The Flocculating Properties of Chitosan-*graft*-Polyacrylamide Flocculants (II)—Test in Pilot Scale

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Received 26 July 2009; accepted 22 January 2010
DOI 10.1002/app.32143
Published online 5 April 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, the flocculating properties of chitosan-*graft*-polyacrylamide (PAM) copolymer flocculants have been investigated in pilot scale, and the raw water from Zhenjiang part of Yangtse river in China was used as simulated waste water. The influences of dose, mechanical mixing rate, and sedimentation time to the flocculating effects have been investigated in different seasons: summer and winter, respectively. The optimal experimental conditions have been studied by orthogonal test. In addition, the structure effects of the flocculants: the grafting ratio, on the flocculating properties have been also investigated in pilot scale, which results were fully consistent to those from the beaker experiment in laboratory scale using kaolin suspension as simulated waste water. Compared to poly ferric sulfate, current used flocculants in Jinxi Water Factory, chitosan-*g*-PAM copolymer flocculants showed better flocculating properties, which was ascribed to the cooperative effects of the charge neutralization and bridging flocculating mechanisms of polymer flocculants. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2016–2024, 2010

Key words: chitosan-*graft*-polyacrylamide copolymer flocculants; pilot scale; flocculating properties; orthogonal test; grafting ratio

INTRODUCTION

Recently, natural polymer-based flocculants have been paid more attention in water purification, as they are believed as low price, nontoxic, and environment-friendly materials, which have been even acclaimed as "Green Flocculants of 21st Century".[1,2] Chitosan (poly-β-(1→4)-2-amino-2-deoxy-D-glucose), one of the high performance natural polysaccharide materials, is prepared from deacetylation of natural chitin, the second most abundant natural polymers in the world. For those novel characteristics, chitosan has been already applied widely in many fields, such as biotechnology, biomedicine, food, and cosmetics.[3–7] Furthermore, chitosan presents abundant free amino groups along the chain backbone that is cationically charged in a wide range of physiological pHs, and shows prominent flocculating effects in water purification.[1,2,8] However, chemical modified chitosan-based flocculants, such as polyacrylamide (PAM) grafted chitosan,[9–11] would bear more effective flocculating properties, which could overcome many disadvantages of chitosan itself, such as the low molecular weight and bad solubility, in practical application. But, previous study have been always limited in the laboratory scale, there is few report related to the work for investigation of the effects of the natural polymer-based flocculants on the flocculating properties in pilot scale. In this work, the flocculating properties of chitosan-*graft*-polyacrylamide (chitosan-*g*-PAM) copolymer flocculants have been investigated in pilot scale, and the raw water from Zhenjiang part of Yangtse River in China is used as simulated waste water. The influences of three external factors: dose, mechanical mixing rate and sedimentation time, to the flocculating effects have been studied by orthogonal test in different seasons: summer and winter, respectively. In addition, the effects of structure factor: the grafting ratio of the copolymers, on the flocculating properties have been also studied in pilot scale, which results have been compared with those from beaker experiment in the laboratory scale using kaolin suspension as simulated waste water.[12] In terms of the flocculating

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Contract grant sponsor: Key Natural Science Foundation of China; contract grant number: 50633030.
Contract grant sponsor: Research Project of Ministry of Housing and Urban-Rural Development of Chinacontract grant number: 2009-K7-11.
Contract grant sponsor: Directive Project of Zhenjiang Social Development in 2008; contract grant number: FZ2008029.

mechanisms: charge neutralization and bridging flocculating mechanism, the effect of grafting ratio on the flocculating properties have been discussed in detail.

EXPERIMENTAL

Chemicals

Chitosan was purchased from Shangdong Aokang Biological Co. and the degree of deacetylation was 85.2%, and its viscosity average molecular weight was 83.4×10^4 g/mol, calculated from the intrinsic viscosity.[13] Polyferric sulfate ($[Fe_2(OH)_n(SO_4)_{3-0.5n}]$, $n < 2$) was kindly supplied by Zhenjiang Taibaifen Factory. Acrylamide (C.P. grade) from Nanjing Chemical Reagent Co. and ceric ammonium nitrate (A.R. grade) from Sinopharm Chemical Reagent Co. were used without further purification.

Preparation of chitosan-*g*-PAM[14,15]

Chitosan was used as the backbone for all graft copolymerizations. The desired amount of solid chitosan powder was dissolved in 150 mL 1% acetic acid aqueous solution by agitation. After 30 min stirring under N_2, the Ce(IV) initiator and acrylamide monomer were added to the solution. The amount of chitosan was kept a constant, but the amount of acrylamide was changed for each synthesizing experiment in order to prepare a series of PAM grafted chitosan samples with various grafting ratios. The mass ratio of chitosan and acrylamide (AM) was 1 : 1, 1 : 3, 1 : 5, and 1 : 8, respectively. After 3 h for reaction, the polymerization was stopped and the samples were precipitated in acetone. The white products were purified three times by repeated dissolving–precipitating treatment, then by Soxhlet extraction using acetone as solvent further, and finally dried at 50°C in a vacuum oven for 48 h. In addition, the four final graft samples were named chitosan11, chitosan13, chitosan15, and chitosan18, respectively, based on the mass ratio of chitosan and AM before reaction as mentioned above.

The detailed structure characterizations of these graft copolymers have been determined and discussed in previous works,[12,16] and the grafting ratio has been determined by the method of specific refractive index increment measurement in solutions.[12,16]

Flocculating experiment

A set of equipment for flocculating experiment in pilot scale, at Jinxi Water Factory in Zhenjiang of China, was shown in Figure 1, and the capacity of water treatment by this equipment was 1 m^3/h. Figure 2 was the flow chart for this equipment including raw-water tank, triple coagulative precipitation tanks, inclined-tube setting tank, sand-filtering column, clear-water tank and its backflushing system. The detailed flocculating experiment in pilot scale was described below: Firstly, the raw water and the chitosan-*g*-PAM flocculants were mixed in the raw-water tank; then the mixtures was extruded into the triple coagulative precipitation tanks by water pump for sufficient mixing, and then the treated water flowed into the inclined-tube setting tank for separation of precipitates primarily; at last it was filtrated by sand-filtering column for further purification.

Orthogonal test

The raw water was from Zhenjiang part of Yangtse river in China, and the method of orthogonal test has been applied to investigate the flocculating properties of chitosan-*g*-PAM copolymer flocculants in continuous water treating process, and three main external factors: dose of flocculants, mechanical mixing rate, and sedimentation time to the flocculating effects have been investigated in summer and winter, respectively, and three variables have been tried for each factor. The detailed experimental parameters were shown in Table I and II. The dose of flocculants was range from 0.1–1.2 mg/L; The mechanical mixing rates in triple coagulative precipitation tank were 250–100, 100, 50 r/min, respectively; The sedimentation time was adjusted by controlling the flow velocity of raw water into the raw-water tank from 10–20 min. The experimental results have been also compared with those by current used flocculants: poly ferric sulfate, at Jinxi Water Factory.

Other relative experimental conditions were described below: The mechanical mixing rate in raw-water tank was 150 r/min. The height of the silicious sand in the sand-filtering column was 76 cm, and the column was backflushed every 24 h. The soil discharging in the coagulative precipitation tanks was carried out every 12 h. The turbidity values of the treated water have been determined by Turbidity Indicator of ATZ-A22 made in Guangming Instrument Factory of Wuxi in China. The units of turbidity from a calibrated nephelometer were called Nephelometric Turbidity Units (NTU), which was applied in this work.

The effects of the grafting ratio of flocculants on the flocculating properties

The experimental conditions for investigation of the effects of the grafting ratio on the flocculating properties in pilot scale were similar to those in

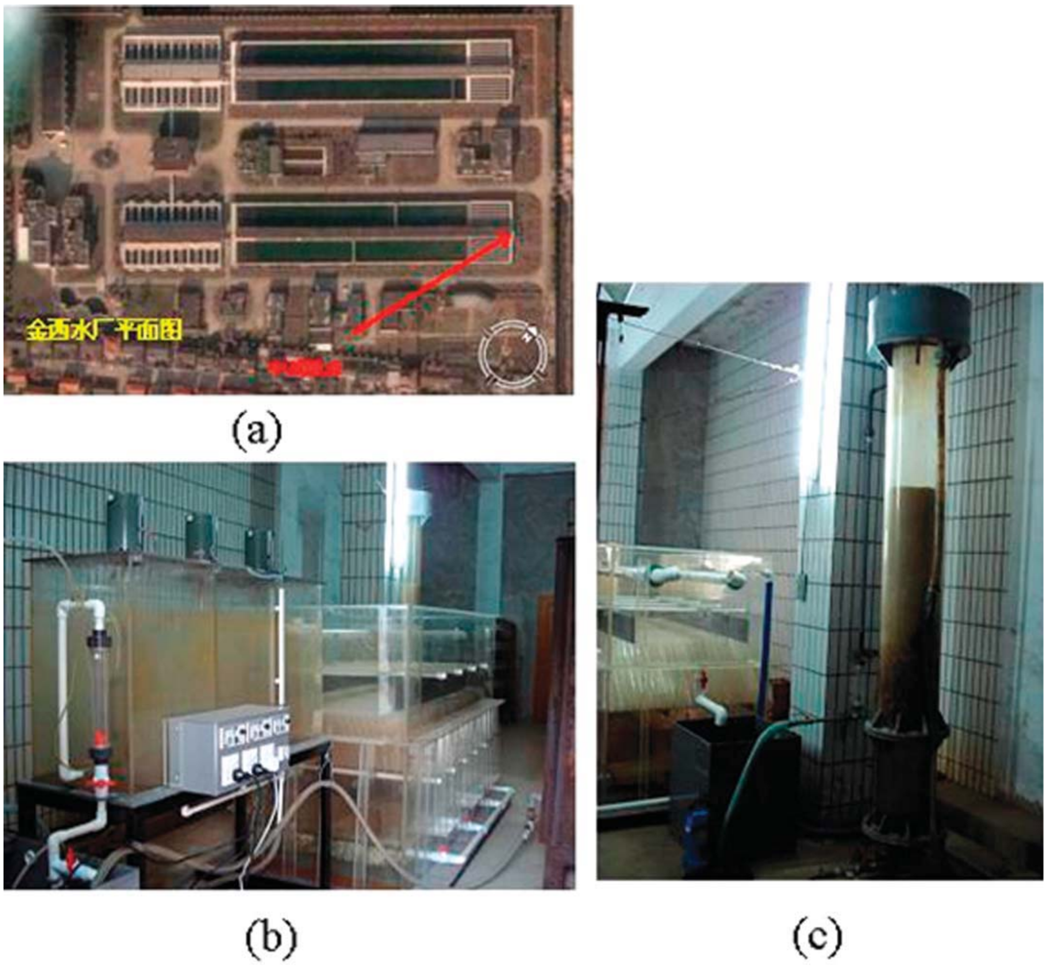

Figure 1 Equipment of flocculating experiment in pilot scale. (a) general location map of flocculating experiment at Jinxi Water Factory in Zhenjiang of China; (b) Coagulative precipitation tanks and Inclined-tube setting tank; (c) Round sand-filtering column. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

orthogonal test as mentioned above. The dose of flocculants was 0.5 mg/L, and the mechanical mixing rates in the triple coagulative precipitation tanks was 150, 100, 50 r/min, respectively, and the sedimentation time was 20 min.

Detection of the content of AM by high performance liquid chromatography (HPLC)

Agilent 1100 liquid chromatography was applied to detect the content of AM in the flocculants products at 35°C. The chromatographical column

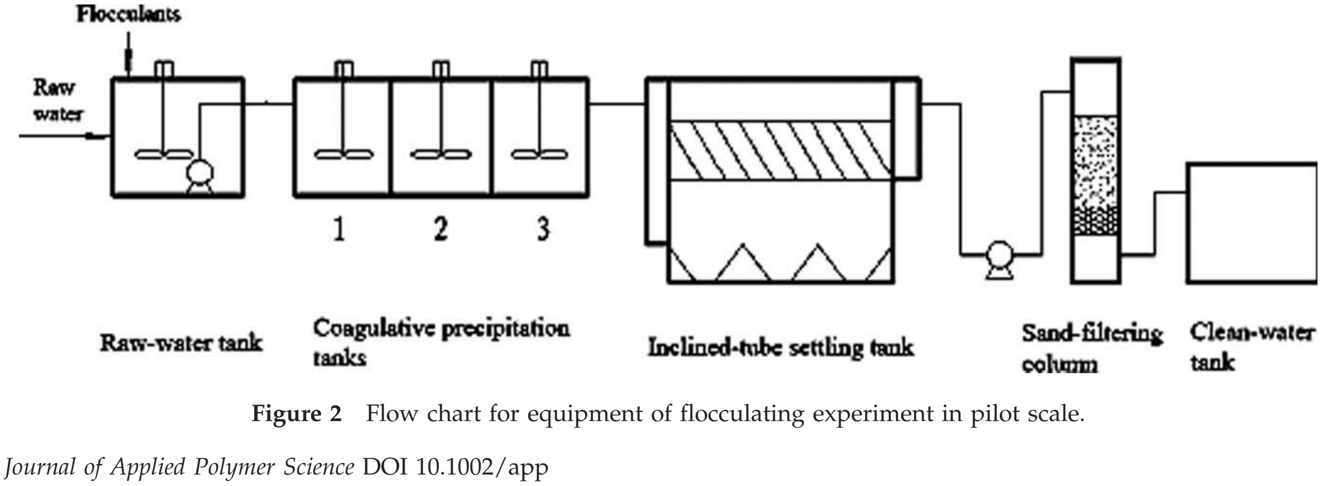

Figure 2 Flow chart for equipment of flocculating experiment in pilot scale.

TABLE I
The Flocculating Experimental Results Using Chitosan15 as Flocculants by Orthogonal Test (in Summer)

No		Dose of flocculants (mg/L, A)	Mechanical mixing rate (r/min, B)	Sedimentation time (min, C)	Water temperature (°C)	Turbidity (NTU)		
						Before sand filtrating (*T*)	After sand filtrating	Raw water
s0		40	150	25	25.0	5.93	0.42	25.60
s1		(1)0.1	(1)150	(1)20	25.8	7.97	1.02	29.60
s2		(1)0.1	(2)200	(2)10	25.9	13.13	1.27	20.30
s3		(1)0.1	(3)250	(3)15	26.0	12.26	1.17	13.26
s4		(2)0.5	(2)200	(1)20	26.0	6.14	0.79	25.20
s5		(2)0.5	(3)250	(2)10	26.0	7.50	0.92	26.30
s6		(2)0.5	(1)150	(3)15	25.8	6.55	0.62	18.87
s7		(3)1.0	(3)250	(1)20	26.0	7.09	1.41	37.30
s8		(3)1.0	(1)150	(2)10	26.0	9.58	1.33	19.73
s9		(3)1.0	(2)200	(3)15	25.6	8.65	1.77	16.73
		(A)	(B)	(C)				
L	(1)	33.36	24.10	21.20				
	(2)	20.19	27.92	30.21				
	(3)	25.32	26.85	27.46				
K	(1)	11.12	8.03	7.07				
	(2)	6.73	9.31	10.07				
	(3)	8.44	8.95	9.15				
R		4.39	1.28	3.00				
S		29.38	2.61	14.17				

s0: Flocculating experiment using poly ferric sulfate as flocculants.

was purchased from Global Chromatography Co. in Suzhou of China, and the detailed parameters about the column were showed below: the packing materials was SP-120-5-ODS-BIO, and column size was 4.6 mm ID × 250 mm Length, which serial No was 518011061; Mobile phase was CH_3OH/0.1 mol/L

TABLE II
The Flocculating Experimental Results Using Chitosan15 as Flocculants by Orthogonal Test (in Winter)

No		Dose of flocculants (mg/L, A)	Mechanical mixing rate (r/min, B)	Sedimentation time (min, C)	Water temperature (°C)	Turbidity (NTU)		
						Before sand filtrating (*T*)	After sand filtrating	Raw water
w0		58	150	20	8.5	5.80	0.56	35.00
w1		(1)0.8	(1)200	(1)20	11.6	3.05	0.45	23.80
w2		(1)0.8	(2)150	(2)15	14.3	2.74	0.23	19.00
w3		(1)0.8	(3)100	(3)10	14.6	3.39	0.20	25.00
w4		(2)1.0	(3)100	(1)20	15.1	1.99	0.18	20.20
w5		(2)1.0	(1)200	(2)15	14.0	2.21	0.22	23.20
w6		(2)1.0	(2)150	(3)10	14.2	3.15	0.18	24.20
w7		(3)1.2	(2)150	(1)20	15.1	2.65	0.21	21.60
w8		(3)1.2	(3)100	(2)15	15.9	3.51	0.31	19.30
w9		(3)1.2	(1)200	(3)10	15.4	5.30	1.24	26.20
		(A)	(B)	(C)				
L	(1)	9.18	9.71	7.69				
	(2)	7.35	10.03	8.46				
	(3)	11.46	8.25	11.84				
K	(1)	3.06	3.24	2.56				
	(2)	2.45	3.34	2.82				
	(3)	3.82	2.75	3.95				
R		1.37	0.59	1.39				
S		2.83	0.598	3.28				

w0: Flocculating experiment using poly ferric sulfate as flocculants

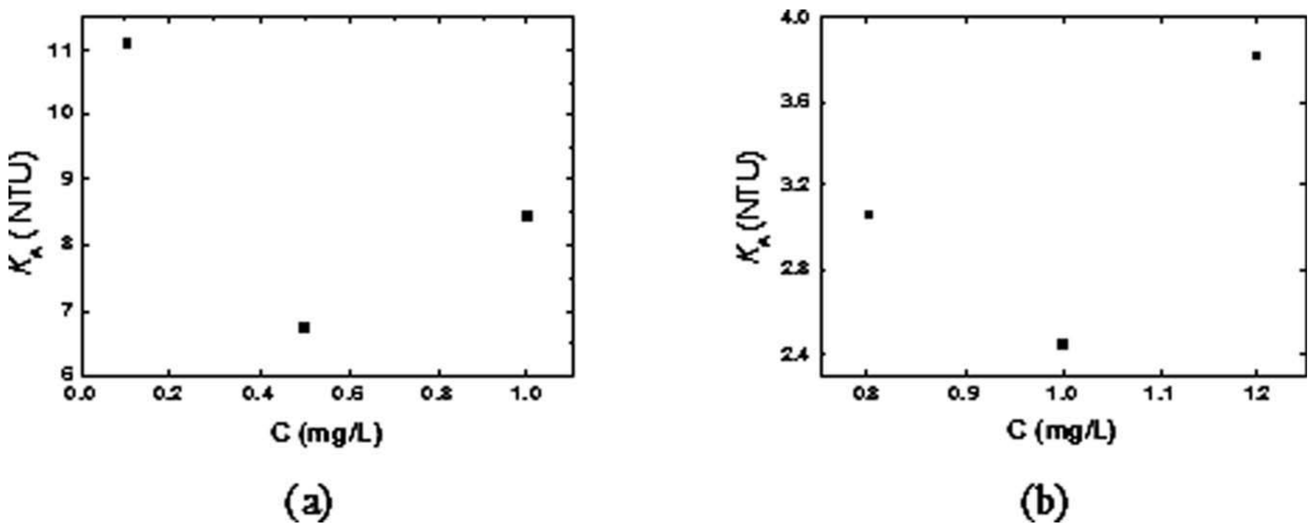

Figure 3 The dose effect on the flocculating properties in pilot scale according to K_A in Table I and II, respectively. (a) in summer; (b) in winter.

ammonium acetate solution with volume ratio of 5/95, and flow rate was 0.8 mL/min; UV detector was used at the wavelength of 205 nm. The recrystallized AM with concentration range from 0.1 mg/L to 12 mg/L was applied to measure the standard curve. The chitosan-*g*-PAM solutions with concentration of 1000 mg/L have been carried out by HPLC to detect the content of AM in the chitosan-*g*-PAM samples.

RESULTS AND DISCUSSIONS

Orthogonal test

The natural polymer-based flocculants have been synthesized according to the reported method.[14,15] The detailed structure characterizations of these graft copolymers including the grafting ratio measurement have been described in previous works.[12,16] Based on the results from beaker experiment in laboratory scale using kaolin suspension as simulated waste water,[12] chitosan15 showed the best flocculating properties, so chitosan15 was studied here in pilot scale for investigation of the effect of three external factors: dose, mechanical mixing rate, and sedimentation time, on the flocculating properties by orthogonal test in different seasons further. Orthogonal test was a scientific method to study the effects of many different factors on certain property of materials, which could reduce the amount of the experiments largely based on the statistic principle. The statistic parameters in Table I and II were defined as:

$$L_{ij} = \sum T_{j(i)} \qquad i = 1, 2, 3;\ j = \mathrm{A, B, C} \qquad (1)$$

$$K_{ij} = \frac{L_{ij}}{3} \qquad i = 1, 2, 3;\ j = \mathrm{A, B, C} \qquad (2)$$

$$R_j = \max(K_{ij}) - \min(K_{ij}) \quad i = 1, 2, 3;\ j = \mathrm{A, B, C} \quad (3)$$

$$S_j = \frac{1}{2}\sum_{i \neq l} (K_{ij} - K_{lj})^2 \quad i = 1, 2, 3;\ j = \mathrm{A, B, C};\ l = 1, 2, 3 \qquad (4)$$

L_{ij} was the sum of the turbidity of the treated water before sand filtrating at a constant of variable in certain condition of j; K_{ij} was the average of L_{ij}; R_j was the largest difference of K_{ij} at certain condition of j; S_j was the square sum of each difference of K_{ij} at certain condition of j.

The final experimental and statistic results were listed in Table I and II, respectively. Based on Table I and II, the dose effects on the flocculating properties in different seasons were shown in Figure 3. It was indicated that the dose of flocculants not only in summer but also in winter, which should be kept neither too high nor too low, could get better flocculating effects. In terms of the charge neutralization mechanism for flocculation, chitosan presented abundant free amino groups along the chain backbone that would be facile cationically charged in acidic media. At a proper amount of the flocculants, the anionic suspension could be efficiently neutralized and coagulated into precipitates. However, if the amount of the flocculants was too high, the excessive cationic flocculants would restabilize the suspension partially in water, which would reduce the final flocculating effects.

Another interesting experimental fact was that the optimal dose of flocculants in winter increased from 0.5 mg/L in summer to 1.0 mg/L. It may be due to that the Brownian motion of the colloidal particles in water decreased with the decrease of water

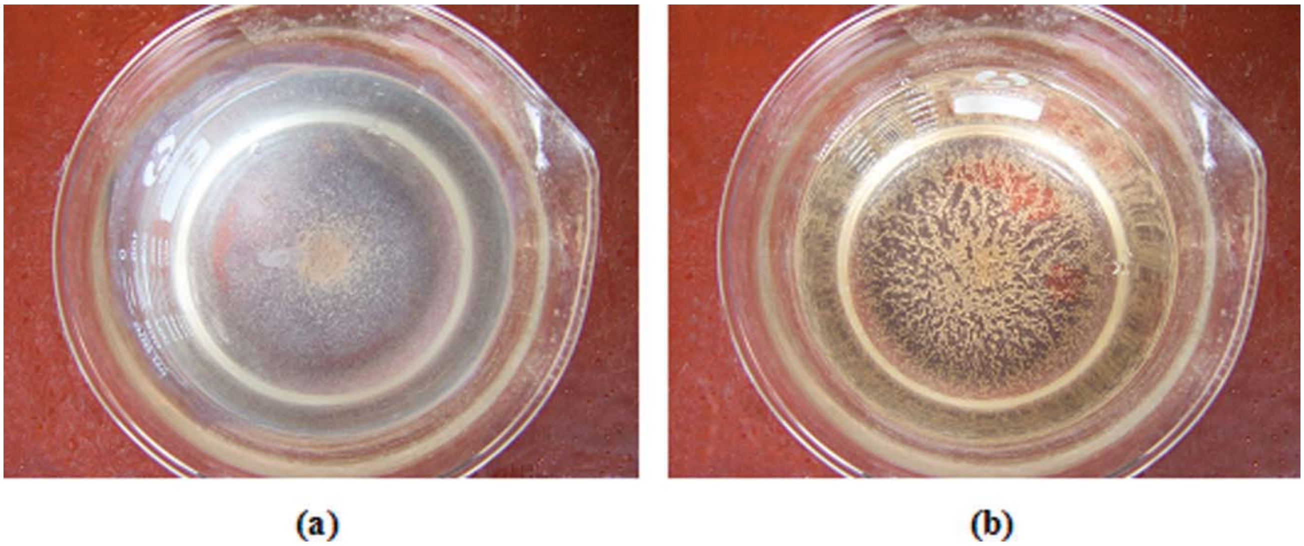

Figure 4 Images of the precipitates produced by different flocculants. (a) poly ferric sulfate; (b) chitosan15. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature, which resulted in the decrease for the agglomeration abilities of colloidal particles. However, comparison to the dose of the poly ferric sulfate, currently used flocculants in Jinxi Water Factory, which was around 40–58 mg/L, the dose of chitosan15 not only in summer but also in winter was much lower to reach similar efficiency in water treatment. Furthermore, from the figures of precipitates produced by different flocculants as shown in Figure 4, the precipitates by chitosan15 showed evidently bigger sizes than that by poly ferric sulfate. From the structure of poly ferric sulfate: $[Fe_2(OH)_n(SO_4)_{3-0.5n}]$, $n < 2$, the main flocculating mechanism of poly ferric sulfate obeyed charge neutralization mechanism. However, chitosan-*g*-PAM, not only a kind of cationic polyelectrolytes, but also organic polymer flocculants, had the characteristic of long flexible chain, so charge neutralization and bridging flocculating mechanisms both affected its flocculating performances.

Besides the dose effect on the flocculating properties, the mechanical mixing rate was another factor. As for the triple coagulative precipitation tank, the mechanical mixing rates in No.2 and No.3 tank as shown in Figure 2, were both kept constant at 100 and 50 r/min, respectively, and that in No.1 tank varied from 100 to 250 r/min. Based on the experimental results shown in Table I and II, the effects of the mechanical mixing rate in No.1 tank on the flocculating properties in different seasons were both showed in Figure 5. It was found that the mechanical mixing rate both kept lower rate would have better flocculating properties. It may be ascribed to that the precipitates with large sized mass were facile to be broken at higher mechanical mixing rate, which would lead to the decrease of the flocculating effects.

However, the sedimentation time was also very important to the flocculating effects, and the sedimentation time could be adjusted by controlling the flow velocity of raw water into the raw-water tank in the continuous water treating process. Based on the experimental results shown in Table I and II, the effect of the sedimentation time on the flocculating time in different seasons were both showed in Figure 6. It was well understood that the flocculating properties could be improved effectively by prolonging the sedimentation time, as the suspensions of treated water were unstable in thermodynamics. But in terms of saving energy, the sedimentation time should be controlled at a proper range.

Above all, according to the experimental results as shown in Table I and II, the optimal experimental conditions of chitosan15 were: the dose of flocculants were 0.5 mg/L for summer and 1.0 mg/L for winter experiment, respectively; the lower of the mechanical mixing rate for No.1 tank in the triple coagulative precipitation tank, and the longer of the sedimentation time would show the better flocculating properties. Furthermore, from the statistical parameters of R and S, the weightiness of the three investigated factors to the actual flocculating properties was dose $>\approx$ sedimentation time $>$ mechanical mixing rate, which indicated that the dose of flocculants was the most important factor to the flocculating properties. In addition, the turbidity values of the treated water after sand filtering in the optimal conditions have been already lower than 1 NTU in both seasons, which were fully measured up the Chinese standard for drinking water quality of GB 5749-2006.[17]

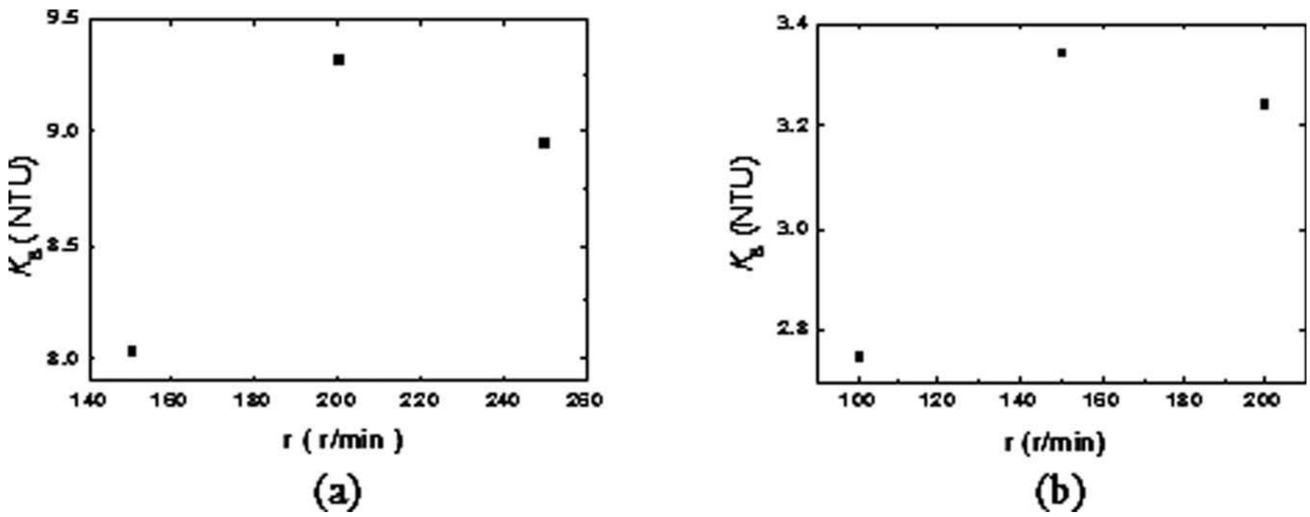

Figure 5 The effect of the mechanical mixing rate on the flocculating properties in pilot scale according to K_B in Table I and II, respectively. (a) in summer; (b) in winter.

Effects of the grafting ratio of flocculants on the flocculating properties

However, the aforementioned factors were all external factors, and the structure factors were more important to properties in practice, as structures of materials would determine their final properties. Based on this viewpoint, the effects of the grafting ratio of chitosan-*g*-PAM flocculants on the flocculating properties have been investigated in pilot scale further. Table III summarized the flocculating properties of chitosan-*g*-PAM samples with different grafting ratio in the same experimental conditions, which indicated that chitosan15 had higher flocculating effect than other flocculants. In terms of the calculated grafting ratio results,[12,16] it was found in Table III interestingly that there was no direct proportion relationship between the grafting ratio and flocculating properties. The flocculating effect increased with the increase of grafting ratio until reaching a maximum, then it was decreased, which results were fully consistent to those from beaker experiment in laboratory scale using kaolin suspension as simulated waste water.[12] It may be due to the cooperative effects of the bridging flocculating and charge neutralization mechanisms of polymer flocculants. Based on the bridging flocculating mechanism, higher grafting ratio was beneficial to increase the molecular weight of flocculants, and improve its actual flocculating capacity. On the other hand, longer and more PAM branch chains would also efficiently shield the cationic groups of $-NH_3^+$ on the chitosan backbone, as shown in Figure 7.

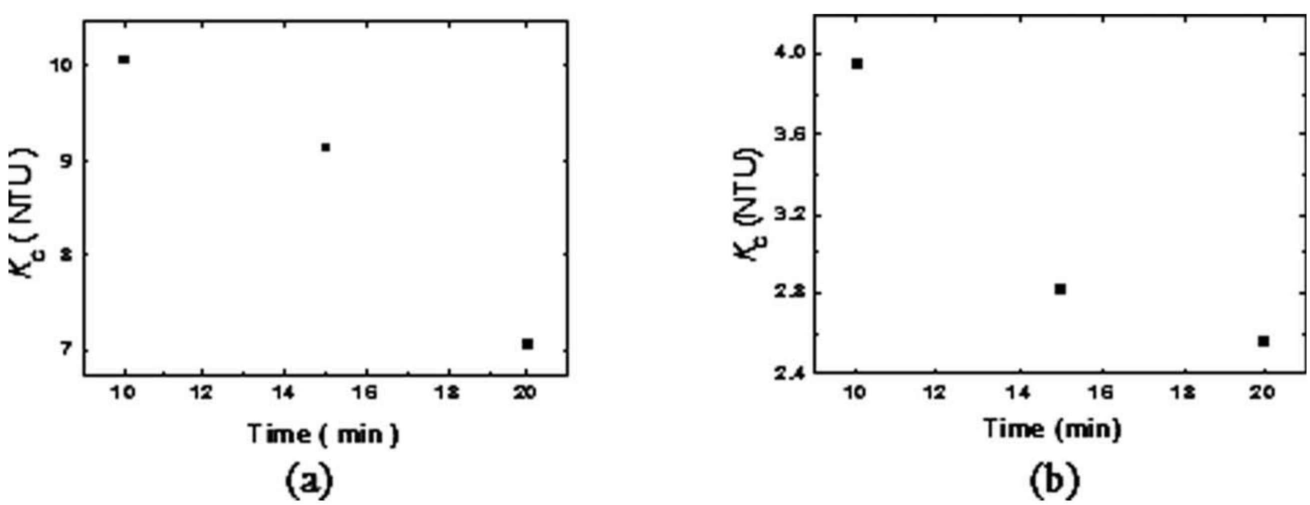

Figure 6 The effect of the sedimentation time on the flocculating properties in pilot scale according to K_C in Table I and II, respectively. (a) in summer; (b) in winter.

TABLE III
The Effects of Grafting Ratio on the Flocculating Properties in Pilot Scale

			Turbidity (NTU)		
Samples	Grafting Ratio[a](%)	Water temperature (°C)	Before sand filtrating	After sand filtrating	Raw water
chitosan11	93	25.0	11.18	2.42	29.90
chitosan13	225	25.0	8.33	1.45	27.90
chitosan15	286	25.0	6.12	0.70	38.60
chitosan18	374	26.0	8.23	0.80	36.60

[a] Grafting ratio $= \frac{W_{Chitosan\text{-}g\text{-}} - W_{Chitosan}}{W_{Chitosan}} \times 100\%$, $W_{Chitosan\text{-}g\text{-}PAM}$ and $W_{Chitosan}$ were the weight of Chitosan-*g*-PAM copolymer and chitosan, respectively.

According to the viewpoint of charge neutralization mechanism, this effect would reduce the flocculating performances. However, the observed experimental facts, related to the effects of grafting ratio on the flocculating properties, should be ascribed to the cooperative effects of charge neutralization and bridging flocculating mechanism. With the grafting ratio increase further, the effects of charge neutralization may be dominant, so the flocculating properties decreased at last. Therefore, chitosan-*g*-polyacrylamide copolymers flocculants should be prepared with a proper grafting ratio to achieve high flocculating properties.

Detection of the content of acrylamide by HPLC

It was well known that PAM had little harmful to human's health, but the monomer of AM was very dangerous. According to the GB 5749-2006,[17] the limit of AM in drinking water was 5×10^{-4} mg/L. However, in this project, it should clarify that how much AM was reserved in the final flocculants products during the preparation processes and final treated water. HPLC has been applied to detect it. Figure 8 was the standard curve of the HPLC for detecting the content of AM, and the detection limit was 0.1 mg/L. Based on the experimental results, AM could not be detected by HPLC in a solution of the flocculants with the concentration of 1000 mg/L, so the percentage of the AM in the flocculants was lower than 0.01%. In terms of the optimal dose of the flocculants, around 0.5–1.0 mg/L as mentioned above, the available content of AM in the treated water was lower than 1×10^{-4} mg/L, which were fully measured up the Chinese standard for drinking water quality of GB 5749-2006.[17] So the chitosan-*g*-PAM flocculants could be applied in water treatment.

CONCLUSION

Based on the experimental results as mentioned above, chitosan-*g*-PAM copolymer flocculants was applicable in water treatment, and also showed better flocculating properties than the traditional flocculants of poly ferric sulfate. The detailed investigations indicated that the dose of flocculants was the most important factor to the flocculating properties of chitosan-*g*-PAM flocculants in pilot scale using the raw water from Zhenjiang part of Yangtse River in China as simulated waste water. Besides, it was

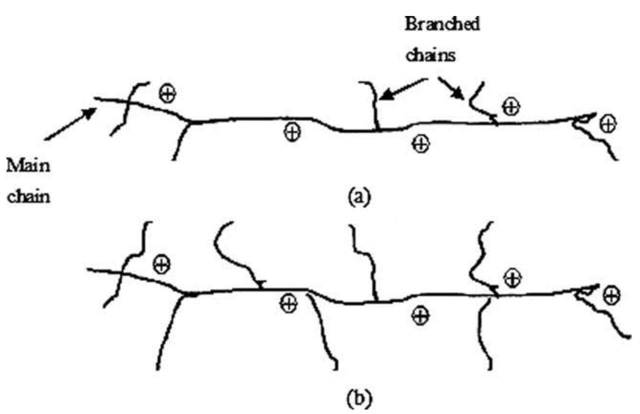

Figure 7 The available structures of chitosan-*g*-PAM samples, with low (a) and high (b) grafting ratio, dissolved in acidic media.

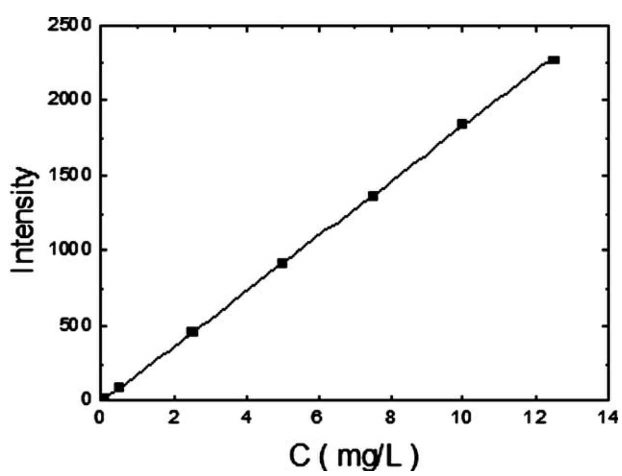

Figure 8 The standard curve of HPLC for detecting the content of AM.

also found that the grafting ratio was one of the key factors to the flocculating properties. The grafting ratio dependence of the flocculating properties showed that the branched PAM chain could efficiently improve the bridging flocculating effect, but also shield the cationic groups on the chitosan backbone, which may reduce the abilities of charge neutralization. However, the final flocculating effects resulted from the cooperative effects of two flocculating mechanisms as mentioned above. Therefore, the chitosan-*g*-PAM flocculants should be prepared with a proper grafting ratio for optimal flocculating properties.

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