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RESEARCH ARTICLE

Xiaojun XU, Xiangyi LIU, Yuming YANG

Synthesis of hydrophobic association cationic starch and its flocculation application on containing algae water of Dianchi Lake

Abstract The hydrophobic formation cationic starch (PSOAMDA) was prepared from starch (St), octadecyl acrylate (OA), acrylamide (AM) and dimethyl diallyl ammonium chloride (DMDAAC) by means of inverse suspension polymerization with redox initiator. Water with algae from Dianchi Lake was tested with PSOAMDA. Results show that when the molar ratio of St: AM: DMDAAC: OA is 4:8:1.5:0.6 and the reaction temperature is 40°C with a reaction time of 3 h, the monomer conversion yield, graft percentage and cationic degree is 92.4%, 63.8% and 7.3%, respectively, and $M_\eta = 3.26 \times 10^6$ g/vmol. It had been found from the flocculation of disposed water with algae from Dianchi Lake that the transparency and COD elimination reach to 93.5% and 70.3%, respectively, with 15 mg/L PSOAMDA and at pH 6, vs. 91.3% and 69.2% obtained with the commercial cationic polyacrylamide (PAM-C). When PSOAMDA dosage is 10–25 mg/L and the pH of aqueous solution is 6–10, the flocculation performance is well capable of dealing with the water with algae from Dianchi Lake.

Keywords hydrophobically associating cationic starch, inverse suspension polymerization, water with algae from Dianchi Lake, flocculation

1 Introduction

The soluble polymer with a few hydrophobic groups on its hydrophilic molecules chain is called the hydrophobic association soluble polymer [1–3]. There is an enormous applied potential in areas such as in the coatings, mining of oil and gas, disposing the sewage water and the preparation of biological macromolecules and nano-particles [4].

The research and application of the starch are always concerned. One of the reasons is that there are many hydroxyls (which can be modified easily by esterification, etherification, oxidation and cross-linking) in the molecules of starch. Another reason is that starch is available and cheap. After the graft copolymerization, it can partly replace the expensive polyacrylamide because the graft copolymerization will greatly increase the activity of the starch. The grafted polymer has a branch structure and the scattered flocculation groups can strongly capture, aggregate, flocculate and precipitate the particles in the suspended liquids. It can improve the flocculation results and satisfy the needs of the different flocculation technologies.

Dianchi Lake used to be called "pearl of the plateau", "the mother lake" of Kunming in Yunnan Province. But, since the 1990s, Dianchi Lake has become more and more eutrophic. The water in the lake has changed becoming a little darker and smells. The water quality is lower than the V level of the water quality (GB3838-88 in China). The index point of the eutrophic TN and TP of Dianchi Lake is at 8.27 mg/L and 0.59 mg/L in Caohai, and 2.13 mg/L and 0.33 mg/L in Waihai, respectively [5]. "Water Bloom" appeared in a large area lasting for a long time resulting in the death and reduction of fish and shrimp populations in the lake. The landscape and usefulness of Dianchi Lake has been badly damaged. The third waterworks of Kunming has been compelled to stop getting water from Dianchi Lake as a supply source.

There are five kinds of pelagian algae in Dianchi Lake. These are cyanobacteria, green algae, diatom, dinoflagellate and yellow algae [5–8]. Most of the algae in Dianchi Lake are green algae and blue-green algae which cover more than 95% of the total. In the blue-green algae,

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Xiaojun XU (✉), Xiangyi LIU, Yuming YANG
College of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China
E-mail: xuxiaojun88@sina.com

Xiangyi LIU, Yuming YANG
Southwest Forestry College, Kunming 650224, China

Microcystis aeruginosa belonging to the microcystic kind is the most important reason of "water bloom". It has been noted based on the result of determinations that *Microcystis aeruginosa* in Dianchi Lake is a poisonous algae which can harm animals' livers. Because it contains a kind of liver toxin, *Microcystis aeruginosa* can cause liver swelling and hyperemia, which may lead to the animals' death. Therefore, it is a potential hazard to the ecological water environment and human health.

The algae characteristically have colloidal sides and airbags. Most of algae are single-cell organisms and have flagella which make them float on water easily. The powerful negative charges on the algae surfaces make them scattered in the water so that the algae in the water is generally difficult to flocculate. The way to solve this problem is to put cationic flocculants into the water to flocculate and remove the algae.

This article reported the results of a study on the polymerization of starch (St), acrylamide (AM), crylic acid, eighteen mellow (OA), and dimethyl diallyl ammonium chloride (DMDAAC) by means of inverse suspension polymerization. The produced polymer is soluble with hydrophobic association cationic starch. It was used as the flocculation agent to flocculate and remove the algae in Dianchi Lake.

2 Experimental

2.1 Materials

Eighteen mellow (OA) was prepared according to the Ref. [9]. Soluble starch (St) (chemical pure) was purchased from the second chemical agent factory in Tianjin. Acrylamide (AM) (analytic pure) was purchased from the third chemical agent factory in Beijing and crystallized in acetone. Persulfate potassium (analytically pure) was purchased from the first chemical agent factory in Shanghai and crystallized in distilled water. Bisulphate sodium (analytic pure) was purchased from the first chemical agent factory in Shanghai and crystallized in distilled water.

Span80 (chemical pure) and Tween80 (chemical pure) were purchased from the chemical glass wholesale station in Dalian medicine company. Dimethyl diallyl ammonium chloride (DMDAAC) (60% aqueous, industrial products), from the Yinhu Chemical Ltd. of Hangzhou, was purified by extracting with anhydrous ether and cyclohexane.

Cationic polyacrylamide (PAM-C) is a commercial product and is used as received for the flocculation. The tested water with algae was from Dianchi Lake during the "Water bloom" outbreak on May 23, 2005. It had a high algae concentration and was light brown with a severe smell and low transmittance.

2.2 Synthesis of hydrophobically associating cationic starch

A three-opening flask installed with the blender, a burette funnel and a gas conduit was put into a water-bath container in which the water temperature was constant at 40°C. After adding cyclohexane 60 mL, Span80 1.2 mL, Tween80 2.4 mL and OA 0.6 mL, into the flask, respectively, the mixtures were emulsified for 30 min under a N_2 atmosphere completely. The 40°C pasted starch, prepared from 4 g starch and 20 mL water at 70°C and cooled to 40°C, was then added and mixed in the flask followed by a 20 min reaction. Subsequently, 0.8 g $K_2S_2O_8$ and 0.8 g $NaHSO_3$ was added for 15 min to the reaction. After 0.75 g DMDAAC was added again, the mixed solution with 0.75 g DMDAAC and 8.0 g AM dissolved in the 10 mL water was dripped at the constant velocity of 1 drop/s and the mix reaction was kept 3 h at 40°C under a N_2 atmosphere. When this mix reaction was finished, the reaction mixture was deposited and washed 3–4 times with the 95% ethanol. Subsequently, the rude graft polymer was received.

If the reactant match rates were changed, the different rude graft polymers could be worked out.

2.3 Rude graft polymers purification

The Quantitative rude graft polymer was put into "SuoShi" distillation utensil and was then dissolved in acetone and extracted after 24 h to remove the homopolymer. The dry and pure graft polymer was achieved after desiccation by using the vacuum drying at the temperature of 60°C.

2.4 Flocculation test on the water with algae from Dianchi Lake

For the water with algae from Dianchi Lake, the algae content is 324 mg/L (determined by filtering Method), the COD is 472 mg/L (determined by $K_2Cr_2O_7$), and pH is 8.6.

For the purifying tests of the water with algae from Dianchi Lake, the water with algae was first mixed for 3 min at the speed of 250 r/min and for 15 min at the speed of 50 r/min after the aqueous solution of the hydrophobically associating cationic starch (PSOA-MDA) was added. Then for 20 min, the algae flock in the treated water was settled. Some of the liquid was drawn from 30 mm below the liquid surface and the light transmission was determined by Spectrophotometer (UNIC apparatus Ltd. in Shanghai). The wavelength used is at 620 nm and the light distance is 1.0 cm with the water as the blank liquid. At the same time, the COD and the PAM-C flocculants were determined under the same conditions.

3 Results and discussion

3.1 Effect of the reaction compounds on the product property

Some conclusions can be reached from the data in the Table 1. With the increase of the dosage of the hydrophobic monomer OA, the polymers' characteristic viscosity and molecular weight was reduced. The dissolution time became longer and the monomer conversion rate and graft rate was reduced. With an increase in the dosage of the cationic monomer DMDAAC, the molecular weight and the monomer conversion rate was reduced, but the solubility was increased.

3.2 Structural characterization of starch and PSOAMDA with IR spectrum

IR spectrums of starch and PSOAMDA are showed in Fig. 1 and Fig. 2.

In Fig. 2, there is an absorption trough at 3024 cm^{-1}. This trough is telescopically vibratile absorption troughs of methyl carbon hydrogen bond on quaternary ammonium. There are also other two troughs at 1481 cm^{-1} and 1479 cm^{-1}. These troughs are telescopically vibratile absorption troughs of carbon nitrogen bond on the quaternary ammonium. Carbonyl telescopically vibratile absorption trough is at 1690 cm^{-1}. Ester C–O–C symmetric telescopically vibratile absorption trough is at 1120 cm^{-1}. It can be seen from the starch's IR that the hydroxy troughs at 1420 cm^{-1} and 1360 cm^{-1} have become obviously weakened or disappeared from the starch's IR and the inherent feature of starch absorb troughs has appeared at 850 cm^{-1}, 750 cm^{-1} and 570 cm^{-1} from Fig. 2. It can be also be proven from the IR spectrum (in Fig. 2) of PSOAMDA removed the homopolymer that the purified graft product is the starch graft copolymer and AM/OA/DMDAAC has been grafted on the starch chain which shows that the separation method and synthesis technology are feasible.

3.3 Effect of the flocculants dosage on the flocculation performance

PSOAMDA-3 samples are used as the flocculants for all tests compared with PAM-C. The influence of the flocculants' dosages of PSOAMDA-3 and PAM-C on the flocculation efficiency and on the COD elimination rate is shown in Fig. 3 and Fig. 4 respectively.

It can be seen from the Fig. 3 that the best dosage of PSOAMDA is 15 mg/L and the change in light transmis-

Table 1 The effect of the reaction compound on product property

m(St):*m*(AM):*m*(DMDACC):*m*(OA)	monomer conversion rate/%	graft degree/%	dissolved time/min	characteristic viscosity/mL·g^{-1}	$M_\eta \times 10^6$	cationic degree/%
4:8:1.5:0	93.2	66.8	24	717.33	4.32	7.7
4:8:1.5:0.2	93.6	65.6	91	681.21	3.99	7.4
4:8:1.5:0.4	92.4	65.3	152	624.63	3.50	7.3
4:8:1.5:0.6	92.4	63.8	226	596.43	3.26	7.3
4:8:1.5:0.8	92.8	62.5	334	511.72	2.57	7.1
4:8:1.5:1.0	92.1	61.6	560	423.62	1.92	6.9
4:8:0:0.6	92.7	71.8	176	577.45	3.11	0
4:8:1:0.6	92.5	67.6	140	548.63	2.88	6.9
4:8:2:0.6	91.9	64.3	127	524.92	2.69	10.6
4:8:3:0.6	91.1	61.8	103	496.58	2.47	13.7
4:8:4:0.6	90.1	59.5	92	463.22	2.21	15.4

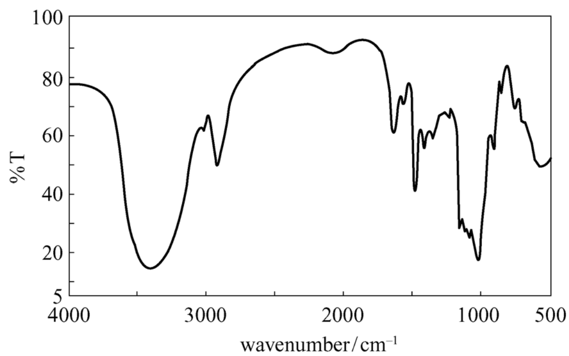

Fig. 1 IR spectrum of starch

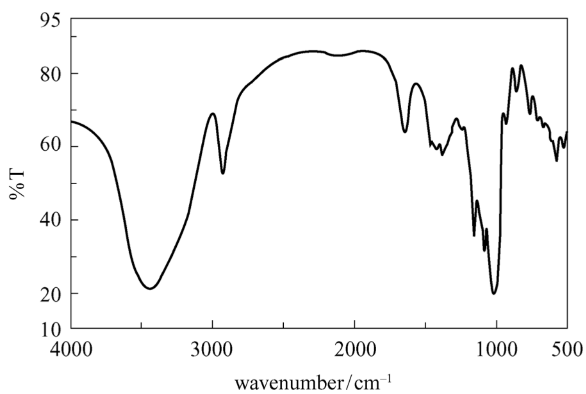

Fig. 2 IR spectrum of PSOAMDA

sion is gentle in the dosage range of 10–25 mg/L. These results show the range for the best dosage is wide and the effectiveness of the removal of algae is high with PSOAMDA. The COD elimination rate is increased with the increase of the flocculant dosage and the change will become gentler until it reaches the maximum. These results show that PSOAMDA is good for practical applications. Although light transmission gets its maximum at very low PAM-C dosage (10 mg/L), the best dosage range for PAM-C is quite narrow because light transmission is reduced rapidly when PAM-C dosage increases.

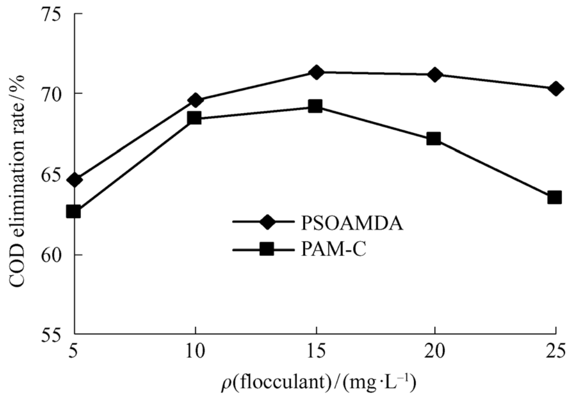

Fig. 3 The effect of the flocculants' dosage on the flocculating efficiency

It can be seen from the Fig. 4 that the trend of the COD elimination rate is similar to Fig. 3 with the PSOAMDA dosage's change. It has been also found in the tests that with the increase of flocculant's dosage of PSOAMDA, the floccule settling time becomes clearly shorter. The light transmission of the water is markedly increased and the flocculation deterioration phenomenon doesn't appear in the test dosage. The settlement time of the PSOAMDA's floccule is faster than PAM-C's with the same dosage. The light transmission of the water by-product by PSOAMDA is bigger than PAM-C. These differences are mainly induced by the special molecular structure of PSOAMDA. Firstly, PSOAMDA has two chemically active monomers linking with starch by grafting and the molecular weight of PSOAMDA is bigger than PAM-C so that the flocculation ability and effectiveness are markedly increased. Secondly, starch is the half rigid chain macromolecule and has a very strongly hydrophilic nature and will have a bigger volume when it expands in water. For PSOAMDA, there are the flexible polyacrylamide, polydimethyldiallyl ammonia chloride, polyacrylic eighteenth ester branched chain on the big molecular skeleton of starch. Therefore, it is obvious that as PSOAMDA is a large net molecule with both rigid and flexible characteristics. It has a better ability to capture suspended particles, especially, the superfine particles. When the hydrophobically associating cationic starch (PSOAMDA) can be synthesized to appropriate component proportions and can form a large net molecule with both rigid and flexible characteristics, the flexible phase (monomer branched-chain) and the rigid phase (starch) in PSOAMDA will have a synergistic effect on improving its flocculation performance.

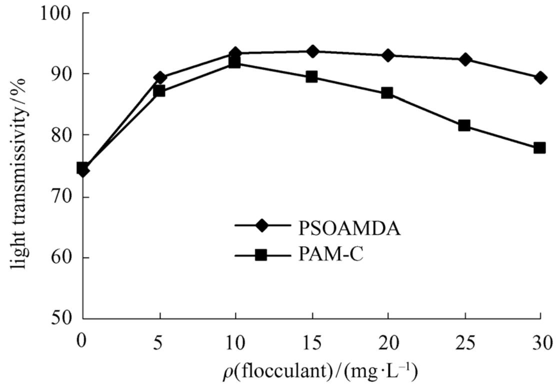

Fig. 4 The effect of the flocculants dosage on the COD elimination rate

3.4 Effect of pH on the flocculation performance

Adjusting the pH with NaOH and HCl at room temperature, the effect of the different pH on the flocculation performance is shown in Fig. 5 and Fig. 6 using PSOAMDA-3 and PAM-C as the flocculants.

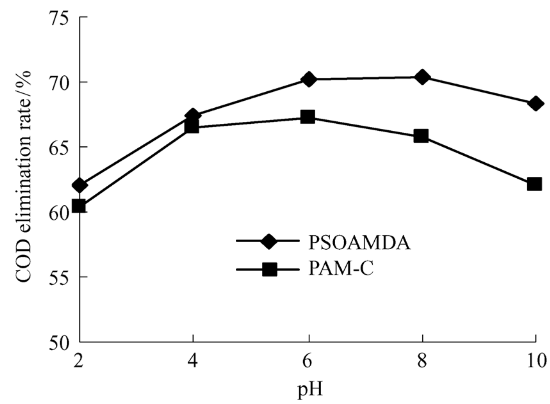

Fig. 5 The effect of pH on flocculation performance

It can be seen from Fig. 5 and Fig. 6 that when the pH value of the water with algae from Dianchi Lake is 6–10, PSOAMDA has a good flocculating effect and its adaptability to pH is obviously better than PAM-C in treatment of the water with algae. It has come to light that the wastewater pH can change the extension morphology of the organic macromolecule flocculants in water which will produce an obvious influence on the flocculation effect. Because the molecular chain of PAM-C is flexible, the molecular chain morphology of PAM-C in water is sensitive to pH change. However, PSOAMDA is modified by polyacrylamide, polydimethyldiallyl ammonia chloride and the polyacrylic eighteenth ester on starch so that its

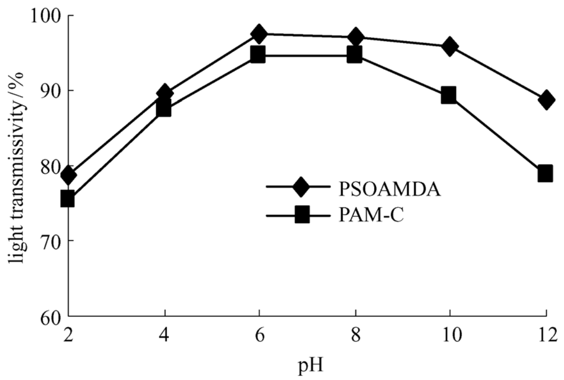

Fig. 6 The influence of pH on COD elimination rate

molecular chain has both rigid and flexible characteristics. Because the molecules are supported by the rigid molecular chain structure, pH only produces a small effect on the extension morphology of PSOAMDA in water so that the adaptability of the PSOAMDA to pH is obviously better than PAM-C in dealing with polluted water.

3.5 Effect of the cationic degree on the flocculation performance

The effect of the cationic degree of PSOAMDA on the flocculating performance can be seen in Fig. 7.

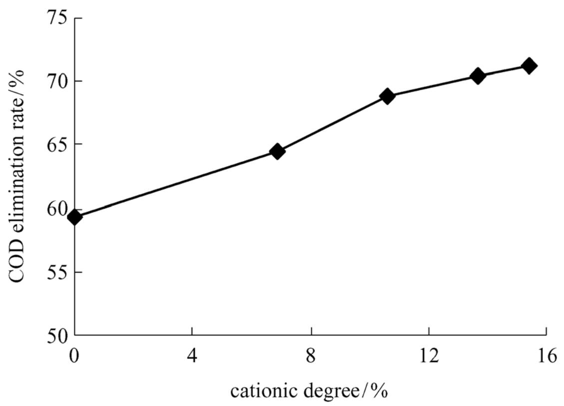

Fig. 7 The effect of the cationic degree on the COD elimination rate

It has been pointed from Fig. 7 that the COD elimination rate increases with the increase of the cationic degree of PSOAMDA. The main reasons are that starch is linked with the branched chains of polyacrylamide and polydimethyldiallyl ammonia chloride which have good flocculating functions. The branched chain of cationic polydimethyldiallyl ammonia chloride is a quaternary ammonium salt which can be almost completely ionized in water so that PSOAMDA, with the high positive charge density, can effectively catch the floating algae with a negative charge. Moreover, the branched chain of polyacrylamide in PSOAMDA can promote inorganic suspended substance settling, which is similar as a flocculation accelerator. Polyoctadecanolacrylate can adsorb on the sides and gasbags of the algae's colloid as it is hydrophobic. For the three different branched chain groups in PSOAMDA can bring into play the well differently absorbing and flocculating actions and produce the perfectly synergistically flocculating effects. PSOAMDA has the good flocculating performance on the processing of the water with algae.

4 Conclusions

(1) The graft polymerization of starch with acrylamide (AM), dimethyl diallyl ammonia chloride (DMDAAC), and acrylic eighteenth ester (OA) can be initiated to form the hydrophobically associating cationic starch (PSOAMDA) by means of the redox initiator of polymerization. It has been pointed out from IR spectrum that AM/OA/DMDAAC is grafted on the starch chain. When the ratio of *m*(St):*m*(AM):*m*(DMDAAC):*m*(OA) is 4:8:1.5:0.6, the reaction temperature is 40°C, and reaction time is 3 h, the monomer conversion rate, graft percentage and cationic degree are 92.4%, 63.8% and 7.3% respectively, and $M_\eta = 3.26 \times 10^6$.

(2) For the PSOAMDA, with the increases of the dosage of hydrophobic monomer OA in the reactants, the polymer's characteristics viscosity, molecular weight (M_η), monomer conversion rate and graft degree will reduce, but the dissolved time of the polymer in water increases. However, with the increase of the dosage of cationic monomer DMDAAC in the reactants, the polymer's cationic degree and water-solubility will increase, but molecular weight and monomer conversion rate will reduce.

(3) The well flocculating effect can be obtained with 93.5% light transmission and 71.3% COD elimination rate after water with algae from Dianchi Lake is treated with the dosage of 15 mg/L PSOAMDA and at pH 6.0. But the light transmission and COD elimination rate are only 91.3% and 69.2% respectively with PAM-C at the same conditions. Otherwise, the COD elimination will increase with the increase of cationic degree of PSOAMDA.

(4) For the flocculation process of the water with algae from Dianchi Lake, PSOAMDA can be provided with the properties of the wide dosage scope and strong adaptability to pH. Its treating results are better than the commercial PAM-C.

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