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Study and Application of a Novel Tap Water Flocculant

Defang Zeng[1], Yong Zhai[1], Shuisheng Zhang[2], Fujun Ding[2]

[1]School of Resource and Environmental Engineering, Wuhan University of Technology, Hubei Key Lab of Mineral Resource Processing and Environment, Wuhan, China; [2]Hubei Shilu Chemical Coat Company, Yingcheng, China.
Email: zhaiyong2005@126.com

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ABSTRACT

By using polyaluminum chloride (PAC), chitosan (CTS) and montmorillonite (MM) as the main raw materials, a novel tap water flocculant had been prepared. The optimal mass proportion of this flocculant was 1 $g \cdot L^{-1}$ chitosan:50 $g \cdot L^{-1}$ PAC:3$g \cdot L^{-1}$ MM = 30:11:7. Compared with the traditional polyaluminum chloride (PAC), the concentration of aluminum ion (Al^{3+}) and suspended solids (SS) in the exit dropped 66.19% and 5.80% respectively, moreover, the cost was decreased by 9.95%. This flocculant was not only cheaper, but also provided improved flocculating function compared with traditional flocculant. The concentration of Al^{3+} in exit water was decreased greatly so the drinking water would be much safer.

Keywords: Water Treatment; Composite Flocculant; Flocculant; Aluminum Ion

1. Introduction

Currently the polyaluminum chloride (PAC) has been widely used in tap water treatment [1,2]. With the application of this chemical, it is generally inevitable to produce secondary pollution resulted from Al^{3+} [3], which brings threats and harms to human health [4]. Thus, there is a demand for an eco-friendly alternative to ensure treatment effect and human health.

In the study, a novel tap water flocculant was discovered based on lower concentration of Al^{3+} in exit water. The novel flocculant was made by polyaluminum chloride (PAC), Chitosan (CTS), and montmorillonite (MM). Owing to the decreased dosage of PAC, the concentration of Al^{3+} in exit water was significantly reduced. Besides, a large number of amino (NH_2) and hydroxyl (OH) groups on the molecular chain of CTS could form stable cheated compounds with Al^{3+} so as to remove part of metal ions from water. MM mainly play an adsorption role in tap water treatment to reduce the SS in exit water.

2. Experiments

2.1. Main Apparatus

Magnetism msier (78-1, Ronghua Equipment Manufacture Co., Ltd, Jiangsu, China); Scattering-type optoelectronic SSmeter (WGZ-100, Jinziguang Apparatus Company, Beijing, China); Digital electronic scale (BA210, Ohaus, Berlin, Germany) accurate to 0.0001 g; Electrical inductive coupling plasma mass spectrometer (ELAN6000, Sigma, Boston, USA); High-speed disperser (GFJO4A, Coating Industry Factory, Shanghai, China); Digital PH meter (pHS-25, Lida Apparatus Company, Shanghai, China); Air dry oven (FN101-3A, Apparatus Company, Changsha, China); Quartz automatic triple water distiller (1810-C, Kanghua Electronic Apparatus Factory, Jiangsu, China).

2.2. Main Reagents

Chitosan (CTS) with a viscosity of about 30 - 3000 mPa·S at 25 degrees Celsius and a degree of deacetylation of about 85% - 98%; Poly (aluminum chloride) with an Al_2O_3 content of more than 32%; Polymerized ferrous sulfate (PFS) with an Fe content of more than 22%; Natural montmorillonite (MM) with its content more than 70%, fineness less than 0.043 μm and specific surface of 260 $m^2 \cdot g^{-1}$; Cationic polyacrylamide (CPAM) with molecular weight of about 3 - 15 million and degree of cationic of about 5% - 80%; Acetic acid with an HAc content of more than 99%.

2.3. Raw Water

The raw water was obtained from The Yangtze River of Wuhan in China (SSvalue = 85.6 NTU, water temperature of about 21 - 25 degrees Celsius, pH = 7.2).

2.4. Preparation of the Composite Flocculant

There were 5 steps in the process of single-component flocculant preparation: 1) CTS was first dissolved in acetic acid. This formed suspension was diluted with water and stirred for 3.5 h at 25 degrees Celsius to prepare CTS working solution of 50 mg·L^{-1}. 2) Similarly PAC was mixed with water to form working solution of 1 g·L^{-1}. It took about 5 min to dissolve completely under stirring at 25 degrees Celsius. 3) MM was mixed with water to form working solution of 3 g·L^{-1}. It took about 6 h under stirring at 25 degrees Celsius. 4) CPAM was diluted with water and oscillated for 4 h at 25 degrees Celsius to form CPAM solution of 1 g·L^{-1}. 5) PFS was mixed with water and stirred for 5 min at 25 degrees Celsius to prepare PFS solution of 1 g·L^{-1}.

2.5. Experimental Methods

Eight samples of 200 mL raw water were placed into eight 250 mL beakers, and various different categories and dosages of flocculants were added under stirring. The solution was quickly stirred for 4 min at a speed of 260 r·min^{-1} and then slowly stirred for 8 min at the speed of 65 r·min^{-1}. The liquid was transferred to a separating funnel, where the floc was allowed to settle for 30min. A small volume of the upper layer was removed from the funnel, and the concentration of Al^{3+} and turbidity in exit water in this liquid were measured. In this way, a set of data were obtained.

The liquid was stirred by magnetism msier. The turbidity in exit water was measured by Scattering-type optoelectronic turbidity meter. The concentration of Al^{3+} was measured by electrical inductive coupling plasma mass spectrometer.

3. Results and Discussion

3.1. Confirming the Optimal Prescription

Based on reaching lower cost than that of traditional flocculant, three single-component flocculant were selected as a group and mixed in the proportion of 1:1:1. Eight specimens were designed and tested to determine the optimal prescription in terms of lower cost and better removal rate of SS.

Taking the higher accuracy and lower cost into account, we used 0.1 mL as the volume unit. The flocculant category and experimental data could be seen in **Table 1**.

The SS of 8 treatments in exit water was all higher than 16 NTU (**Table 1**). The treatment effect of the composite flocculant which contained CPAM was not satisfactory. The specimens containing both CPAM and MM were worse than other specimens. On the whole, the specimen 4 had the best effect and it was the optimal combination to be used. Its turbidity in exit water was only 16.2 NUT and removal rate of SS reached 81.07%. So the optimal prescription was made by 1 g·L^{-1} PAC, 50 mg·L^{-1} CTS, and 3 g·L^{-1} MM.

3.2. Confirming the Optimum Dosage

The optimum dosage of single-component flocculant was determined based on lower cost and better treatment effect. Thus this flocculant was superior to traditional one for the improved performance-price ratio and strong market competitiveness.

3.2.1. Confirming the Optimum Dosage of PAC

With the content of CTS and MM maintaining to 0.1 mL, the dosage of PAC was gradually changed in order to determine its optimum dosage.

Figure 1 showed that the larger the dosage of PAC; the lower the turbidity in exit water. When the dosage of PAC was less than 0.6 mL, with the dosage of PAC increasing, the turbidity in exit water was significantly decreased. When the dosage of PAC was more than 0.6 mL, the treatment effect of tap water was not very satisfactory with the dosage of PAC increasing. When the dosage of PAC was 1.0 mL, the turbidity in exit water was 3.12 NTU and the removal rate of SS was 96.3%. However, the cost of composite flocculant was higher than that of traditional flocculant.

Figure 1 showed that the larger dosage of PAC was added, the higher concentration of Al^{3+} was in exit water.

Table 1. The treatment results of 8 specimens.

NO.	Flocculant category (1:1:1)	Turbidity in exit water (NTU)	Removal rate of SS (%)
1	PAC + CPAM + CTS	21.5	74.88
2	PAC + CPAM + MM	22.7	73.48
3	PAC + PFS + CTS	18.3	78.62
4	PAC + CTS + MM	16.2	81.07
5	PFS + CPAM + MM	23.9	72.08
6	PFS + PAC + MM	20.1	76.52
7	PFS + PAC + CTS	20.4	76.17
8	PFS + CPAM + CTS	18.1	78.86

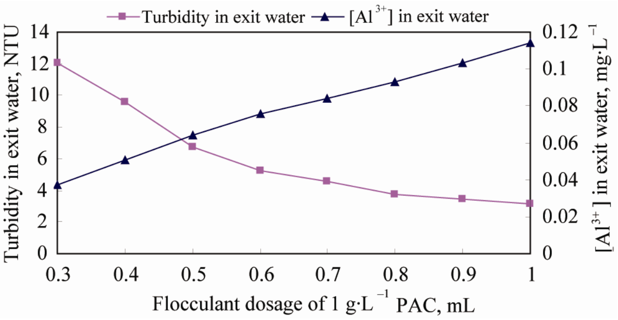

Figure 1. Relationship between dosage of PAC and turbidity, [Al^{3+}] in exit water.

So the optimum dosage of PAC was 0.6 mL. The cost of composite flocculant and concentration of Al^{3+} in exit water was decreased; what's more, the tap water treatment effect was better than that of traditional flocculant.

3.2.2. Confirming the Optimum Dosage of CTS

In a similar way, the dosage of PAC and MM was maintained to 0.6 mL and 0.1 mL respectively. The dosage of CTS was gradually changed in order to find the optimum dosage.

Figure 2 showed that with the dosage of CTS increasing, the turbidity in exit water was decreased at the beginning and then increased suddenly. If the dosage of CTS was very large, the treatment effect of tap water was not very satisfactory. When the dosage of CTS reached 0.22 mL, the turbidity in exit water was 1.28 NTU and the concentration of Al^{3+} was 0.065 $mg \cdot L^{-1}$, showing the best treatment effect of tap water. So the optimum dosage of CTS was 0.22 mL.

3.2.3. Confirming the Optimum Dosage of MM

Similarly, the dosage of PAC and CTS was maintained to 0.6 mL and 0.1 mL respectively. The dosage of MM was gradually changed in order to determine the optimum dosage.

Figure 3 showed that when the dosage of MM was lower than 0.14 mL, with the dosage of MM increasing, the turbidity in exit water was significantly decreased. However, when the dosage of MM was higher than 0.14 mL, the turbidity in exit water was significantly increased. This is because the MM suspension was a kind of emulsion which had a negative influence on the transparency of exit water. When the dosage of MM was 0.14 mL, the turbidity in exit water was only 0.65 NTU and the concentration of Al^{3+} was 0.057 $mg \cdot L^{-1}$. So the optimum dosage of MM was 0.14 mL.

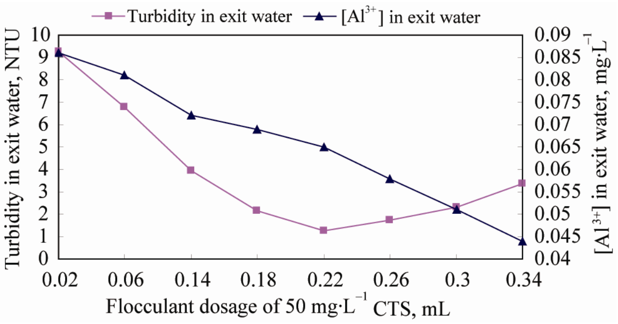

Figure 2. Relationship between dosage of CTS and turbidity, [Al^{3+}] in exit water.

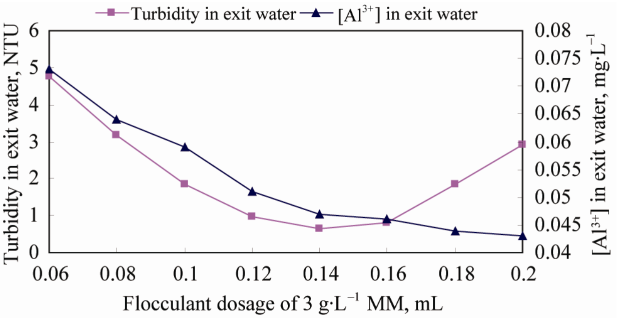

Figure 3. Relationship between dosage of MM and turbidity, [Al^{3+}] in exit water.

In conclusion, the novel composite flocculant was prepared in the weight proportions: 1 $g \cdot L^{-1}$ PAC:50 $mg \cdot L^{-1}$ CTS:3 $g \cdot L^{-1}$ MM = 30:11:7. The removal rate of SS reached 99.24%. The reasons were as follows: The concentration of Al^{3+} was decreased by using less dosage of PAC, at the same time, the CTS and MM played the role of flocculation and adsorption.

3.3. Confirming the Optimum Reaction Conditions

3.3.1. Confirming the Optimum Reaction Temperature

When the PH value was 7 and other conditions were confirmed, we conducted the tests to determine the optimal reaction temperature of composite flocculant (**Figure 4**).

The results of the experiment showed that the removal rate of SS was enhanced when the reaction temperature in the range from 0˚C to 30˚C, and then decreased when the temperature was higher than 30˚C. The Al^{3+} in exit water was decreased when the reaction temperature in the range from 0˚C to 40˚C, and then enhanced when the temperature was higher. It showed that when the temperature was from 10˚C to 40˚C, the flocculation effect was very good.

3.3.2. Confirming the Optimum Reaction pH Value

When the water temperature was 30˚C and other conditions were confirmed, a series of tests were conducted to study the flocculation effectiveness of composite flocculant under various pH value conditions.

Figure 5 showed that the optimal flocculation effect of composite flocculant at pH value 7. When the pH was higher than 7, the removal rate of SS was slightly in-

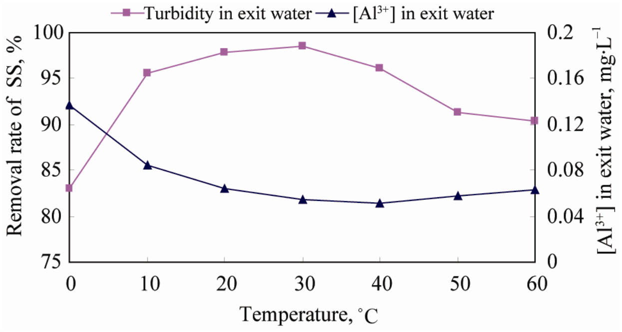

Figure 4. Influence of temperature on flocculation effect.

creased and Al^{3+} in exit water was slightly decreased. As the pH of raw water is 7, from the aspects of low cost and high efficiency, 7 is the optimal pH.

3.4. The Treatment Results of Traditional Flocculant (PAC)

The tap water treatment results of traditional flocculant (PAC) were as follows.

Figure 6 showed that when the dosage of PAC was 1.3 mL, the turbidity in exit water was 0.81 NTU higher than that of composite flocculant. What's more, when the dosage of PAC was 1.4 mL, the turbidity in exit water was higher than that of composite flocculant, and the cost of traditional flocculant was higher than that of composite one too. **Figure 6** showed that whether the dosage of traditional flocculant (PAC) was 1.3 mL or 1.4 mL, the concentration of Al^{3+} was both higher than that of composite flocculant. In conclusion, the performance-price ratio of composite flocculant was higher than that of traditional flocculant.

3.5. Comparison between Composite and Traditional Flocculant (PAC)

Comparing the novel composite flocculant to traditional flocculant, we could get the main economic indicators (**Table 2**).

Table 2. The result of competition on main economic indicators.

Category of flocculant	Traditional flocculant (PAC)	Novel composite flocculant
Turbidity in exit water (NTU)	0.69	0.65
Removal rate of SS (%)	99.15	99.24
Decline rate of SS (%)		5.80
$[Al^{3+}]$ in exit water ($mg\cdot L^{-1}$)	0.139	0.047
Decline rate of Al^{3+} (%)		66.19

Table 2 showed that the treatment effect of novel composite flocculant was better than that of traditional flocculant. The concentration of Al^{3+} and SS in exit water was decreased by 66.19% and 5.80% respectively; moreover, the cost of this flocculant was decreased by 9.95%. The composite flocculant could bring environmental and economic benefits greatly. The concentration of Al^{3+} in exit water was 0.047 $mg\cdot L^{-1}$, and it was lower than 0.05 $mg\cdot L^{-1}$. With the application of this composite chitosan flocculant in tap water treatment, harms caused by aluminum ions to human and environment were greatly reduced, showing a significant market prospect in tap water treatment.

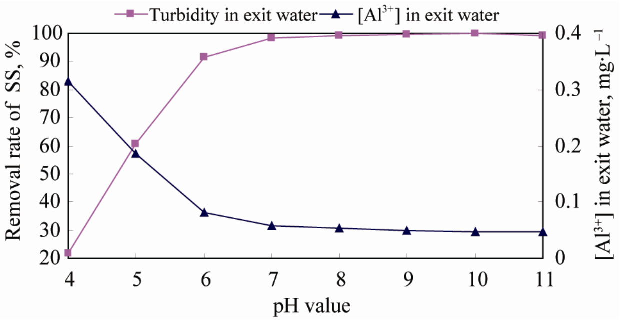

Figure 5. Influence of pH value on flocculation effect.

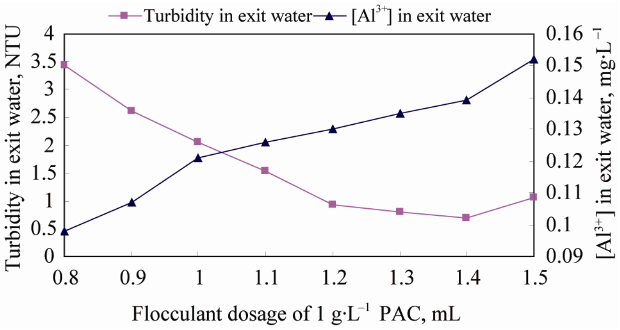

Figure 6. Relationship between dosage of traditional flocculant (PAC) and turbidity, $[Al^{3+}]$ in exit water.

3.6. The Mechanism of Flocculation Effect

3.6.1. PAC Plays the Role of Neutralization, Adsorption and Bridge

PAC can make a more stable rearrangement structure on the surface of the colloidal solid after dissolution [5]. PAC with high quantity of electric charge is able to significantly increase the power of neutralization [6]. The groups of OH can link the flocs and metal ions together and form bigger floc particles [7].

3.6.2. CTS Play the Role of Bridge, Neutralization and Chelation [8]

A large number of amino (NH_2) and hydroxyl (OH) groups on the molecular chain of CTS carry non-bonded pairs of electrons which can donate to empty d-orbital of metal ions and form stable chelated compounds [9]. So chitosan can be used to remove many deleterious metal ions from water [10], including Al^{3+}, Zn^{2+}, Cr^{3+}, Hg^{2+}, Ag^{+}, Pb^{2+}, Ca^{2+}, Cu^{2+} and Cd^{2+}. The active amino groups can also be protonated with H^{+} in water to form a cationic polyelectrolyte. Because of this cationic polyelectrolyte's static attraction and adsorption, chitosan can make colloidal particles to sedimentation [11,12].

3.6.3. MM's Adsorption Is Very Strong

The MM has a strong adsorption as the surface area and ion exchange capacity is enlarged through modification [13].

3.6.4. The Complex of CTS, PAC and MM Has the Effect of Complementary and Synergy Advantages

The neutralization effect of PAC and adsorption of MM can form a strong adsorption. The adsorption and bridge of CTS can flocculate particles into bigger floc that could settle out. The combination use of CTS and MM make destabilization of colloidal particles and improvement of coagulation velocities [14,15].

4. Conclusions

Compared with traditional chemical flocculant (PAC), the novel composite flocculant had the following advantages: higher removal efficiency for SS and Al^{3+}, lower material cost, easier treatment of tap water, and less pollution. Results showed that this flocculant with good properties played a positive role in tap water treatment. It was also observed that the novel composite flocculant was prepared in the weight proportions: 1 $g \cdot L^{-1}$ PAC:50 $mg \cdot L^{-1}$ CTS:3 $g \cdot L^{-1}$ MM = 30:11:7.

PAC and CTS both have the effect of neutralization, bridge and adsorption. But PAC mainly plays a part in neutralization and adsorption, while CTS mainly has a role in bridge and flocculation. MM has a strong adsorption. In conclusion, the synergism in the three flocculants provides excellent flocculation effect in water treatment.

Compared with traditional chemical flocculant (PAC), the concentration of Al^{3+} and SS in exit water was decreased by 66.19% and 5.80% respectively; moreover, the cost of this flocculant was decreased by 9.95%. Hence it is likely to gain wide acceptance and application for tap water treatment. There will be economic and environmental benefits on using this novel composite flocculant as an alternative to the traditional flocculant PAC in water treatment.

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