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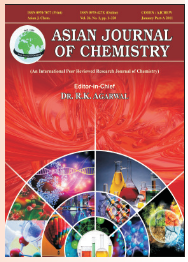

Fabrication and Experimental Study on PAC/CMCS Composite Flocculant for Treating Domestic Wastewater

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A novel composite flocculant was successfully prepared based on polymeric aluminum chloride (PAC) and carboxymethy1 chitosan (CMCS). The flocculation behaviors of the PAC/CMCS products were studied and evaluated by the removal rate of COD and turbidity of domestic wastewater. The result indicates that the process parameters have remarkable effect on the coagulating activity of PAC/CMCS flocculant. It achieved the best coagulating effect when the dose ratios of PAC to CMCS was 2:1, the reaction time was 0.5 h, the reaction temperature was 30 °C and pH value was adjusted to 4. In addition, the PAC/CMCS composite flocculant exhibited much enhanced flocculation performance compared with the conventional single flocculant such as polymeric aluminum chloride or carboxymethyl chitosan.

Keywords: PAC/CMCS, Composite flocculant, Wastewater, COD, Turbidity.

INTRODUCTION

Recently, the shortage of water resources and environmental problems have become serious factors in restricting economic growth and social development[1]. As one of main pollution sources for water in the world, the urban domestic sewage has a large amount of discharge and high concentration of pollutants. At the same time, it also contains all kinds of bacteria, parasites or viruses. The domestic sewage produce smelly materials in the action of anaerobic bacterial[2-3]. Therefore, we must pay more attention on pollution problem of urban domestic sewage in order to achieving sustainable development objectives.

As an important physical-chemical method, the flocculant is extensively used to treat domestic wastewater in the process of solid-liquid separations because of low cost, simple technology, some fine particles, upstanding treatment effect in persistent organic pollution, *etc.*[4-6]. Conventionally, the flocculants used in water treatment are classified into three groups: inorganic flocculants, organic flocculants and composite flocculants. Among these flocculants, the inorganic flocculants like chloride or ferrite flocculants have obvious disadvantages of poor adsorption bridging capability and large dosage while it is low cost. Though organic flocculants such as polyacrylamide or chitosan have strong adsorption bridging capability and stable products, the hard degradability and toxic residual monomer restrict its application. In view of complementary on the performance and cost for the above two types of flocculants, the composite flocculants have aroused great interests and become an important hotspot in the field of flocculants[7-10]. Up to now, some composite flocculants have exhibited enhanced flocculation properties for wastewater treatment that resulted partly from the different inorganic flocculant and organic flocculant[11-14]. However, most of the existing composite flocculants involve high cost or complicated process and thus it is still a challenge to develop simple, low-cost, environment-friendly routes for the composite flocculants with controllable process to broaden its industrial applications.

Polymeric aluminum chloride (PAC), a stable inorganic polymer material, is deemed to be one of the most important flocculants for industrial wastewater treatment due to its low cost, easy production process, wide pH adapting range, fast flocs-forming and good flocculation effect at low temperature[15-17]. However, the application of polymeric aluminum chloride poses a limitation in coagulation where the coagulation capacity is lower if it was applied individually. To overcome this limitation, organic carboxymethyl chitosan (CMCS) polymer material are introduced to prepare inorganic-organic hybrid flocculant with improved flocculant stability. The obtained PAC/CMCS composite flocculant is used for treating domestic wastewater, which shows enhanced flocculation performance compared with the conventional single flocculant such as PAC or CMCS.

EXPERIMENTAL

Carboxymethyl chitosan (CMCS) with molecular weight of 5×10^4 made in laboratory. All other chemical reagents in this work were used without further purification. In addition, the raw domestic wastewater used in the study was obtained from Huainan Sewage Treatment Plant in China, COD = 59 mg/L, turbidity value = 24, pH = 7.3. The fourier transform infrared spectroscopy was performed with a Nicolet 380 FTIR spectrometer. The removal rate of turbidity was performed on WGZ-1 Digital turbidity meter. The removal rate of COD were performed on a SP-722E visible spectrophotometer.

Synthesis of PAC/CMCS composite flocculant: Firstly, PAC and CMCS were dissolved in the three-necked flask with deionized water according to a certain proportion. Then, the mixture was constantly stirred under the power electric mixer and acetic acid was added gradually in the mixture to adjust pH. The resulting mixing solution was sealed and left for 1 h. After the drying and grinding, PAC/CMCS composite flocculants with the different molar were obtained. The investigation of optimum synthesis conditions was carried out by altering certain experimental parameters, such as dose ratios of PAC to CMCS (g/g), the reactive temperature (°C) and reaction time (h) and the value of pH.

Flocculation tests: The flocculation tests was investigated using domestic sewage of Huainan Sewage Treatment Plant as a probe and a Pyrex beaker (500 mL) as the photoreactor vessel. The reaction system containing 200 mL of domestic sewage solution and composite flocculants (0.05 g) was magnetically stirred at a constant speed of 150 rpm for 10 min to complete flocculation. The solution was poured into pear-shaped separatory funnel for standing layering. After 0.5 h, the liquid on the upper layer is used for flocculation tests. The experiments were carried out by measuring absorbance at 340 nm wavelengths and the removal rate of turbidity and organic contaminant (COD)[18].

RESULTS AND DISCUSSION

FTIR spectra characterization: The infrared spectroscopy of CMCS and PAC-CMCS are shown in Fig. 1. Compared with CMCS, the absorption peaks at 1621 cm^{-1} (vibrating adsorption of C=O) and 1421 cm^{-1} (vibrating adsorption of C-O) become weaker and the new peak at 1652 cm^{-1} (vibrating adsorption of -OH) appears in the spectrum of PAC-CMCS. It suggests that PAC with constitution water and absorbed water has been grafted into carboxyl of CMCS. At the same time, the peak at 1070 cm^{-1} disappears and the new absorbed peaks at 1085 cm^{-1} and 994 cm^{-1} emerge in the spectrum of PAC-CMCS, which shows the absorbed peak of Al-OH-Al bending vibration existing in the polymer. In addition, the phenomenon of the weaker peak at 560 cm^{-1} indicates that part of carboxymethyl have been replaced by polymeric aluminum. These small change demonstrates that the PAC-CMC composite flocculants has been prepared successfully.

Effect of process parameters on flocculating activity: In order to obtain the optimum composite flocculants, we discussed the effect of process parameters of PAC/CMCS composite flocculants on flocculation efficiency for domestic wastewater. In treating wastewater, the highest COD and turbidity removal are the main characteristics to determine the flocculation performance of flocculants. Fig. 2 showed the effect of the mixed ratio of PAC and CMCS on flocculating activity of PAC/CMCS composite flocculants. As can be seen from the diagram, the mixed ratio of PAC to CMCS showed a significant influence on COD removal. The COD removal rate of wastewater initially increased and then decreased with the variation of mixed ratio (PAC: CMCS) from 5:1 to 1:5. The optimum mixed ratio of PAC to CMCS was 2:1 based on COD and turbidity removal for 72.23 and 96.02 %, respectively. It indicated an appropriate ratio of CMCS could improve the flocculating activity due to its strong adsorption bridging capability, but excessive mass of CMCS which was water insoluble may induce water solubility decline of the flocculant. In this case, further increase in CMCS ratio would result in the decrease of COD removal rate.

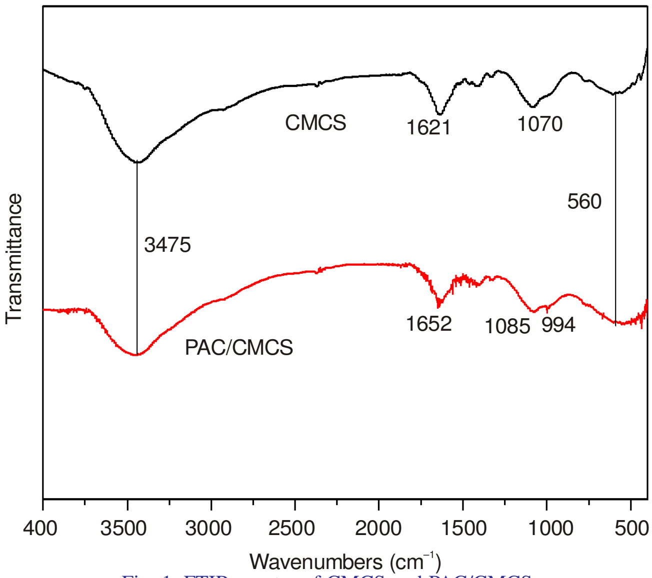

Fig. 1. FTIR spectra of CMCS and PAC/CMCS

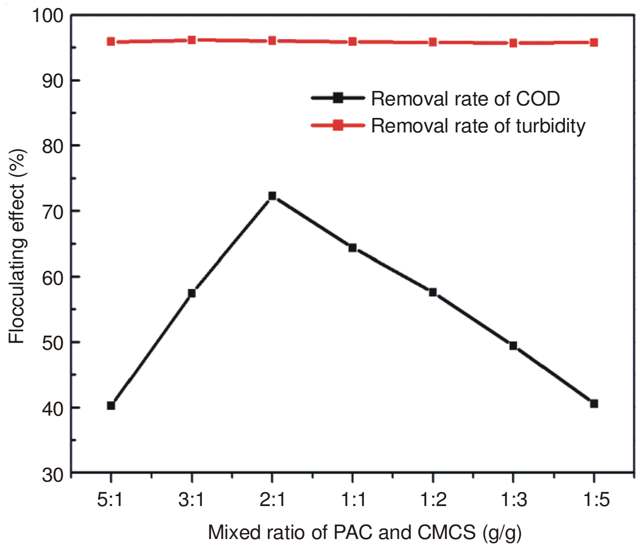

Fig. 2. Effect of the mixed ratio of PAC and CMCS on flocculating activity of PAC/CMCS composite flocculants. The cross-linking temperature, time and pH of the mixed solution was 30 °C, 2 h and 4, respectively

The value of pH is one of important factors for organic-inorganic composite flocculants. Fig. 3 shows the effect of pH on flocculating activity of PAC/CMCS composite flocculants when the mixed ratio of PAC and CMCS, cross-linking temperature and time was 2:1, 1 h and 30 °C respectively. It was found that the removal rate of COD and turbidity are presented with curve distribution with the increase of pH value from 2 to 5. When the value of pH was between 3 and 4, the removal rate of COD and turbidity attained its maximum performance. When the value of pH was smaller than 3, $-NH_2$ in carboxymethyl chitosan would be changed into $-NH_3$, which could decrease the flocculating effect. When pH value was more than 4, surface charge of colloidal particles in compounding flocculant increased accordingly with the increase of pH, resulting in the flocculating reaction more difficult. In a word, pH with 4 is considered to be best in the present experiment.

The flocculating activity at various reaction times for the synthesis of PAC/CMCS composite flocculants was shown in Fig. 4. As other factors were constant (the mixed ratio of PAC and CMCS, cross-linking temperature and pH respectively was 2:1, 30 °C and 4), reaction time varied from 1 to 4 h. The removal rate of COD and turbidity increased gradually in the first 2 h as the reaction time extend and reached a peak value when the reaction time was 2 h. With the further extension of reaction time, cross-linking between the reactants increased and the molecular weight of the product got larger continuously until the reaction reached its limits as the reduction of reactants. However, the removal rate of COD and turbidity become decreased or keep unchanged after the reaction time is longer than 2 h. This could be attributed that cross-linking reaction between PAC and CMCS had been completed when the the reaction time reached to 2 h, so too long time would make molecular chain of composite flocculants corrupted instead, which induced the flocculating activity decreased. Thus, the flocculating activity reached maximum when reaction time prolonged to 2 h.

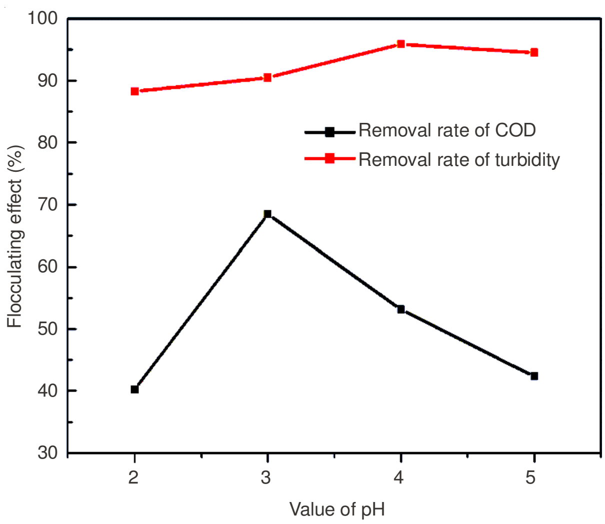

Fig. 3. Effect of pH on flocculating activity of PAC/CMCS composite flocculants. The mixed ratio of PAC and CMCS, cross-linking temperature and time was 2:1, 1 h and 30 °C, respectively

In order to evaluate the effect of cross-linking temperature on flocculating activity of PAC/CMCS composite flocculants,

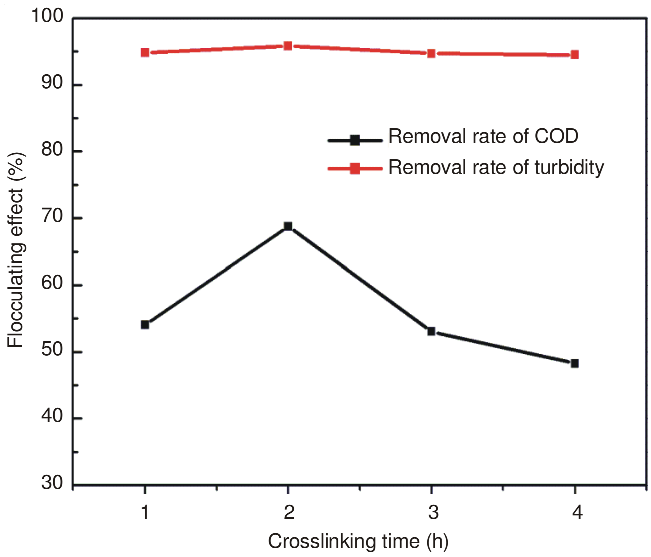

Fig. 4. Effect of cross-linking time on flocculating activity of PAC/CMCS composite flocculants. The mixed ratio of PAC and CMCS, cross-linking temperature and pH was 2:1, 30 °C and 4, respectively

experiments were conducted at five different cross-linking temperatures. Mixed ratio of PAC and CMCS, cross-linking time, pH was 3:1, 2 h and 4, respectively. As shown in Fig. 5, the flocculating activity increased as cross-linking temperature increasing from 20 to 30 °C, reaching a peak value at 30 °C, but then decreased gradually when the temperature was higher than 30 °C. It could be explained as follows: Firstly, the hydrolysis of inorganic salt coagulants belongs to endothermic reaction, which will lead to the hydrolysis of PAC that is tardy and incomplete under the condition of low temperature. Secondly, Brownian movement will restrict and reduce the opportunity of crashing between PAC and CMCS. So low temperature is harmful for the promoting of the degree of cross-linking and the molecular weight of PAC/CMCS. This is because higher temperature will cause the aging of CMCS and even decomposing into the insoluble substance[19-21], which

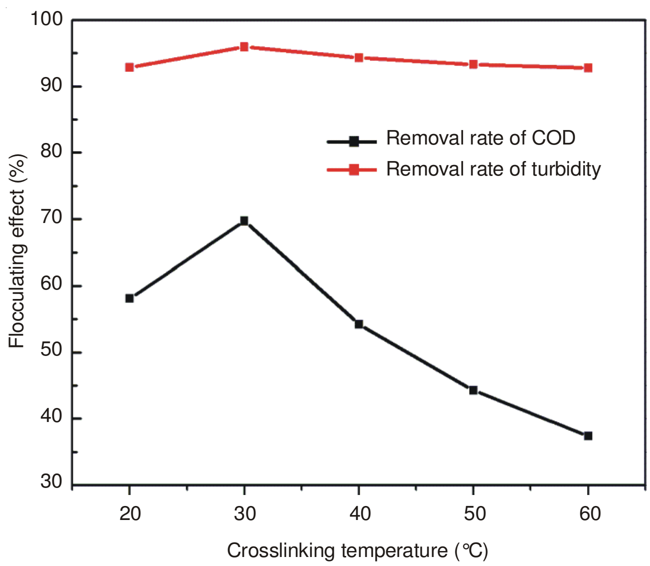

Fig. 5. Effect of cross-linking temperature on flocculating activity of PAC/CMCS composite flocculants. The mixed ratio of PAC and CMCS, cross-linking time and pH was 3:1, 2 h and 4, respectively

would bring the breakage of molecular chain and bridging flocculation of PAC/CMCS, resulting in lowered flocculation efficiency of PAC/CMCS composite flocculants.

Comparison of flocculating performance of different flocculants: To demonstrate the favorable flocculating activity of the coupled PAC/CMCS composite flocculant obtained by the optimal condition, its activity for treating domestic sewage was compared with pure PAC and CMCS components. Table-1 shows the results of COD and turbidity removal in the presence of different flocculants. For pure PAC flocculant, the removal rate of COD and turbidity are about 67.45 % and 57.14 % at 2 h, respectively. For pure CMCS flocculant, the removal rate of COD and turbidity are about 62.37 % and 79.69 % at 2 h, respectively. For PAC/CMCS composite flocculant, the removal rate of COD and turbidity reached 79.23 % and 96.82 % at 2 h, respectively. It indicated that compared with those of the pure single components, the PAC/CMCS composite flocculant exhibited an enhanced flocculating activity for COD and turbidity removal in domestic sewage. It will be of great and practical value for domestic sewage treatment industry.

TABLE-1

Flocculants	COD removal rate (%)	Turbidity removal rate (%)
PAC	67.45	87.14
CMCS	62.37	79.69
PAC/CMCS	79.23	96.82

Possible flocculation mechanism: For the enhanced flocculating activity of PAC/CMCS composite flocculant, there are two primary reasons in the present system: one is likely due to the good adsorption of CMCS component and the other is the synergistic effect of PAC and CMCS flocculants. There are large amounts of -OH in the molecular chain of CMCS, it can compound with organic materials containing $-NH_2$ or -COOH groups in water solution by forming hydrogen bond, which is beneficial to adsorb and remove COD of the organic contaminants in water.

On the other hand, flocculating activity of flocculants for the degradation of wastewater is related to its adsorption and bridging. For PAC/CMCS composite flocculant, the match of inorganic polymer flocculant (PAC) with adsorption and organic polymer flocculant (CMCS) with bridging in PAC/CMCS composite are suitable to promote polymerization and cohesion strengthen of colloidal particle, forming much larger and denser flocs, thus strongly enhancing sedimentation rate and adsorption rate[22]. Therefore, PAC/CMCS composite flocculant exhibited a superior flocculating activity than other single flocculants.

Conclusion

A novel PAC/CMCS composite flocculant with improved flocculation performance was successfully prepared and evaluated in removal of COD and turbidity for treating domestic wastewater. It was found that the removal rate of COD and turbidity of PAC/CMCS composite achieved the best coagulating effect with 79.23 % and 96.82 % respectively when mixed proportion of PAC to CMCS was 2:1, the reaction time was 0.5 h, the reaction temperature was 30 °C and pH value of was 4. It shows an enhanced flocculation performance than the conventional single flocculant such as PAC or CMCS. Therefore, this work not only demonstrated a facile route to the synthesis of inorganic-organic composite flocculant with improved performance, but also provided massy theoretical foundation for domestic sewage treatment application in the future.

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