

3.2Effect of PFASSB dosage

Taking the same batch of wastewater, different doses of flocculant named PAFSSB were added respectively. According to the set procedures to do experiments, experimental phenomena were observed. The supernatant were analyzed after the experiments and the results were shown in Figure 2.

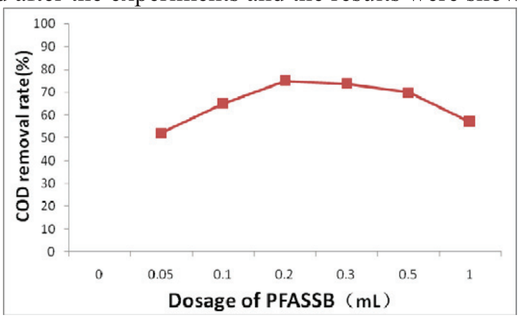


Figure 2. COD removal at different dosage of flocculant

Flocculant dosage was related to the suspended solids content in the solution. In general, flocculation effect would strengthen with the increase of the flocculant dosage, and it reached a peak at a certain dosage. When the dosage was continued to increase, the flocculation got worse. Because when flocculant dosage was excessive, it would produce colloid protecting function. After the adsorption surface of the entire colloidal particle were covered by polymer, when two particles were closed, it would be mutually exclusive by polymer and not together. The results showed that, with large alumen ustum and dense flocs, the optimum dosage of PAFSSB was 1.3mL/L with the COD removal efficiency of 75%.

3.3Effect of initial pH of wastewater

Taking the same batch of wastewater, pH was adjusted to different values. The same dose flocculant was added to do flocculating and stirring experiments. Then the supernatant were analyzed for the COD content, and the results were shown in Figure 3.

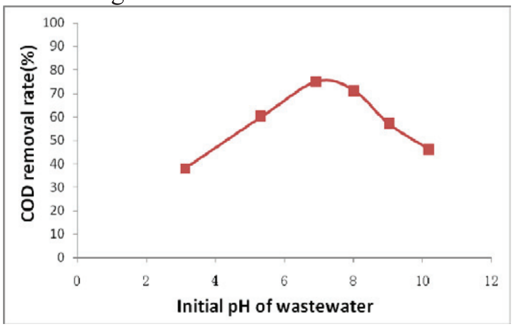


Figure 3. COD removal at different initial pH of wastewater

The pH has a great influence on Z charge of colloidal particles surface charge, the nature and function of flocculants, flocculating effect and so on. In decentralized system the adjustment of pH means adding H+ or OH-. These ions compress double electric layer and play a role of electrical neutralization. At this time H+ or OH- becomes positioning ion on the surface of these particles. When pH is adjusted to an appropriate range, the hydrolysis products of flocculants are in the form of groups or ions, which can give full play to agglomeration, so flocculating effect is the best. Therefore, the study on flocculating effect must study the impact of pH [15]. By the test results, when the optimal pH range was 6.5-7.5 with COD removal efficiency of 72%-75%.

The pH of pulp and paper wastewater used in the test was 6.92, so in the experiments pH adjustment step could be omitted to simplify operation.

3.4Effect of kinetic factors

After adding flocculants, in order to increase the particle collision frequency and the contact opportunity between particles and flocculants, stirring was used. Stirring process was divided into two parts, rapid stirring and slow stirring. In general, when the flocculants dissolved, in order to accelerate the dissolution rate, promote flocculants dispersed in water, and increase with the contact and collision between particles and flocculants, rapid stirring was used. In flocs growth stage in order to form large flocs which were conducive to sedimentation, slow stirring was used. In the experiments stirring speed and time were changed. The experimental results were shown in Figure 4.

Learned from the observation of the experimental phenomenon, if rapid stirring time was shorter, the alumen ustum would appear later after entering into the slow stirring. As flocculants and pollutants could not be fully contacted, the flocculants on colloid capture was affected. Meanwhile uneven distribution of the flocculants was not conducive to play a role [16]. Slow stirring could make formed flocs by the role of bridges and enmeshment to become large alumen ustum in order to accelerate sedimentation. With the increase of stirring time, flocculation was faster and more obvious, then formation flocs increased. However, if the stirring time was too long, formed large particulate matter would be broken into small particles that were difficult to precipitate, which would affect the flocculation effect. The experiment results showed that the optimal kinetic factors were at rapid stirring speed of 300r/min (60s) and at slow stirring speed of 50r/min (10min).

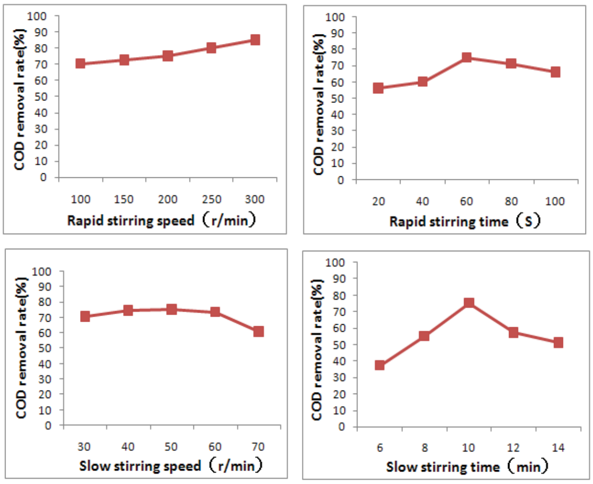
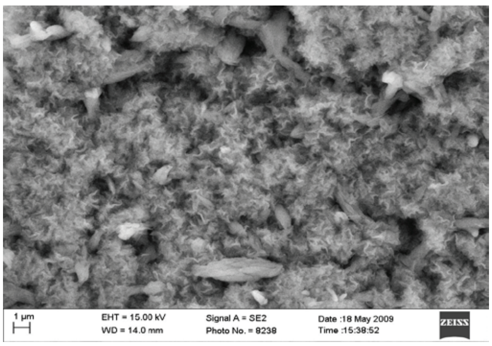


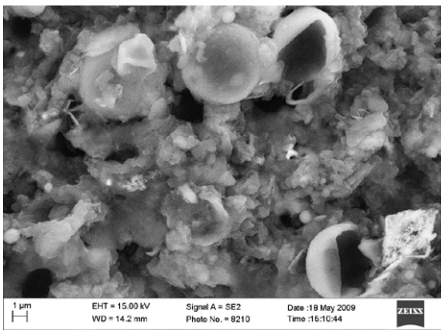
Figure 4. COD removal at different kinetic factors

3.5Mechanism analysis of flocculation

By scanning electron microscopy (SEM), the morphology of flocs after treatment was observed, as shown in Figure 5.



(a) SEM of flocs with PAC

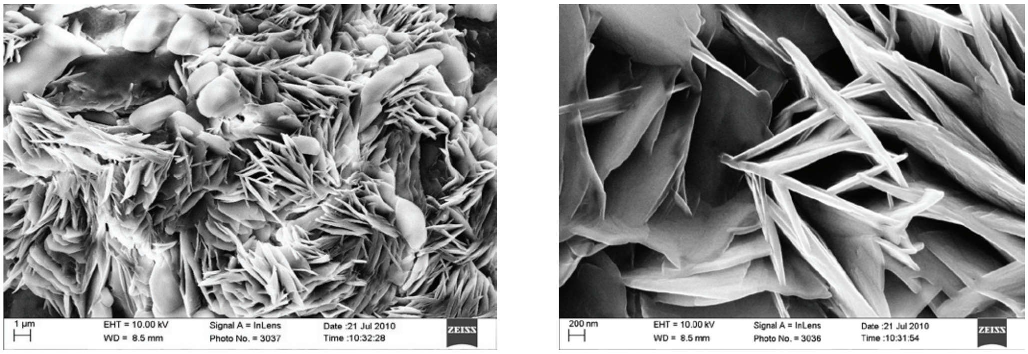


(b)SEM of flocs with PAFSSB

Figure 5. Transmission electron microscopy image of flocs in RO pre-treatment

After PAC added, the phenomena of the aggregation and flakiness between suspended solids in wastewater were obvious. But colloidal particles simply attached to large size flocs, and the density of each parcel was not enough, so they did not form a stable whole.

After PAFSSB added, the size of flocs was large, the density was enough, and the shape was regular with a ball chain or long chain. This bridge chain could make more small particles stick together to step up the field. Seen from the floc shape angle, PFASSB has a strong adsorption bridging and precipitation enmeshment effect, which was also conducive to the aggregation and deposition of unstable particles. Combined with the figures, various substances contained in flocs were analyzed. Large and dense flocs packaged a lot of suspended solids and colloidal particles, which closely combined to form a stable whole. Meanwhile, many small particles tightly attached to the floc structure that was formed by the suspended solids, colloidal particles and the coagulant hydrolysis products. Such floc structure could not be easily damaged because particles wrapped tightly each other to be strong stability.



(a) Magnification for 10k (b) Magnification for 50k

Figure 6. Transmission electron microscopy image of PAFSSB structure

Seen from the point of flocculation mechanism, PFASSB has a strong decontaminating capability, because sulfate, silicate, boron, aluminum, iron and other groups formed PAFSSB by polymerization. Hydrolysis products of Al^{3+}, Fe^{3+} ions and boron were adsorbed and chelated in the polysilicate particle surface, which had some form of linkage with polysilicate in order to enhance the adsorption bridging effect, so that the flocculating ability doubled, shown in Figure 6. In addition, simple complex compound after hydrolysis through hydroxyl bridged and polymerized with silicate ions. Polymerization, combination was random, while the polymer with unstable structure depolymerized at any time and rearranged, until stable spatial structure was formed.

4. Conclusions

Based on the contrasting experiments, the treatment effect of efficient composite flocculant named PAFSSB was better than other types of flocculants, which could effectively reduce the COD content in pulp and paper wastewater. The optimal dosage was 1.3ml/L at pH 6.5-7.5 after rapid stirring time of 60s (300r/min) and slow stirring time of 10min (50r/min). At this time COD removal rate could reach 75%. Flocs were observed by SEM, and further analysis combined with flocculation mechanism was done.

Sulfate, silicate, boron, aluminum, iron and other groups formed PAFSSB by polymerization. Hydrolysis products of Al^{3+}, Fe^{3+} ions and boron were adsorbed and chelated in the polysilicate particle surface, which had some form of linkage with polysilicate in order to enhance the adsorption bridging effect, so that the flocculating ability doubled.

In summary, this method used in pulp and paper wastewater was simple, effective and low cost, so it had very broad application prospects.

Acknowledgements

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