J. Ocean Univ. China (Oceanic and Coastal Sea Research)
DOI 10.1007/s11802-011-1741-5
ISSN 1672-5182, 2011 10 (1): 42-46
http://www.ouc.edu.cn/xbywb/
E-mail:xbywb@ouc.edu.cn

Preparation of Cationic Chitosan-Polyacrylamide Flocculant and Its Properties in Wastewater Treatment

WANG Ben[1), *], ZHANG Yulian[2)], and MIAO Chunbao[2)]

1) *School of Environment and Safety Engineering, Qingdao University of Science & Technology, Qingdao* 266042, *P. R. China*
2) *Qingdao Hygain Chemical* (*group*) *Co., LTD, Qingdao* 266042, *P. R. China*

(Received March 3, 2010; revised April 19, 2010; accepted September 5, 2010)

Abstract Chitosan derived from crab shells, was used to prepare the graft polymer in aqueous solution with acrylamide (AM) and methacrylatoethyl trimethyl ammonium chloride (DMC) as raw materials and ceric ammonium nitrate (CAN) as initiator. The flocculation ability of the resulting polymer (PCAD) was studied in waste water treatment experiments. Its properties were determined on the basis of the transmittance of waste water after flocculation. The effects of chitosan and DMC content on PCAD's flocculation ability were studied. Flocculation experiments were also undertaken under various pH conditions. According to the experimental data, the flocculation ability could be improved when chitosan content decreased in the raw material, but the monomer conversion would decrease obviously. When the chitosan's content was more than 65%, AM and DMC groups were less on each chitosan molecule. So PCAD's flocculation ability was poor. Similarly, high content of DMC would result in low monomer conversion and high flocculation ability. PCAD molecules with more DMC group had more positive charges. It was favorable to flocculation. However, monomer conversion would decrease with the increase of DMC content. The suitable conditions were that chitosan and DMC contents were 65% and 15-20%, respectively. The experiment data showed that PCAD had good flocculation ability under weak acidic condition. Its ability would be weakened by strong acidic or alkaline condition. The flocculation efficiency was the best at pH of 5.5 when PCAD's dosage was $8 mg \cdot L^{-1}$. Compared with cationic polymer (the copolymer of AM and DMC, PAD), PCAD showed better flocculation ability under acid and neutral conditions, but worse ability under alkaline condition.

Key words Chitosan; marine chemicals; graft polymer; cationic polymer; flocculant

1 Introduction

Chitosan is a partially N-deacetylated derivative of chitin, which is commonly found in shells of insects and crustaceans, as well as cell walls of some fungi, and is known as the second most abundant biopolymer in nature after cellulose (Roberts, 1992; Chang *et al.*, 2008). More and more researchers are focusing on it all over the world because it is of high-quality, non-pathogenic and biodegradable as water treatment flocculant (Knorr, 1984; Zeng and Ruckenstein, 1998; Divakaran and Sivasankara Pillai, 2002). Chitosan, a natural poly (aminosaccharide), is non-toxic and easily bioadsorbable (Liu *et al.*, 2007; Zhou *et al.*, 2007). This biopolymer is a weak base with an intrinsic pKa of 6.5 and with a gel-forming ability at low pH. In acidic solutions, the amine groups of chitosan are protonated and form a cationic macromolecule. Chitosan has been successfully used to prepare Semi-IPN Hydrogels (Mahdavinia *et al.*, 2008), membranes (RMP, 2008), flocculant (Laue and Hunkeler, 2006; Chu and Sun, 2008), porous beads resin (Cai, 1999), sizing agent (Hebeish *et al.*, 2006) and paper-strengthening agent (Ma and Qiu, 2007).

Flocculation is an efficient and cost-effective method for water and wastewater treatment. Flocculants are classified into two categories, *i.e.*, inorganic and organic ones. Inorganic flocculants are usually salts of multivalent metals like aluminum or iron. Compared with the organic flocculants, the inorganic ones have several disadvantages, *e.g.*, greater dosage, larger volume of sludge and pH sensitivity. On the other hand, synthetic organic polymers have some advantages, such as insensitiveness to pH changes, formation of large cohesive floc and wide applicability. Among the organic polymer flocculants, cationic ones have better flocculation ability, as they can work efficiently through both bridging and charge neutralization (Wang *et al.*, 2009). Polymeric flocculants are typically synthetic water-soluble macromolecules, usually with high molar mass. For municipal waste water treatment, synthetic cationic polymers are almost exclusively employed. In recent years, graft copolymers of chitosan were prepared to treat wastewater (Feng *et al.*, 2005; Lin

* Corresponding author. Tel: 0086-532-84023844
E-mail: wangben@qust.edu.cn

et al., 2005; Laue and Hunkeler, 2006; Chu and Sun, 2008), most of which are of limited charge. The flocculation in many applications requires high molar charge densities. So, the means to increase the charge on polysaccharides are of interest.

In the present work, the modified chitosan flocculant, chitosan-graft-poly (acrylamide-methacrylatoethyl trimethyl ammonium chloride) (PCAD), was made by grafting acrylamide and methacrylatoethyl trimethyl ammonium chloride (DMC) onto chitosan under the suitable condition. PCAD, a cationic graft copolymer, was synthesized with a variety of chitosan and DMC contents. The polymer was used to treat the wastewater collected from a waste water treatment plant. The effects of chitosan and DMC contents on PCAD's flocculation ability were studied.

2 Material and Methods

2.1 Materials

Acrylamide (AM, AR) from Beijing Chemical Reagent Co. was further purified by three-time recrystallization. Methacrylatoethyl trimethyl ammonium chloride (DMC, 76%) was from Befar Group, Binzhou, China. Sodium hydroxide, acetic acid and ceric ammonium nitrate (CAN) were of analytical grade from China National Medicines Corporation Ltd. Chitosan (the degree of deacetylation, 90.8%) was self-made. Cationic polyacrylamide was self-made with ionic degree 20(mol)% with AM and DMC as comonomer. Deionized water was used throughout this work.

2.2 Synthesis of Polyacrylamide

Predetermined amount of chitosan with the deacetylation rate of 90.8% was dissolved into1% acetic acid solution. Then, it was poured into a 500 mL three-neck separable flask and heated to 50℃ at agitation of 100 rounds per minute. After purging with nitrogen for 30 min, CAN solution was added into the flask. AM and DMC were added into the reaction after 30 min. The flask was kept at constant temperature and nitrogen atmosphere for 5 h to make monomers react completely. After adding some alcohol, NaOH solution was used to adjust pH to weak alkaline. The polymer would phase out and be separated by pumping filtration. The product was washed several times by alcohol and dried at vacuum and at 60℃ to constant weight. Monomer conversion rate was measured. A certain amount of PCAD was dissolved into acetic acid solution (1%) to yield PCAD solution (2500 mgL^{-1}).

2.3 Flocculation Properties of PCAD

Flocculation ability of graft polymer was evaluated using the wastewater collected from the waste water treatment plant. The flocculants in solution form were added into each sample of 1000 mL waste water. The waste water was immediately stirred at a constant speed of 200 $rmin^{-1}$ for 2 min, followed by a slow stirring at 40 $rmin^{-1}$ for 10 min. Thereafter, the waste water was allowed to be settled down for 5 min. At the end of settling, the solution transmittance was measured with a spectrophotometer (UV-9100, Ruili Co., China) at a wavelength of 550 nm (Wang *et al.*, 2009).

3 Results and Discussion

3.1 Effect of chitosan content on PCAD properties

Several PCADs were synthesized with various chitosan content and constant monomer concentration. These graft polymers were used to treat the waste water with PCAD dosage of 8 mgL^{-1}. The data are shown in Fig.1.

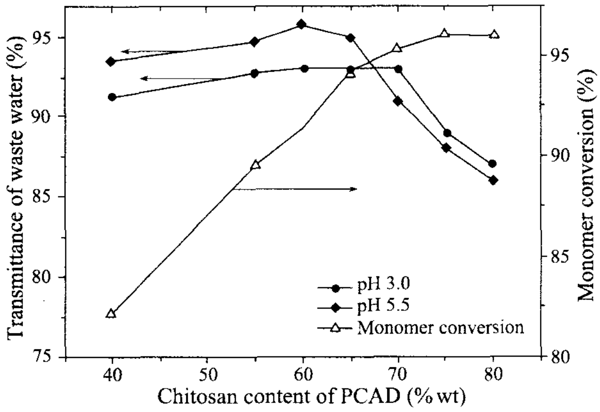

Fig.1 Experimental data with various chitosan contents. The solid spots are for transmittance and the open ones for monomer conversion.

It is obviously seen that the flocculation ability of PCAD was high when chitosan content was below 65%. However, it decreased rapidly with chitosan content exceeding 65%. When chitosan content was low, AM and DMC could graft on the backbone of chitosan efficiently. So chitosan molecules had more AM and DMC groups. Good flocculation ability was achieved with larger branched-chains and more charges (Ma and Shao, 1999). When chitosan content was high, AM and DMC concentration was relatively low for the chitosan. So, AM and DMC groups was less on chitosan molecules. Consequently, the flocculation ability of the resulting graft polymer was weak.

It is also shown in Fig.1 that the flocculation ability of PCAD at pH 3.0 was better than that at pH 5.5 when chitosan content was higher than 70%. However, when chitosan content was lower than 65%, PCAD's ability at pH of 5.5 was better than that at pH 3.0. PCAD prepared with chitosan content of lower than 65%, had relatively more DMC groups. Therefore, it was affected by acid (Wang *et al.*, 2007). However, for PCAD prepared with chitosan content higher than 70%, the positive charges were due to the amine groups of chitosan. Under such cir- cumstances, acid condition was beneficial to flocculation.

Meanwhile, monomer conversion changed obviously with various chitosan content. When chitosan content was low, monomer conversion was also low. The reason was that less chitosan had less radicals. So AM and DMC could not react sufficiently. The monomer conversion changed less when chitosan content was higher than 70%. Based on flocculation ability and monomer conversion, the optimal content of chitosan was determined as 65%.

3.2 Effect of DMC Content on PCAD Properties

PCAD was prepared with various DMC contents, but chitosan and AM was constant. These graft polymer was used to treat the waste water with pH of 5.5 and PCAD dosage of 8 mgL^{-1}. The data are shown in Fig.2.

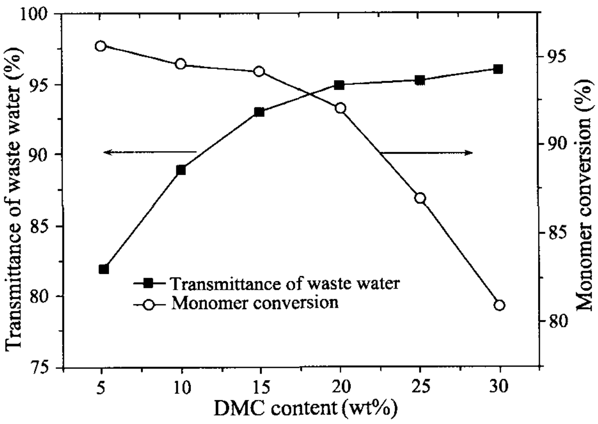

Fig.2 Experiment data with various DMC contents. The solid spots are for transmittance and the open ones for monomer conversion.

It is shown in Fig.2 that the flocculation ability of PCAD was stronger with more DMC in the raw material. When more DMC was added into the reaction system, the resulting polymer would have more DMC groups. So they would have more positive charges in the solution. Then the colloidal particles would be flocculated efficiently. However, as shown in Fig.4, the monomer conversion decreased with DMC content in raw material. The radicals became less when chitosan concentration decreased. The monomer reacted insufficiently and some of them became residues. In the view of flocculation ability and monomer conversion, the optimal content of DMC was 15-20% in the raw material.

3.3 pH Effect on PCAD Properties

Waste water was treated by the graft polymer (PCAD) and cationic polyacrylamide (PAD) under various pH conditions. The effects of flocculant dosage were also studied. PCAD was prepared with the mass ratio of chitosan: (AM+DMC) as 2:1 and the mole ratio of AM: DMC as 4:1. The flocculation results of PCAD and PAD at pH 3.0, 5.5, 7.0 and 9.6 are illustrated in the Fig.3 (A–D). The floc image of some experiments is shown in Fig.4.

Compared with PAD, PCAD showed better flocculation ability under acid and neutral conditions, but worse under

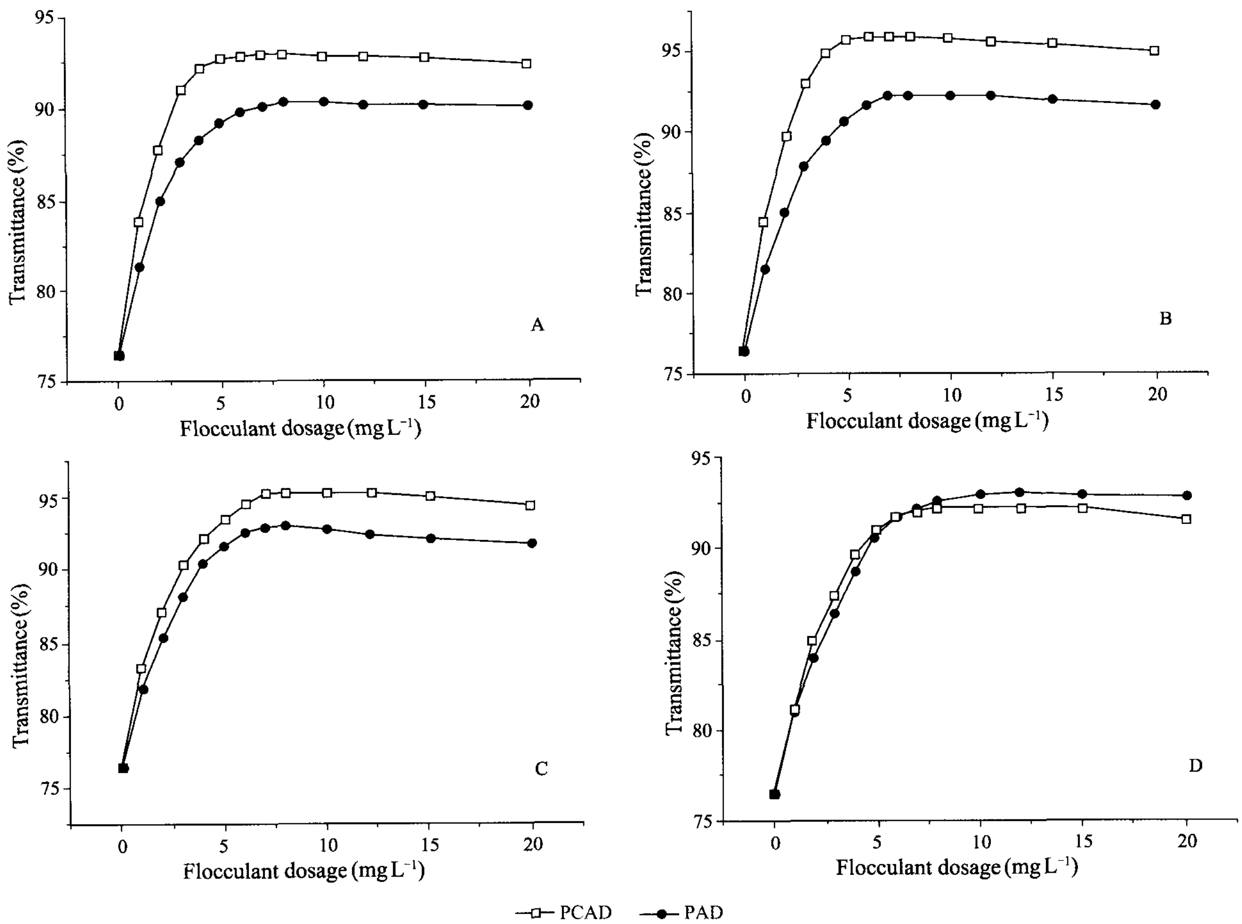

Fig.3 Flocculation performance of PAM and the copolymer in waste water at pH values of 3.0 (A), 5.5 (B), 7.0 (C) and 9.6 (D). The solid spots are for graft polymer (PCAD) and the open ones for cationic polyacrylamide (PAD).

alkaline conditions. At pH 4.0 (Fig.3A), the transmittance of waste water was 95.8% after being flocculated with PCAD at a dosage of 7.0 mgL^{-1}, but 92.3% with PAD. Under neutral conditions (pH 7.0, Fig.3B), at the optimal dosage of 8.0 mgL^{-1}, the transmittance of waste water was 95.4% after being flocculated by PCAD, but 93.1% by PAD. On the other hand, at pH 9.6 (Fig.3C), the transmittance of waste water was about 92.3% after the flocculation with PCAD at a dosage range of 8.0 mgL^{-1}, while PAD showed a little better flocculation effect on the wastewater with the transmittance of 92.9%.

With increasing flocculant dosage, adsorbing and bridging effects were enhanced. So more waste was flocculated and the transmittance rate increased accordingly. When most waste was separated, more flocculant had less effect. However, if flocculant dosage was above the optimal value, some polymer would act as stabilizer. The transmittance of waster water decreased because flocculation efficiency became weaker.

It was known that the amine groups of chitosan were protonated and formed cationic groups under acid conditions. They were favorable to flocculation because the colloidal particles in the waste water had negative charges. The molecules of PCAD would have more positive charge under acid conditions. So PCAD showed better flocculation ability than it did under alkaline condition. Similarly, PCAD was a better flocculant than PAD under acid condition, but a worse one under alkaline conditions. When pH value was 3.0, the flocculation ability of both PCAD and PAD was worse. The reason was that large amount of acid caused chain segments of AM and DMC coiled. These groups could not act with colloidal particles in waste water efficiently.

Fig.4 shows the floc images of some flocculation experiments. Obviously, the floc became bigger with increasing PCAD dosage. When PCAD dosage was lower than 8 mgL^{-1}, the flocs were smaller and settled slowly. When PCAD dosage was larger than 8 mgL^{-1}, the flocs were obviously bigger and could settle fast. The results were consistent with that of transmittance. According to the above facts, the optimal dosage of PCAD was 8 mgL^{-1} at pH 5.5.

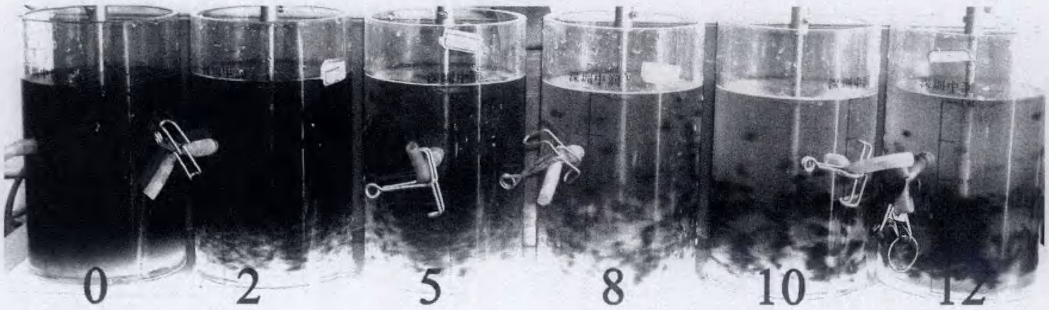

Fig.4 The floc image of flocculation experiments (mgL^{-1}).

4 Conclusions

The chitosan, derived from crab shells, was used to prepare the flocculant with two monomers of AM and DMC. The graft polymer was used to treat the waste water. The experiment data indicated that the graft polymer (PCAD) had good flocculation ability. Compared with PAD, PCAD showed better flocculation ability under acid and neutral conditions, but worse ability under alkaline condition. The flocculation ability of PCAD was high when chitosan content was below 65%. However, it decreased rapidly when chitosan content exceeded 65%. When chitosan content was high, AM and DMC concentration was relatively low for the chitosan. So AM and DMC groups were less on chitosan molecules. Consequently, the flocculation ability of graft polymer was weak. When more DMC was added into the reaction system, the resulting polymer would have more DMC groups. So they would have more positive charges in the solution. The colloidal particles would be flocculated efficiently. PCAD's flocculation ability was obviously affected by pH value of wastewater. PCAD performed well when the waste water was under weak acidic condition (pH=5.5). The optimal synthesis conditions were chitosan content 65% and DMC content 15%–20%.

Acknowledgements

This study was supported by Young Scientist Foundation (2008BS09001) from the Department of Science and Technology of Shandong Province.

References

Cai, B. X., 1999. Development of porous beads chitosan resin from marine biology. *Donghai Marine Science*, **17** (2): 39-42.

Chang J., Liu, W., Han, B., and Liu, B., 2008. The Evaluation on Biological Properties of Carboxymethyl-chitosan and Carboxymethyl-chitin. *Journal of Ocean University of China*, **7** (4): 404-410.

Chu, Y. Y., and Sun, X. J., 2008. Study on the Treatment of Coke-oven Plant Wastewater with Chitosan-Acrylamide Flocculant. *Pollution control technology*, **20** (2): 6-8.

Divakaran, R., and Sivasankara Pillai, V., 2002. Flocculation of river silt using chitosan. *Water Research*, **36** (9): 2414-2418.

Feng, S., Xiang, B., Shao, J. Y., Li, Y. J., and Wang, F., 2005. Effects of modified chitosan on dewatering performance of sludge. *Industrial Water and Wastewater*, **36** (4): 62-67.

Hebeish, A., Higazy, A., and El-Shafei, A., 2006. New sizing agents and flocculants derived from chitosan. *Starch-Starke*, **58** (8): 401-410.

Knorr, D., 1984. Use of chitinous polymers in food: A challenge for food research and development. *Food Technology*, **38** (1): 85-88.

Laue, C., and Hunkeler, D., 2006. Chitosan-graft-acrylamide polyelectrolytes: Synthesis, flocculation, and modeling. *Journal of Applied Polymer Science*, **102** (1): 885-896.

Lin, J., Suo, Z. Q., Wang, G., and Liu, Y. P., 2005. Study on Modified Chito san Flocculant in Dyeing Wa stewater Treatment. *Environmental Protection Science*, **31** (6): 16-18.

Liu, C., Tan, Y,. Liu, C., Chen, X., and Yu, L., 2007. Preparations, Characterizations and Applications of Chitosan-based Nanoparticles. *Journal of Ocean University of China*, **6** (3): 237-243. DOI 10.1007/s11802-007-0237-9.

Ma, X. P., and Shao, D. B., 1999. The synthesis and flocculating property of cationic polyacrylamides. *Oilfield Chemistry*, **16** (1): 37-40.

Ma, Y. S., and Qiu, H. Y., 2007. Study of Selecting Proper Chitosan from Various Chitosan Sample as Wood Pulp Strengthening Agent. *Heilongjiang Pulp and Paper*, (1): 1-4.

Mahdavinia, G. R., Pourjavadi, A., and Zohuriaan-Mehr, M. J., 2008. Synthesis and properties of highly swelling PAAm/ chitosan semi-IPN hydrogels, *Macromolecular Symposia*. **274** (1): 171-176.

RMP, D. S., 2008. Poly (N-isopropylacrylamide) surface-grafted chitosan membranes as a new substrate for cell sheet engineering and manipulation. *Biotechnology and Bioengineering*, **101** (6): 1321-1331.

Roberts, G., 1992. *Chitin Chemistry*, MacMillan Press, London. 350 pp.

Wang, F. H., Lei, W., Xia, M. Z., and Wang, F. Y., 2009. Flocculation Process in Suspension Medium of PAM by Reverse Microemulsion Polymerization. *Envirbnmental Science and Technology*, **32** (9): 45-48.

Wang, Y. F., Shi, B. Y., and Hui, R., 2007. Preparation of Dispersion Polymeric Cationic Polyacrylamide and Application as Flocculant on Bamboo Pulp Waste Water. *Paper and Paper Making*, **26** (6): 69-73.

Zeng, X., and Ruckenstein, E., 1998. Cross-linked macroporous chitosan anion-exchange membranes for protein separations. *Journal of Membrane Science*, **148** (2): 195-205.

Zhou, L., Xu, J., Song, Y., Gao, Y., and Chen, X., 2007. Preparation and *in vitro* Release Performance of Sustained-elease Captopril/ Chitosan-gelatin Net-polymer Microspheres. *Journal of Ocean University of China*, **6** (3): 249-254. DOI 10. 1007/s11802-007-0249-5.

(Edited by Ji Dechun)