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Preparation and Characterization of Chitosan-Graft-Polyacrylamide and its Application in Wastewater Treatment

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Graft copolymerization of acrylamide over chitosan has been performed. The effect of reaction variables such as type and dosage of the initiator, total concentration of the reactants, reactants ratio, nitrogen blowing time, temperature and reaction time were investigated. The orthogonal experiment indicated that the most important factor was the ratio of reactor, next the concentration of the initiator and lastly was reaction temperature. The flocculants were detected and characterized with IR spectroscopy and scanning electron microscope. The adsorption capacity for removal of Cu(II) and Cr(VI) were up to 96.31 % and 84.17 %, respectively.

Key Words: Chitosan-graft-polyacrylamide, Polymer composites, Copolymerization, Heavy metal ions, Wastewater treatment.

INTRODUCTION

Increasing demand for environmentally friendly technologies has promoted the interest for natural polyelectrolytes, which can replace synthetic flocculants, in such fields as water treatment, food and beverage industry, biotechnology and medicine. Since most of the natural colloids are negatively charged, cationic polyelectrolytes are of particular interest for application as flocculants[1]. Chitosan, the main derivative of chitin, a copolymer that is primarily composed of β(1-4) linked 2-amino-2-deoxy-d-glucopyranose units and residual 2-acetamido-2-deoxy-d-glucopyranose units, is a chemical derivative obtained by alkaline deacetylation of chitin and is also found naturally in some fungal cell walls[2]. Chitin is a white, hard, inelastic nitrogenous polysaccharide found in the outer skeleton of insects, crabs, shrimps and other marine animals[3]. Annual production of chitosan by deacetylation of chitin, the second most abundant natural polymer polysaccharide with an estimated annually production in the range 1-10 billion ton that is almost the same as that of cellulose, is expected to increase with future development of chitosan-based products and technologies[1]. Owing to its non-toxic, hydrophilic, biodegradability and biocompatibility, chitosan is an attractive material in various fields of applications ranging from environmental protection and agriculture to food industries[4-6]. It has been used for removal of humic substances from drinking water, treatment of wastewater from distilleries, removal of oil from waste waters, treatment of food processing wastes, lignin removal as well as other applications[7,8]. The other uses of chitosan is (are) for the removal dye wastewater[9,10]. Another benefit of chitosan application is in sludge dewatering[1]. This implies that chitosan is an important polymer flocculant in water treatment and sludge dewatering.

Several methods have been used to modify raw chitosan flake. Graft copolymerization is a useful technique for modifying the chemical and physical properties of natural polymers, is the most attractive method to improve chitosan solubility and widen its applications[11]. Chitosan bears two reactive groups that can be grafted; firstly, the free amino groups on deacetylated units; secondly, the hydroxyl groups on the C_3 and C_6 carbons on acetylated or deacetylated units. Grafting of chitosan allows the formation of functional derivatives by covalent bonding of a molecule, the graft, onto the chitosan backbone[12]. Modified chitosan has better flocculate ability than chitosan itself and also has a variety of applications. This is attributed to the special molecular structure of chitosan, which is characterized by the active amido and hydroxide on the chain side and other advanced structure. Some mechanism had been presumed, that was chitosan with moderate molecular weight had both functions of counteracting charge and building bridge[2,13].

Many investigations have been carried out on the graft copolymerization of chitosan in view of preparing polysaccharides based advanced material with unique bio-activities thus widening their application in the environmental field. Gorochovceva *et al.*[14] studied the synthesis of Chitosan-*N*-

poly(ethylene glycol) by modification of chitosan with reductive amination); Ganji and Abdekhodaie[15] synthesized a novel thermo-sensitive hydrogel chitosan-PEG diblock copolymer by grafting PEG onto chitosan through block copolymerization. Hu *et al.*[13] synthesized poly(ethyleneglycol)-g-chitosan (PEG-g-CS) by *N*-substitution of triphenylmethyl chitosan with MPEG iodide in organic medium and subsequent removal of protecting groups, which can be soluble in water over wide pH range.

In this study, (CTS-AM) was synthesized by the graft copolymerization of acrylamide (AM) over chitosan (CTS). The structure and morphology of CTS-AM synthesized and chitosan were detected and characterized by IR spectra and scanning electron microscope, respectively. The effects of reaction variables such as dosage, kind of initiator, total concentration of the reactants, reactants ratio, nitrogen blowing time, temperature and the reaction time on graft polymerization were studied. Lastly, the turbidity removal rate of the flocculating agent on simulated wastewater solutions and the trapping and removal properties with respect to some heavy metal ions were also studied.

EXPERIMENTAL

All reagents used were analytical grade except chitosan, which was the commercial grade. Chitosan (49 % de-acetyl-degree, molecular weight, 2.8 × 105) was obtained from Zhejiang Aoxing Biotechnology Co. Ltd., Acrylamide was obtained from Beijing Chemical Plant. Ceric ammonium nitrate was obtained from Shanghai Chemical Reagent Co. China. Acetic acid, acetone and ethanol were obtained from the China Chongqing Chuandong Chemical Group Co. Ltd., $CuSO_4{\cdot}5H_2O$ and $K_2Cr_2O_7$ were used for the preparation of Cu(II) and Cr(VI) stock solutions, respectively. All aqueous solutions and standard solutions were prepared with distilled water. The pH of the heavy metal ions solution was adjusted with a sodium hydroxide solution or a hydrochloric acid solution.

Synthesis procedure of CTS-AM and purification of the product: A three-necked, round-bottom flask (250 mL) was used as the reaction vessel. A given mass of acetic acid solution (1 % mass ratio) and chitosan were added to the flask in a water bath at a constant temperature of 30 ºC. The mixture was then stirred until the chitosan was completely dissolved using electric agitator for 3 min at the speed of 280 r/min. Acrylamide monomer was then added. Nitrogen gas was introduced into the reaction vessel to remove oxygen. Under the protection of nitrogen, the initiator ceric ammonium nitrate (CAN) was added and then the reaction vessel was sealed. The reaction was allowed to proceed under a constant temperature for a scheduled time. The reaction vessel was then removed from the warm water bath and then placed into a cold-water bath, to terminate the polyreaction. All procedures were carried out in stirring condition.

Then the product was mixed with acetone and stirred until a white precipitate was formed. It was then immersed in the mixture of ethanol and water (volume ratio of ethanol to water was 7:3) for 12 h to remove the unreacted monomer and the homopolymer. The precipitate was dried at 80 ºC until a constant weight was reached in a vacuum. Then the solid product of CTS-AM was obtained.

Adsorbing and removal of turbidity with CTS-AM: A ZR 4-6 stirring machine (Shenzhen Zhongran Water Industry Technology Development Co. Ltd., Shenzhen, China) with six stirrers was used in this experiment. Simulation wastewater was prepared by weighing 5 g of kaolin in a 1 L beaker and then added 1 L of distilled water. The mixture was stirred with glass rod to form a suspension liquid. Under different conditions, A CTS-AM solution and chitosan were added to a wastewater analogue (200 mL) containing kaolin (5 g/L). The mixture was stirred for 5 min at 40 rpm followed by 120 rpm for 2 min. Then, the solution was filtered after 5 min of sedimentation. The turbidity of the solution was assayed by ultraviolet-visible (UV-VIS) spectrophotometer.

Trapping and removal of heavy metal ions with CTS-AM: A ZR4-6 stirring machine (Shenzhen Zhongrun Water Industry Technology Development Co. Ltd., Shenzhen, China) with six stirrers was used in this experiment. Under different conditions, a CTS-AM solution was added to a waste water analogue (100 mL) containing Cu(II) (100 mg/L) or Cr(VI) (100 mg/L). The mixture solution was stirred for 3 min at 100 rpm followed by 300 rpm for 2 min. The solution was filtered after 10 min of sedimentation. Concentration of Cu(II) or Cr(VI) was analyzed by ultraviolet-visible spectrophotometer.

Grafting rate and grafting efficiency: Grafting ratio and grafting efficiency were defined as follows:

$$\text{Grafting rate} = \frac{W2\ - W1}{W1} \times 100\,\% \qquad (1)$$

$$\text{Grafting efficiency} = \frac{W2 - W1}{W3} \times 100\,\% \qquad (2)$$

where, W1 is the initial amount of chitosan (g), W2 is the amount of CTS-AM, which was purified (g) and W3 is the amount of acrylamide monomer (g) grafted onto chitosan.

IR spectra: IR spectra of CTS-AM was analyzed using a Magna-IR model spectrometer(Thermo Nicolet Corporation Madison, WI, USA) in the range of 4000-500 cm^{-1} with KBr as dispersant.

It was evident that the original strong absorption peak (Fig. 1) at 3427 cm^{-1} migrated to 3408 cm^{-1}. The new absorption peak at 2931 cm^{-1} is ascribed to the distortion vibration peak of $-CH_2$ for acrylamide. During the chemical reaction, characteristic peak at 1643 cm^{-1} migrated to 1655 cm^{-1} and generated new absorption peak at 1316 cm^{-1}. The presence of these main functional groups proved that the graft copolymerization of acrylamide onto chitosan initiated by Ce^{4+} occurred.

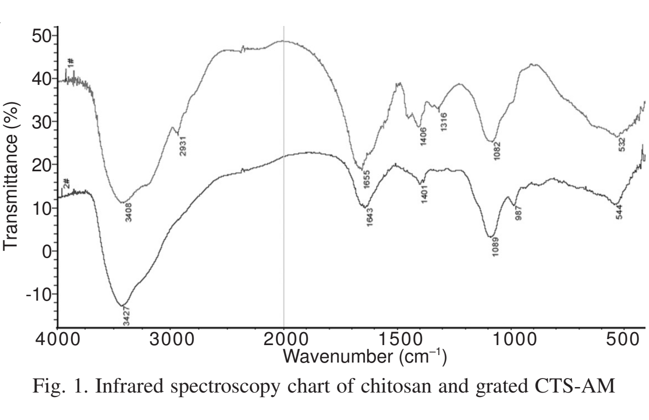

Fig. 1. Infrared spectroscopy chart of chitosan and grated CTS-AM

Electron microscope scanning: The SEM images of chitosan and CTS-AM are depicted in Fig. 2. It can be seen that there is a significant difference in surface morphology of the two forms of chitosan. A striking feature of this image is the appearance of porous internal structure for CTS-AM. The chitosan (Fig. 2a) displayed a smooth and nonporous surface, while the CTS-AM (Fig. 2b) displayed a rough and microporous structure, which may offer more adsorption sites for adsorption and improve the bridging ability. This result also indicated that chitosan has been chemically modified.

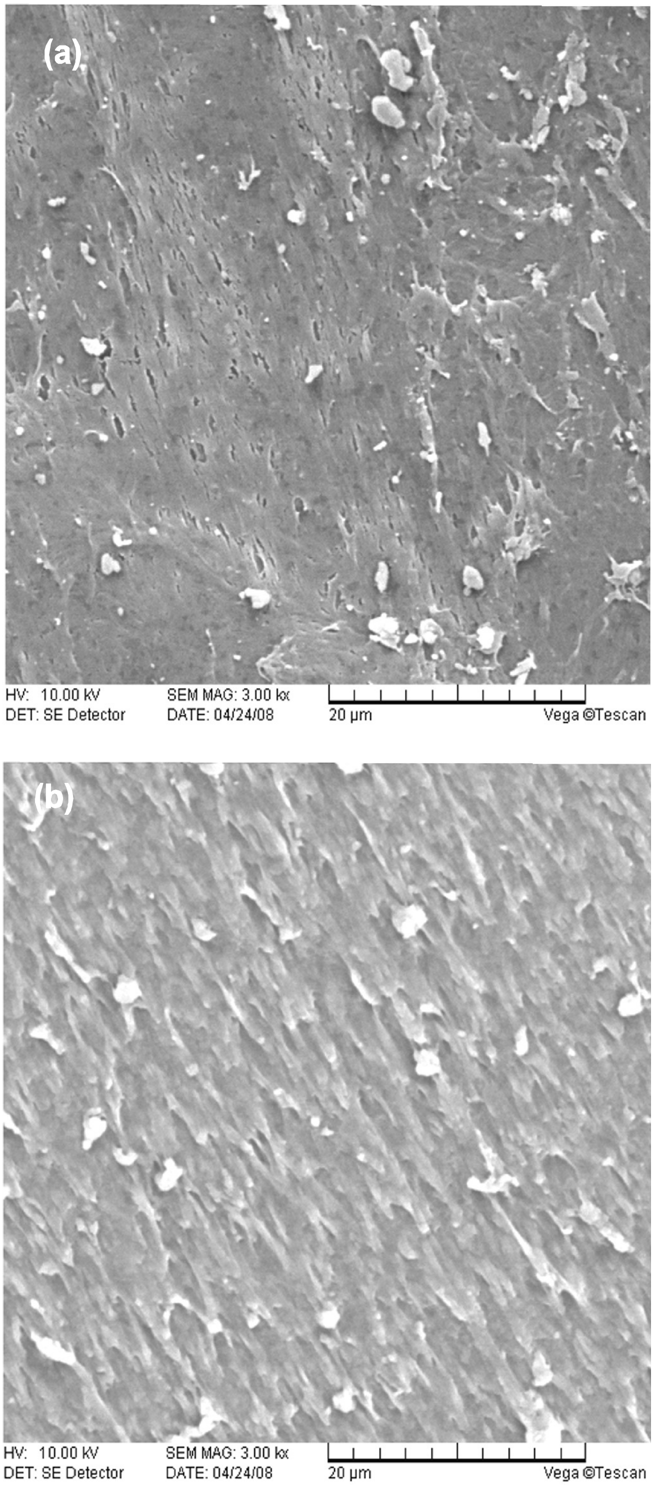

Fig. 2 (a) SEM images of chitosan and (b)grafted CTS-AM

RESULTS AND DISCUSSION

Synthetic conditions

Effect of the initiator on the production rate: The effect of the initiator was studied through changing the types of the initiator in this experiment. In theory, any material, which can generate free radicals can initiate a polymerization reaction. The commonly used initiators are ammonium persulfate [$(NH_4)_2S_2O_8$], azo initiator V-50 as well as the complex initiation system composed of a mixture of the oxidant, ammonium persulfate with reducing agent sodium sulfite constituting a certain percentage. Ceric ammonium nitrate (CAN), $(NH_4)_2S_2O_8$, V-50, $(NH_4)_2S_2O_8$-Na_2SO_3 (mass ratio was 3:1) were used as initiators in this experiment.

The reaction temperature was maintained at 45 ºC. Table-1 shows that ceric ammonium nitrate was the high efficiency initiator and this was related to the particular trigger mechanism. Actually, in most of the research, Ce^{4+} was used as the initiator in graft copolymerization of chitosan. However, theoretically and some research work has reported that other types of initiators could also initiate the reaction of chitosan, but in this study the reactions could not be initiated. On the other hand, there is a probably that we had not yet found the right dosage or other suitable reaction conditions.

TABLE-1
SELECTION OF THE INITIATOR

Dosage (%)	CAN	$(NH_4)_2S_2O_8$	V-50	$(NH_4)_2S_2O_8$-Na_2SO_3
0.04	*	-	-	-
0.06	**	-	-	-
0.08	***	-	-	-
0.10	**	*	-	-

Effect of the total concentration of reactants on the grafting rate and grafting efficiency: The effect of the total concentration of reactants on the grafting rate and grafting efficiency were studied through changing the total concentration of reactants from 7 to 15 %. The results are given in Fig. 3.

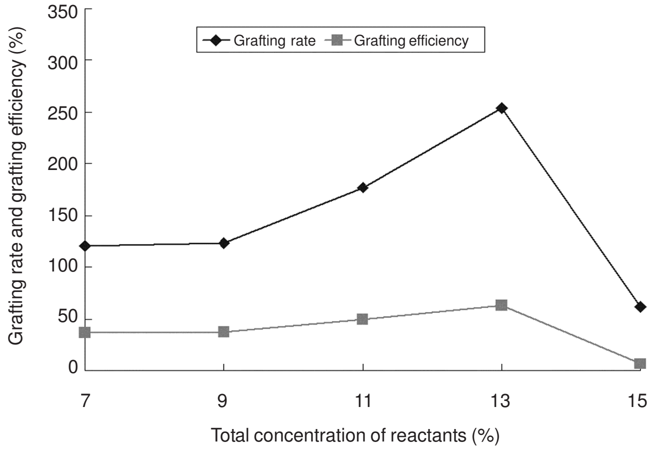

Fig. 3. Effect of the total concentration of reactants on the grafting rate and grafting efficiency

Fig. 3 showed that when the total concentration of reactants was in the range 7-13 %, the grafting ratio and grafting efficiency increased while increasing the total concentration of reactants beyond 13 % the grafting ratio and grafting efficiency decreased. Therefore, the maximum grafting rate of 253.98 % and grafting efficiency of 63.50 % were achieved at 13 % total concentration of reactants. The reasons were that, firstly, with the increase of chitosan and acrylamide, the system presented a high viscous state, some raw materials cannot be completely dissolved and therefore, not participate in the reaction. In addition, if the stirring time is prolonged, the dissolved chitosan may be partially hydrolyzed and the test conditions will be difficult to control. Thus, the high concentration was not beneficial to the reaction. The reaction conditions were as follows: the mass ratio of chitosan to acrylamide, 1:4; the reaction temperature, 45 ºC; percentage of initiator concentration to the total mass of the reaction system (including the aqueous solution), 0.04 %; nitrogen running time, 20 min; reaction time, 3.5 h.

Effect of the reactants ratio on the grafting rate and grafting efficiency: When the other reaction variables were fixed, the effect of the reactants ratio on the grafting rate and grafting efficiency was studied.

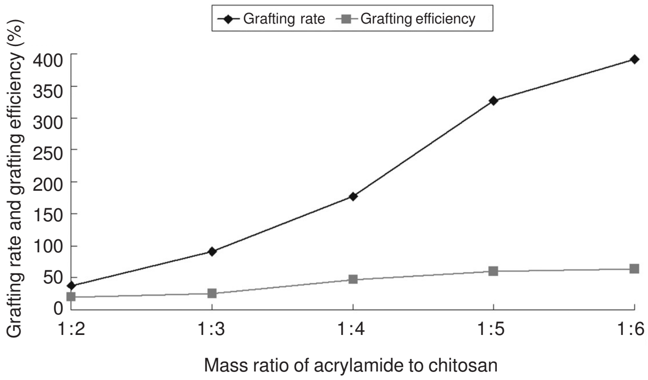

Fig. 4. Effect of the reactants ratio on the grafting rate and grafting efficiency

Fig. 4 shows that the optimum ratio of chitosan to acrylamide was 1:6. The grafting rate significantly increased with the increasing mass ratio of acrylamide to chitosan. However, there was a slight increase in the grafting efficiency after reaching a certain degree. When increasing the acrylamide monomer, it resulted in the increase in collision opportunity between the acrylamide monomer and chitosan molecules, which was beneficial to the grafting of the chitosan macromolecules. However, the increase of acrylamide also promoted the formation of polyacrylamide, resulting in low utilization of acrylamide monomer. In chitosan molecule, the quantity of sugar residues was fixed and could receive a certain amount of acrylamide, so there was an optimal value of the ratio of monomers. Continuing to increase the mass of acrylamide, may decrease the reaction degree.

Effect of the concentration of the initiator on the grafting rate and grafting efficiency: When the other reaction variables were fixed, the effect of the concentration of the initiator on the grafting rate and grafting efficiency was investigated. Fig. 5 shows that when the mass fraction of the initiator was lower than 0.02 %, the free radicals were insufficient and the initiated reaction was difficult to proceed. When it increased to 0.06-0.08 %, the reaction proceeded steadily. The effect of the initiator excessive phenomenon was not experienced in this experiment, but in theory, the excess initiator causes the low grafting degree and low molecular weight of the product. Because as the concentration of initiator increases, massive free radicals will be produced instantaneously, active centers created excessively and short chain material formed. Moreover, the collision of the active group may cause the chain transfer to hinder the reaction to proceed further.

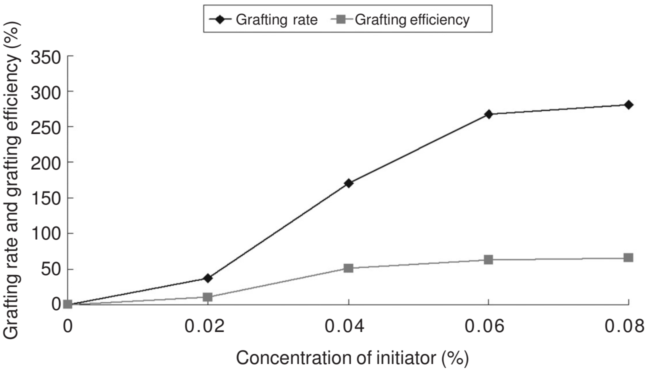

Fig. 5. Effect of the concentration of initiator on the grafting rate and grafting efficiency

Effect of the reaction temperature on the grafting rate and grafting efficiency: When the other reaction variables were fixed, the effect of the reaction temperature on the grafting rate and grafting efficiency was studied. Fig. 6 shows that the lower temperature was helpful to the formation of high polymer, but the initiation must reach a certain temperature to produce free radicals. Therefore, at 35 ºC, the reaction was almost impossible to proceed. When at 45 ºC, the optimum polymerization efficiency was reached, while continuing to raise the temperature, the grafting rate and grafting efficiency decreased. The high temperature was harmful to the stability of the active center of chitosan and thus could reduce the free radical initiation ability. Simultaneously, the chain transfer and the chain termination would obviously increase, enhancing the homopolymerization, which will hinder the graft copolymerization.

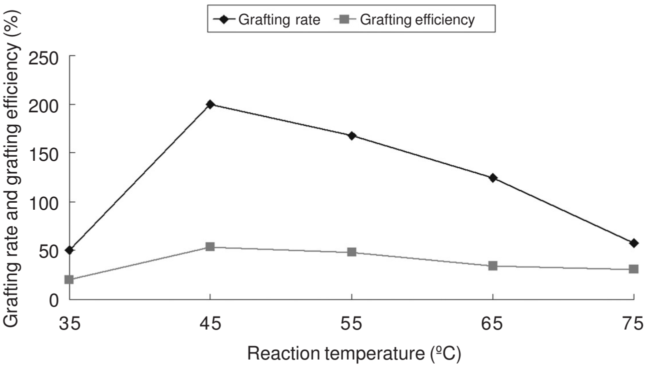

Fig. 6. Effect of the reaction temperature on the grafting rate and grafting efficiency

Effect of the nitrogen blowing time on the grafting rate and grafting efficiency: When the other reaction variables were fixed, the effect of the nitrogen blowing time on the grafting rate and grafting efficiency was studied. Fig. 7 shows that the oxygen in the air was an inhibitor to the copolymerization and the reaction would not continue if there was micro oxygen in the system. Therefore, it was necessary to blow nitrogen into the vessel and eliminate oxygen and thus protecting the reaction. Blowing nitrogen for 10 min could achieve the desired results, however, continuing blowing nitrogen, the grafting rate and the grafting efficiency increased. Therefore, when considering the effects and costs, blowing nitrogen for 20 min was suitable.

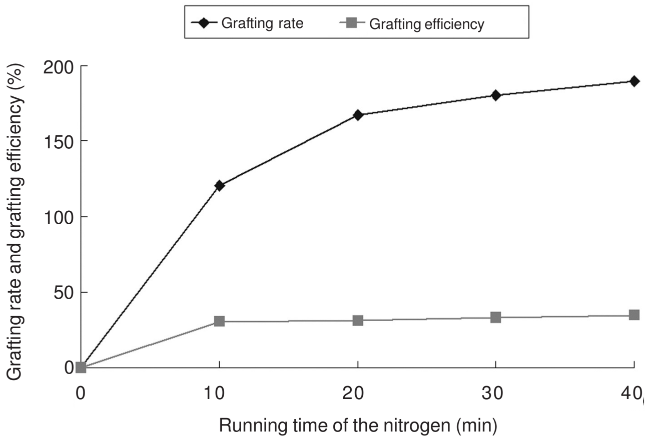

Fig. 7. Effect of the running time of the nitrogen on the grafting rate and grafting efficiency

Effect of the reaction time on the grafting rate and grafting efficiency: When the other reaction variables were fixed, the effect of the reaction time on the production rate was investigated. Table-2 shows the results on the effect of reaction time on the grafting rate and efficiency. It was observed that during the reaction process, solution became transparent and the surface appeared as small grains, finally generating a homogeneous gel that has a certain degree of flexibility and mechanical strength. However, prolonging the reaction time resulted in the growth of graft chains and an increase in viscosity. Therefore, it was difficult to make monomer spread to the active center and grafting rate and grafting efficiency tended to be stable. Continuing to extend the reaction time was not beneficial to homopolymerization, leading to a difficulty in the separation of product, thereby showing a decrease of grafting rate and efficiency. Therefore, extending the reaction time tends to go against the graft copolymerization. The optimum reaction time was 3.5 h.

TABLE-2
EFFECT OF REACTION TIME ON THE REACTION EXTENT

Reaction time (h)	State of reactants
0	Viscous and light yellow solution
0.5	Solution turn into transparent colour, the surface appears small grain
1.5	Become the mixture of colloid particles and solution
2.5	Large amount of colloid particles, large viscosity
3.5	Homogeneous jelly, a certain degree of flexibility and mechanical strength

Orthogonal experimental design: Comprehensive considerations of the influence of the above factors, orthogonal experiments was designed in order to find out the optimum reaction conditions and study on the various factors that influence the degree of the reaction. According to the single factor test condition and experimental phenomenon, initiator concentration was chosen as the reaction factor. The total concentration of reactants was 11 %, nitrogen blowing time of 20 min and reaction time at 3.5 h were fixed. Single factor tests and orthogonal test showed that, the grafting ratio could reach 396.40 %.

It was concluded from Tables 3 and 4 that the optimal condition of extraction was as follows; the monomer ratio of 1:8, reaction temperature of 45 ºC and the initiator concentration of 0.06 %. Orthogonal experimental design indicated that for the influence response the primary factor was the reactant mass ratio, followed by the initiator density and finally was the reaction temperature.

TABLE-3
ARRANGEMENT OF FACTORS AND LEVELS OF L9 (34) ORTHOGONAL ARRAY EXPERIMENTS

Factor level	A (reactants ratio)	B (concentration of initiator) (%)	C (reaction temperature) (ºC)
1	1:4	0.04	45
2	1:6	0.06	55
3	1:8	0.08	65

TABLE-4
DESIGN AND RESULTS OF L9 (34) ORTHOGONAL ARRAY EXPERIMENTS

Factor number	A	B	C	Grafting rate (%)
1	1	1	1	327.2
2	1	2	2	350.4
3	1	3	3	336.3
4	2	1	2	344.8
5	2	2	3	348.0
6	2	3	1	355.8
7	3	1	3	358.1
8	3	2	1	396.4
9	3	3	2	354.7
K1	338.0	343.4	359.8	
K2	349.5	364.9	350.0	
K3	369.7	348.9	347.5	
R	31.7	21.5	12.3	

Study on the properties of removing turbidity: The effect of dosages of chitosan and CTS-AM on turbidity removal rate was studied at the dosage range from 1 mL to 5 mL. The results are given in Fig. 8. Fig. 8 shows the CTS-AM graft copolymer had better flocculation characteristics than chitosan. The residual turbidity was about 7.57 NTU by using CTS-AM while the residual turbidity was about 47.31 NTU by using chitosan when the dosing quantity was 2 mL. Henceforth, with the increasing of dosage, while the residual turbidity may change reversely. The results showed that the graft copolymerization introduced the acrylamide to the chitosan macromolecule effectively, which prolonged the side chain of chitosan and introduced the amido to the chitosan. This proved that the CTS-AM possessing perfect chelating capability and adsorption capacity.

Heavy metal ions trapping and removal properties: Effect of the product dosage on the heavy metal ions removal

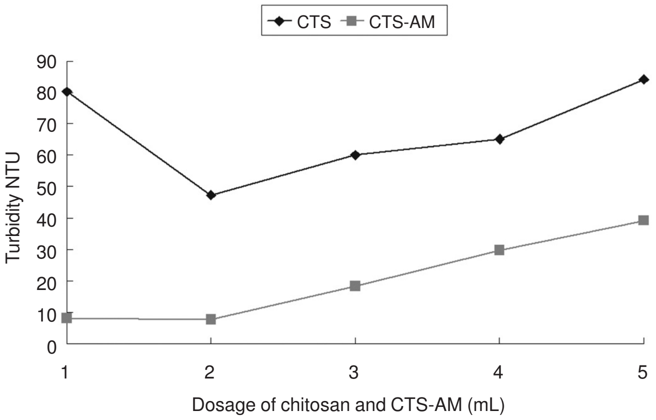

Fig. 8. Effect of the product dosage on turbidity removal effect

rate. The effect of the CTS-AM dosage on the heavy metal ions removal rate was studied in the dosage range of 0.5-3.0 mL. The results are given in Fig. 9.

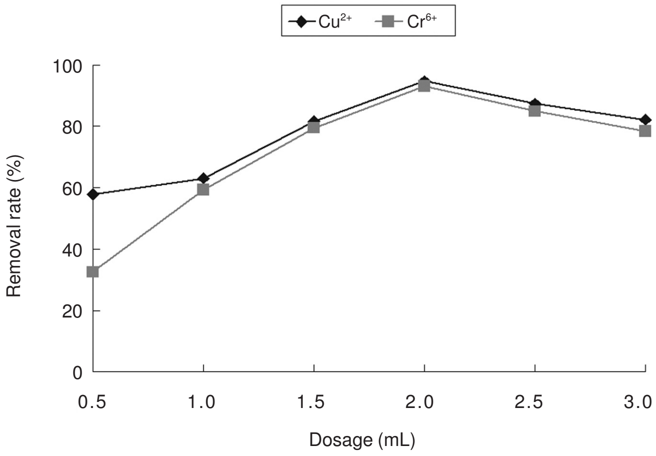

Fig. 9. Effect of the addition of CTS-AM on the removal of heavy metal ions

Fig. 9 shows that the removal rate of Cu(II) changed from a low value of 57.90 % at 0.5 mL to its maximum of 94.78 % at 2.0 mL. The Cr(VI) removal rate changed from a low value of 32.40 % at 0.5 mL to a maximum of 93.18 % at 2.0 mL. However, the removal rate of Cu(II) or Cr(VI) decreased as the dosage increased from 2 to 3 mL. The influence of the product dosage on the removal of heavy metal ions can be explained on the basis of charge neutralization and adsorption bridging mechanism. As the dosage of the product was increased, some hydroxyl of the product chelated with the heavy metal ions, but the excess hydroxyl carried negative charges, thereby, causing electrostatic repulsions between these negative charges. As the dosage of the product increased excessively, the blank position of the product was quickly occupied by its own molecule and therefore, could not generate adsorption bridging action any more. This resulted in a decrease in the removal rate of heavy metal ion[16].

Effect of the pH on the heavy metal ions removal rate: Heavy metal ions solutions (100 mg/L) with different pH and CTS-AM solutions (10.0 g/L) were prepared. The effect of the pH on the heavy metal ions removal rate was studied in the pH range of 2.0-11.0. The results are given in Fig. 10.

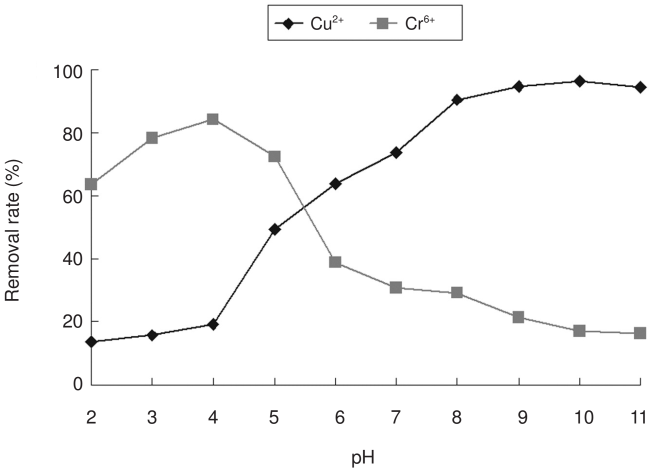

Fig. 10. Effect of the pH on the removal of heavy metal ions

Fig. 10 shows that the removal rate of Cu(II) increased when the pH changed from 4 to 8 and then stabilized within the pH range from 8 to11. When the pH was 10, the removal rate of Cu(II) was up to its maximum value of 96.31 %. In alkaline conditions, complete sorption was observed, but in this pH region the Cu(II) removal originates from precipitation of $Cu(OH)_2$ rather than from sorption. The effect of pH on sorption of Cr(VI) ions onto the CTS-AM can be seen. Contrary to Cu(II) ions, high sorption percentages were observed in the acidic pH region. The removal rate of Cr(VI) increased when the pH changed from 2 to 4 and then decreased as the pH value increased from 4 to 11. The maximum removal of Cr(VI) ions of 84.17 % was observed at pH 4. Below this pH of CTS-AM, sorbent is positively charged with the quaternary ammonium salt, whereas the adsorbate is negatively charged, Cr(VI) exists as $HCrO_4^-$. So the charge neutralization by CTS-AM played the important role in the sorption.

Conclusion

The graft copolymerization (CTS-AM) of acrylamide (AM) over chitosan (CTS) was synthesized under simple conditions and the main synthetic conditions were studied. This reaction was affected by the total concentration of reactants, the ratio of reactor, the concentration of the initiator, temperature and some other factors. Regard the percentage of adding on as an index, orthogonal experiments showed when all the reagents contents were 11 %, nitrogen blowing time of 20 min, reaction time was 3.5 h, m (CTS) : m (AM) = 1:8, the concentration of the initiator was 0.06 % and the temperature was 45 ºC, the reaction reached the best value of 396.4 %. The orthogonal experiments indicated that the most important factor affecting the reaction was the ratio of reactor, then the concentration of the initiator and lastly was reaction temperature. The structure of the graft copolymer of chitosan and acrylamide flocculants synthesized in this work was detected and characterized by IR spectra and electron microscope scanning. The turbidity removal effect of the flocculating agent to some kaolin simulated wastewater solutions were studied and experimental results showed that the flocculating agent had good removing property to turbidity. By using CTS-AM, the removal effect of turbidity much better than using chitosan. The results for trapping and removal properties of flocculating agent with respect to heavy metal ions showed that the CTS-AM had good trapping and removal properties with respect to some heavy metal ions. The removal rate of Cu(II) and Cr(VI) were up to 96.31 % and 84.17 %, respectively.

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