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Application of a chitosan flocculant to water treatment

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Abstract

A novel composite chitosan flocculant was made from chitosan, polyaluminium chloride (PAC) and silicate. Compared with the conventional flocculant such as PAC, the percentage of removing COD, SS and Al^{3+} in the treated water using this novel composite chitosan flocculant were enhanced by 1.8–23.7%, 50% and 61.2–85.5%, respectively, and its cost was cut down 7–34%. So this composite chitosan flocculant is of better environmental and economic benefits than that of conventional flocculant in water treatment

Keywords: Chitosan; Composite flocculant; Water treatment

1. Introduction

Chitosan as a cationic polysaccharide is an important polymer flocculant in water treatment (Juang, Tseng, Wu, & Lin, 1996; Lasco & Hurst, 1999). We know that in chitosan's molecular structure, there are many amino groups ($–NH_2$) and hydroxyl groups (–OH) on the molecular chain. These –OH and $–NH_2$ groups contain single-pair electrons that can offer the electron pair to empty d-trajectories of metal ions; then they chelate into a steady complex compound (–N–M–O–) (Zhang, 1979). Chitosan can therefore be used for removal of many unwanted metal ions in water such as Al^{3+}, Zn^{2+}, Cr^{3+}, Hg^{2+}, Ag^{+}, Pb^{2+}, Ca^{2+},Cu^{2+} and Cd^{2+} etc. (Bassi, Prasher, & Simpson, 2000; Muzzarelli, Weckx, Fillippini, & Sigon, 1989; Pesic, Oliver, Raman, & Lasko, 1994). Because the active amino groups ($–NH_2$) in the chitosan molecule can be protonated with H^+ in water into a cationic polyelectrolyte (Jaafari, Elmaleh, Coma, & Bankhouja, 2004) the molecule has powers of static attraction and adsorption. Thus chitosan can also flocculate particles into bigger flocs which become deposited. So chitosan can be effectively used for removing COD (organic contaminant) (Ishii, Koyama, & Mitani, 1995), and SS (solid suspending substances) in water treatment (Bolto, 1995).

Compared with traditional chemical flocculants, chitosan has the following advantages: the required dosage is less, a quicker depositing velocity, a higher efficiency of removing COD, SS and metal ions, easier sludge treatment, and there is no further pollution. Chitosan, however, as a flocculant for treating water, will have a higher cost than that of the traditional chemical flocculants. Therefore the objective was to prepare a cheaper composite chitosan flocculant material and to make this up from lobster shells (Defang, Gang, & Penyi, 2002) and other chemical flocculants. This composite chitosan flocculant was planned not only to reduce flocculation cost but also to improve flocculating function, comparing with single chitosan flocculant and the traditional chemical flocculant poly(aluminium chloride) (PAC).

2. Experiments

2.1. Raw water

Sewage of Tsinhua University in Beijing, China (COD = 200–400 mg L^{-1}, SS = 100–300 mg L^{-1}); and the

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raw water from the sewage treatment plant of Gao Beidian in Beijing of China (COD = 1200–1800 m L^{-1}, SS = 300–500 m L^{-1}).

2.2. Main reagents

Chitosans whose viscosities and deacetylating degrees are about 30–000 mPa S (at 25 °C) and 85–98%, respectively.

Poly(aluminium chloride) (PAC) in which Al_2O_3 is more than 32%. The molecular formula of PAC is $[AI_2(HO)_nCl_{6-n}XH_2O]_m$, $n = 1$–5, $m \leqslant 10$. It is a conventional flocculant used for water treatment. The formula of aluminium chloride is $AlCl_3$ and it is a monomer, and not polymer and it is not suitable used for water treatment, it is only a raw material for synthesizing PAC.

Polymerized ferrous sulfate (PFS), in which the content of Fe is more than 22%. The molecular formula of PFS is $[Fe_2(OH)_2(SO_4)]_m$, $m = 5$–10. It is made from $FeSO_4$ monomer. It is also a conventional flocculant.

Acetic acid >99%, was used as solvent for dissolving chitosan in preparing composite chitosan flocculant.

2.3. Main apparatus

Six-combined mixer (S2-1#, Scientific Apparatus Company, Shenzhen City, PR China); COD auto-measuring apparatus (TL-IA#, HACH Company, New York, USA); Spectrophotometer (722s#, Analytic Apparatus Company, Shanghi, PR China); Electrical inductive coupling plasma mass spectrometer (ELAN6000#, Sigma Company, Boston, USA).

2.4. Preparation of composite chitosan flocculant

The chitosan solution was prepared at 1% w/w in 1% w/w aqueous HAc. It takes about 3–5 h to dissolve chitosan completely under stirring at 25 °C.

PAC solution was prepared at 2% w/w in water; it takes about 5 min to dissolve PAC completely under stirring at 25 °C.

The working liquid of composite chitosan flocculant was made up from 1% chitosan: 2% PAC: accelerant in the ratio 1:100–200:10–20 (w/w). After mixing and dissolving them completely at room temperature, the working liquid of composite chitosan flocculant was a yellow transparent liquid.

2.5. Usage of multiple chitosan flocculant

Raw water pH 6–7 (500 ml) was placed in a 1000 ml funnel, and under stirring, 3–10 g working liquid of flocculant composite was added (the higher the concentration of COD, SS and metal ions in the raw water, the bigger the dosage of the working liquid). After shaking this funnel for 5 min, it was kept still for 5–30 min to ensure that deposition was complete. The upper layer was measured for the concentrations of COD, SS and metal ions.

2.6. Experimental methods

Raw waters were dispensed into 500 ml beakers and different categories and dosages of other flocculants were added with a stirring rate of 150 r $\min^{-1}$. After starting continuously for 10 min; the mixtures were transferred into 1000 ml separating funnels and the floc allowed to settle in the water for 30 min. Aliquots of the upper liquid were used to measure the concentrations of COD, SS and Al^{3+} in this liquid.

2.7. Comparing methods and confirming the optimal prescription

Firstly, typical domestic sewage was treated with pure PAC, and for the optimal dosage and the cost of PAC, different prescriptions of composite chitosan flocculant were designed for cheapness. Use of these composites provided data to allow useful comparisons and recommendations to achieve the reduced cost and the increased rate of removing COD, SS and metal ions with the optimum composite chitosan flocculant, compared with pure PAC.

3. Results and discussion

3.1. Results of live sewage treatment in Tsinghua University of China

Table 1 shows that the removal rate of COD by composite flocculant is higher than that of pure PAC; furthermore, the dosage of PAC (200 ppm) in the composite flocculant is less than that of pure PAC (320 ppm). This composite chitosan flocculant cannot only enhance COD's removal efficiency, but also reduce PAC's dosage, compared with pure PAC. And it also shows that the composite chitosan flocculant is of very obvious advantage of removing SS in water; at the optimal point in Fig. 3; not only its dosage of PAC reduces about 1/3, but also the concentration of SS in exit water is cut down more than 50%, compared with pure PAC under the same conditions.

Compared to 1# flocculant (pure PAC), firstly Table 2 shows that by using 2# flocculant the $[Al^{3+}]$ in exit water is reduced to 61.2%. The dosage of PAC in the composite flocculant is reduced by 37.5% and 23.7% Al^{3+} in the exit water is adsorbed by chitosan. So it proves that the effect of chitosan adsorbing Al^{3+} in water is very obvious. Secondly, Table 2 shows that by using 4# flocculant, the COD in exit water is reduced by 4%, and the $[Al^{3+}]$ in the exit water is reduced by 85.8%. Thirdly, the results of 3# and 4# in the Table 2 show that adding a small amount of PFS to composite flocculant can enhance the removal rate of COD and Al^{3+}. So the effect and dosage of 4# composite chitosan flocculant are the best.

Fig. 1 shows that the removal rate of COD of composite chitosan flocculants were enhanced by 1.8–23.7% compared with pure PAC.

Fig. 2 shows that the composite chitosan flocculants were reduced by 7–34% compared with pure PAC.

Table 1
The relationship between flocculant dosage and removal rate for COD and solid suspension in exit water

No.	Flocculant's category and dosage		Removal rate of COD (%)	COD in exit water (mg L^{-1})	Removal rate of SS (mg L^{-1})	Absorbency (610 nm)
	CTS (ppm)	PAC (ppm)				
1	0	120	38.55	203.84	23	0.055
2	0	200	51.84	159.74	26	0.045
3	0	320	73.11	89.19	36	0.029
4	0.6	120	61.15	128.88	32	0.038
5	0.6	200	58.49	137.70	30	0.04
6	0.6	320	77.10	75.96	33	0.026
7	1.2	120	74.44	84.78	34	0.028
8	1.2	200	86.40	45.10	15	0.019
9	1.2	320	73.11	89.19	36	0.029
10	1.8	120	79.76	67.14	39	0.024
11	1.8	160	73.11	89.19	23	0.029
12	1.8	200	90.39	31.87	32	0.019
13	1.8	320	63.81	120.06	39	0.036

Table 2
Comparison of removal rates of COD and Al^{3+} by composite chitosan flocculant and PAC

No.	Flocculant category and dosage			COD removal rate (%)	COD in exit water (mg L^{-1})	$[Al^{3+}]$ in exit water (mg L^{-1})
	Chitosan (mg L^{-1})	PAC (mg L^{-1})	PFS (mg L^{-1})			
1	0	320	0	52.5	89	1.34
2	1.8	200	0	52.5	89	0.52
3	0.6	200	40	44.3	111	0.49
4	1.2	200	40	54.1	85	0.19

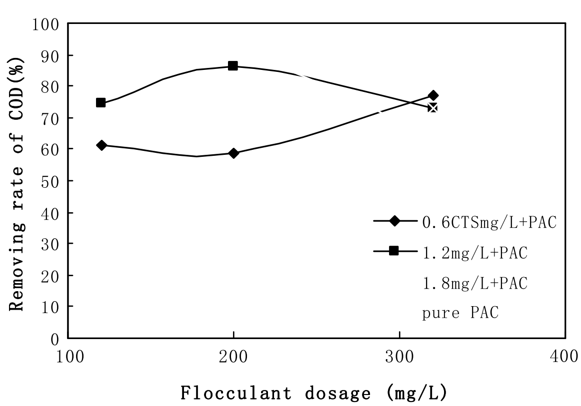

Fig. 1. Comparison of removal rate of COD between composite chitosan flocculant and PAC.

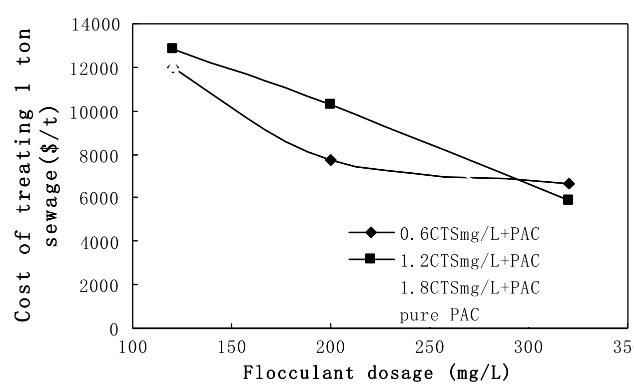

Fig. 2. Comparison of cost of treating 1 ton sewage between composite chitosan flocculant and PAC.

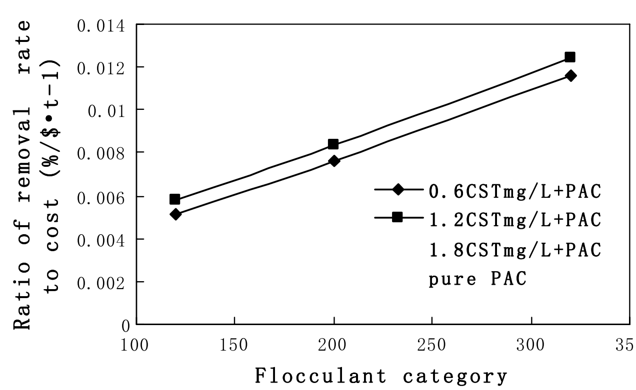

Fig. 3. Comparison of ratio of removal rate to cost between composite chitosan flocculant and PAC.

Fig. 3 shows that the that ratios of performance to price of composite chitosan flocculants are higher than that of pure PAC. The ratio of performance to price of composite chitosan flocculant of 1.8 mg/L CTS plus 320 mg/L PAC is the highest one which is 1.755 times as that of pure PAC. So the composite chitosan flocculant of 1.8 mg/L CTS plus 320 mg/L PAC is the best one among all the 10 flocculants.

3.2. Results of sewage treatment in Gao Beidian sewage treatment plant of China

Tables 3 and 4 show that the average value of COD in the exit water is lessened by using composite chitosan flocculant than by using pure PAC. And they also show that relationship between flocculant dosage and solid suspension of the exit water by measuring the absorbency of upper liquid; as the flocculant dosage increases, the absorbency of upper liquid reduces, and the concentration of SS reduces too. Besides, the removal rate of composite chitosan flocculant for SS is higher than that of pure PAC.

Table 3
The removal rate of COD, absorbency of upper liquid of pure PAC

No.	Flocculant's category and dosage		Removal rate of COD (%)	COD in exit water (mg L^{-1})	Absorbency (610 nm)
	CTS (ppm)	PAC (ppm)			
1	0	6	84.42	220.60	0.058
2	0	12	86.54	204.80	0.054
3	0	18	94.12	98.01	0.02
4	0	24	92.00	133.29	0.028
5	0	30	93.59	106.83	0.022
6	0	36	91.21	146.52	0.031
7	0	42	92.00	133.29	0.028
8	0	48	91.74	137.70	0.029
9	0	54	91.74	137.70	0.029
10	0	60	92.53	124.47	0.026
11	0	66	92.27	128.88	0.027
12	0	72	92.27	128.88	0.027

Table 4
The removal rate of COD, absorbency of upper liquid of flocculant dosage

No.	Flocculant's category and dosage		Removal rate of COD (%)	COD in exit water (mg L^{-1})	Absorbency (610 nm)
	CTS (ppm)	PAC (ppm)			
1	0.6	6	86.98	217.07	0.047
2	0.6	12	88.57	190.61	0.041
3	0.6	18	94.65	89.19	0.018
4	0.6	24	94.12	98.01	0.02
5	0.6	30	94.91	84.78	0.017
6	0.6	36	94.91	84.78	0.017
7	0.6	42	95.44	75.96	0.015
8	0.6	48	95.44	75.96	0.015
9	0.6	54	95.44	75.96	0.017
10	0.6	60	94.91	84.78	0.017
11	0.6	66	94.12	98.01	0.02
12	0.6	72	94.65	89.19	0.018

3.3. Confirming the optimal prescription and dosage of composite chitosan flocculant

Figs. 1–3 show that the optimal prescription of composite chitosan flocculant is that of composite chitosan flocculant of 1.8 mg/L CTS plus 320 mg/L PAC, because its ratio of performance to cost is highest in all of the flocculants tested. Generally speaking, the higher the concentration of COD and SS in water are, the more the dosage of composite chitosan flocculant is. The flocculant dosage has the direct relationship to the value of COD in water, and the relationship between them is on the basis of the following proportion:

Dosage of composite chitosan flocculant (mg L^{-1}): concentration of COD (mg L^{-1}) = 1:8.0–8.8 (w/w).

3.4. Environmental benefit of this composite chitosan flocculant

The removal rate of this composite chitosan flocculant for Al^{3+} in water is 85%. Once it is used in the city's sewage treatment, the second pollution resulting from Al^{3+} will be reduced greatly. Because the sludge treated by PAC backfills into the farm, the Al^{3+} will pollute farm land and cause the crop output to fall. If these aluminium ions flow into the water supply channels such as rivers, lakes and groundwater, the drinking water will be polluted, and it will directly and adversely mankind's health. Because the Al^{3+} will induce many diseases such as premature aging, dementia disease etc., it is unfortunate that PAC is a main flocculant nowadays. Therefore there is a strong case for the introduction and use of this composite chitosan flocculant instead of PAC in the water treatment; the potential harm of Al^{3+} for mankind will be greatly reduced.

3.5. Economic benefit of this composite chitosan flocculant

Cost of this composite chitosan flocculant reduced 7–34% (or cut 7–34% down), compared with that of pure PAC. Nowadays the dosage of pure PAC used for city's sewage and feedwater treatment is about 50,000 tons in China every year. The price of PAC's is about 241 US dollars per tonne. If the cost of one tonne of PAC were to be cut by 30%, the costs of flocculant used for sewage treatment plant and feedwater plant in China would save over 3,615,000 US$ every year. So the economic benefit of using this composite chitosan flocculant is very obvious.

4. Conclusions

A novel composite chitosan flocculant has been prepared according to the weight proportions, 1% chitosan:2% PAC:sodium silicate = 1:100–200:10–20 (w/w). Its optimal dosage in treating water was on the basis of the weight proportion, composite chitosan flocculant (mg L^{-1}): COD in the water (mg L^{-1}) = 1:8.0–8.8 (w/w). Compared with the conventional flocculant such as PAC, the percentage of removing COD, SS and Al^{3+} in the treated water using this novel composite chitosan flocculant were enhanced by 1.8–23.7%, 50% and 61.2–85.5%, respectively, and its cost was cut down 7–34%. It will bring greater economic and environmental benefits if this composite chitosan flocculant is used to replace the traditional flocculant PAC in water treatment.

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