



Synthesis and characterization of hydrophobically associating cationic polyacrylamide

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ABSTRACT

P(AM-DMDAAC-BA), one kind of hydrophobically associating cationic polyacrylamide, was synthesized with acrylamide (AM), dimethylallylammonium chloride (DMDAAC) and butylacrylate (BA) by the micellar free radical copolymerization technique. The copolymer was characterized by means of Nuclear Magnetic Resonance Hydrogen Spectroscopy (^1H NMR), Transmission Electron Microscopy (TEM) and Thermal Gravimetric Analysis (TGA). The effect of flocculant dosage on oil removal efficiency and synergistic effect of the copolymer with other reagents were studied with respect to oily wastewater treatment. ^1H NMR results proved the formation of the hydrophobically associating cationic copolymers. TEM showed that adsorption bridging property of P(AM-DMDAAC-BA) was significantly enhanced along with the increase of hydrophobic group content in the copolymer. TGA results indicated that the copolymer has favorable thermal stability. It was found that the oil removal efficiency of P(AM-DMDAAC-BA) could reach 93.4% at dosage of 50 mg/L. P(AM-DMDAAC-BA) had good synergistic effect with soluble starch and $\text{Al}_2(\text{SO}_4)_3$. The oil removal efficiency could be improved if $\text{Al}_2(\text{SO}_4)_3$ was added prior to P(AM-DMDAAC-BA).

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1. Introduction

Hydrophobically associating water-soluble polymers are hydrosoluble polymers containing a small number of hydrophobic groups attached directly to the polymer backbones [1]. The incorporation of a few hydrophobic groups in a hydrophilic macromolecule chain results in systems with unique rheological characteristics. In aqueous solutions, the hydrophobic groups of these polymers can aggregate together and result in intra and intermolecular associating to minimize their exposure to the solvent, similar to the formation of micelles by a surfactant above its critical micelle concentration [2,3]. These associations result in an increase in the hydrodynamic size of the polymer that increases solution viscosity, as well as the association reaction between hydrophobic groups of these polymers and the organics in the wastewater. The potential exists to use water-soluble associating polymers as flocculants and mobility control agents in oil recovery [2–7].

The hydrophobically associating cationic polyacrylamide, one kind of water-soluble hydrophobically associating copolymers, was polymerized by cationic monomer, hydrophobic monomer and acrylamide. As can be imagined, both cationic group and hydropho-

bic group were incorporated into the polymer molecule chain. The P(AM-DMDAAC-BA) is an amphiphilic cationic polyelectrolyte containing both hydrophobic groups (methyl groups, backbone chain and so on) and hydrophilic groups (positively charged tertiary amine and acrylamide groups) [8]. Therefore, the electro-neutralization effect, adsorption bridging effect and hydrophobic association effect could together contribute to oil removal during the treatment of oily wastewater.

The hydrophobically modified water-soluble polymer was one typical kind of organic copolymers and it had strong degreasing performance and could improve the oil recovery [9,10]. However, raw materials used in the synthesis of the copolymer were a little more expensive and dosage of the polymer during wastewater treatment might be comparatively higher than those of other traditional organic or inorganic flocculants. Therefore, it would lead to the high operating cost during the treatment of oily wastewater [3,11]. Moreover, up to now, the hydrophobic association water-soluble polymers have not been applied widely. Many problems appearing in synthesis and performance limited their usage. For example, the critical aggregate concentration is little high, and their viscosities below the critical aggregate concentration were not high enough to be used in practice. At high temperature, the viscosities may decrease because of weak bond in polymer chemical structure, which result in the breakage of hydrophobic side chain from polymer backbone [12]. So, in order to decrease the operating cost, ensure the treatment efficiency and reinforce the possibility of the

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large-scale industrial application of P(AM-DMDAAC-BA) simultaneously, it seemed necessary and essential to utilize the copolymer together with some cheap natural macromolecule coagulant aids or some inorganic flocculants.

In this paper, the synthesis and characterization of the water-soluble hydrophobically associating cationic polyacrylamide flocculant P(AM-DMDAAC-BA) were investigated. The synthesis was conducted with acrylamide (AM), dimethyldiallylammonium chloride (DMDAAC) and butylacrylate (BA) by the micellar free radical copolymerization technique. The copolymer was characterized by means of ^1H NMR, TEM and TGA technique, respectively. The effect of flocculant dosage and its synergistic effect with soluble starch and $\text{Al}_2(\text{SO}_4)_3$ on degreasing performances were studied with respect to oily wastewater treatment.

2. Materials and methods

2.1. Experimental materials

The oily wastewater used in this experiment was taken from Tuo-1 Joint Station of Sheng Li Oilfield in Dong Ying, Shandong Province, China. The pH of the oily wastewater was 7.0. The contents of oil, SS, COD and total salinity were 35.5 mg/L, 27.8 mg/L, 277 mg/L and 9242 mg/L, respectively.

The monomers acrylamide and butylacrylate were recrystallized from acetone and were obtained from Guangcheng Chemical Reagent Plant, Tianjin, China. The cationic monomer DMDAAC (40%, w/w aqueous solution, 100% charge density, intrinsic viscosity was 1.02 dL/g, provided by manufacture) was obtained from Bin Zhou Chemical Co., Shandong, China. The initiators for the synthesis of the hydrophobically modified polyacrylamides were sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) and potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), analytical pure grade, from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Ethanol and acetone (Damao Chemical Reagent Plant, Tianjin, China), chemical pure, were used for copolymer precipitation and purification. Other analytically pure grade agents, including soluble starch, anhydrous sodium sulfate (Na_2SO_4), concentrated hydrochloric acid (HCl), petroleum ether, aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), cetyltrimethylammonium bromide (CTAB) and azobisisobutyronitrile (AIBN) were used as received, without any further purification, and were purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. The water used was distilled and deionized with an all-glass apparatus. High purity nitrogen (Deyang Special Gas Co., Ltd., Jinan, China) was used in the synthesis of the copolymer in order to drive away the air existing in the reactor.

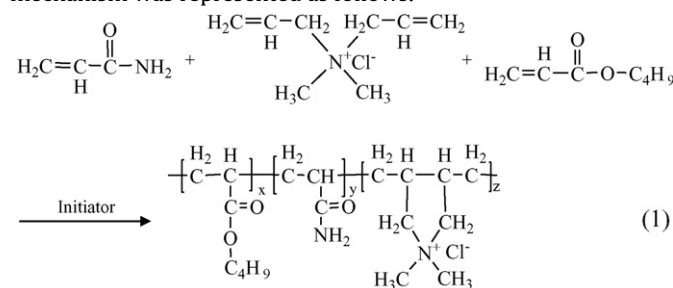
2.2. Experimental methods

2.2.1. Synthesis of P(AM-DMDAAC-BA)

The P(AM-DMDAAC-BA) copolymer was prepared using micellar free radical copolymerization technique [12–14]. The active monomer AM, which had higher reactive activity, was separated into two parts to participate in the copolymerization in order that homogeneous distribution could exist in the polymer molecule chain. In this technique, use of a surfactant is necessary to solubilize the hydrophobic monomer into micelles dispersed in water. Each reaction was conducted in a 500 mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer, a dropping funnel, glass spigot, and high purity nitrogen inlet/outlet. The reactor, containing a cationic surfactant, BA, DMDAAC, half quantity of AM in deionized water, was heated to 30 °C from ambient temperature using a thermostated water bath with continuous stirring under high purity nitrogen to ensure the complete removal of trapped air until the hydrophobic

monomer was solubilized within surfactant micelles and the solution was optically transparent. Then the redox initiators ($\text{Na}_2\text{S}_2\text{O}_3$ and $\text{K}_2\text{S}_2\text{O}_8$) were added to initiate the copolymerization. The remaining aqueous acrylamide solution was transferred into the reaction vessel through a dropping funnel within 1 h. When heat emission peak of the system appeared, the temperature of the system was enhanced to 70 °C and the mixture was kept at the constant temperature with vigorous stirring and under a high purity nitrogen purge for 6 h. At the end of the reaction, either a viscous polymer solution or a viscous polymer gel was obtained and the product was homogeneous and clear.

After cooling the final reaction mixture, the aqueous polymer solution or gel-like samples were washed, precipitated and filtered with ethanol and acetone to remove unreacted monomers and surfactants. The mixture recovered by filtration was continuously dried to constant weight in vacuum oven for a minimum of 24 h in order to allow ethanol and acetone to evaporate. The final product P(AM-DMDAAC-BA) was white powder. It was dissolved in deionized water prior to utilizing. The probable complex reaction mechanism was represented as follows.



The properties of the copolymer for the ^1H NMR, TGA and coagulation experiments were indicated as follows: contents of DMDAAC and BA were 24.3% and 2.0%, respectively and its intrinsic viscosity was 636 mL/g, which was determined through the previous experiments [15]. The molar mass of P(AM-DMDAAC-BA) was about 2,570,000 according to its intrinsic viscosity which was measured through the national standard of the People's Republic of China [16,17]. The three copolymers used in the TEM experiment contained different contents of hydrophobic monomer (BA), which was 0.5%, 1.0% and 2.0%, respectively, in order to observe the influence of the addition of hydrophobic monomer on the copolymer morphology and coagulation performance.

2.2.2. Characterization of P(AM-DMDAAC-BA)

Copolymer composition was determined by ^1H NMR spectroscopy in deuterium oxide using a Bruker ADVANCE 400 MHz spectrometer according to literatures [14,18]. The thermal gravimetric analysis was conducted at a heating rate of 10 °C/min under nitrogen flow of 20 mL/min over a temperature range from room temperature up to 600 °C on a TA SDT Q600 synchronal thermal analyzer, in order to investigate the thermal stability of the copolymer.

The morphology of the copolymer was observed through transmission electron microscopy. The solid sample was prepared as shown in Section 2.2.1 and was diluted in order to get a water solution with concentration of 1 g/L. Several drops of this water solution were added on a copper net with a supporting membrane. After absorbing the excess liquid with filter paper, the copper net was dried (drying time takes about 5–8 min) and the TEM images could be taken through a JEM-100CXII type transmission electronic microscope.

2.2.3. Coagulation experiments

Coagulation experiments for oily wastewater treatment were carried out at room temperature of about 20 °C. The test water of

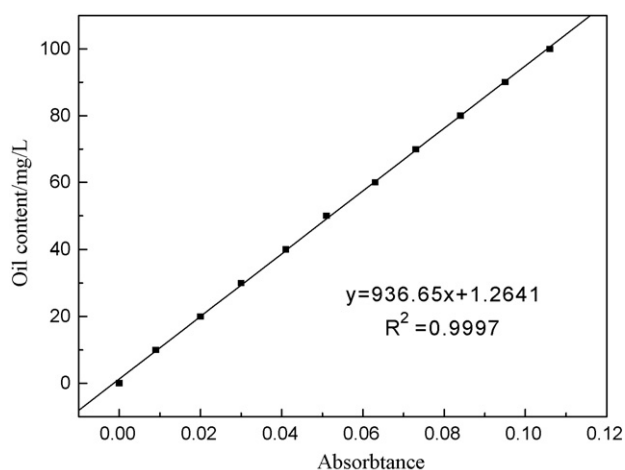


Fig. 1. Standard curve of oil content.

500 mL was added to each of the one-liter beakers and a six-paddled stirrer was used for mixing. The solutions were stirred rapidly at 200 rpm for 60 s after flocculant addition, followed by slow stirring at 40 rpm for 15 min and quiescent settling. After depositing for certain time, middle part of the water was taken for oil content measurements and oil removal efficiency calculation.

2.2.4. Measurement of oil content

Oil content in wastewater was measured according to the petroleum and natural gas industry standard SY/T0530-93 of People's Republic of China [19]. During the experiment, the oil contents of feed and solution after flocculation were analyzed by petroleum ether extraction test. The oil content was obtained through consulting the standard curve of oil content after measuring the absorbance of extracting agent at 430 nm wavelength with spectrophotometer of UV-754 type spectrophotometer. The dehydration should be carried out with anhydrous sodium sulfate if the extract was turbid. And then the oil content-absorbance standard curve could be achieved, in which, the reciprocal of the slope rate indicated the absorption coefficient K , as shown in Fig. 1.

The oil content in the oily wastewater was calculated as follows:

$$C_0 = \frac{EV_0}{KV_W} \times n \quad (2)$$

where C_0 : oil content of test water, mg/L; E : absorbance of test water; V_0 : total volume of the extract, mL; V_W : volume of test water, mL; K : absorption coefficient, L/mg; n : dilution multiple.

3. Results and discussion

3.1. Characterization of P(AM-DMDAAC-BA)

3.1.1. ^1H NMR spectrum of P(AM-DMDAAC-BA) flocculant

The microstructure of the P(AM-DMDAAC-BA) copolymer was determined by ^1H NMR spectroscopy. The spectrum was recorded on a Bruker AVANCE 400 MHz spectrometer at 27 °C and was shown in Fig. 2.

As seen in Fig. 2, the spectrum of P(AM-DMDAAC-BA) showed several characteristic peaks due to the addition of different monomers. The protons in the methenyl connected to amide group in AM were evidenced by the peak at 2.128 ppm. The protons in the methyl group connected to the ammonium group in DMDAAC could be found at 3.135 ppm and 3.038–2.919 ppm. The protons in the methylene group connected to ammonium group in DMDAAC were evidenced by the peak at 3.807 ppm, 3.789 ppm and 3.691 ppm, respectively. The pro-

tons in the terminal methyl group in BA were exhibited at 1.062–1.097 ppm. The protons in the methylene group in BA were indicated at 1.203 ppm. The protons in the methenyl group connected with esterfunction in BA were evidenced at 2.566 ppm [20,21].

3.1.2. Analysis of TEM images

The morphology study of the copolymer was carried out by TEM in order to observe the structure, aggregation and ramification of the organic macromolecule copolymers and to obtain some microscopic and visualized information [22]. The P(AM-DMDAAC-BA) copolymers with different contents of hydrophobic monomer were imaged through TEM technique, as shown in Fig. 3.

As can be seen in Fig. 3, along with the increase of the hydrophobic monomer content in the copolymer, the copolymer gradually aggregated and changed its intrinsic structure. The copolymer existed as spherical aggregates and looked like particles at 14,000 magnifications when the mole content of hydrophobic monomer in the copolymer was 0.5%. The particles are aggregated macromolecules with comparatively lower aggregation intensity and its size was about 0.09–0.34 μm . Fig. 3(b) showed that the aggregated macromolecules began to appear a few ramifications at 14,000 magnifications when the mole content of hydrophobic monomer in the copolymer increased to 1.0%. The size of the aggregated macromolecules synthesized under this condition was about 2.54 μm . Fig. 3(c) showed that when the mole content of hydrophobic monomer in the copolymer increased to 2.0%, the ramifications in the aggregated macromolecules increased significantly at 14,000 magnifications. The size of the aggregated macromolecules synthesized under this condition was about 2.82 μm and the adsorption bridging property of P(AM-DMDAAC-BA) might be significantly enhanced under this molecule structure, which in turn would result in a considerable flocculation performance of the copolymer during wastewater treatment [23]. So, along with the increase of hydrophobic monomer content in the copolymer, P(AM-DMDAAC-BA) showed different morphology and the addition of hydrophobic monomer could change the intrinsic structure of the copolymer and its aggregation intensity.

3.1.3. Thermal gravimetric analysis

The thermal stability of the P(AM-DMDAAC-BA) copolymer was investigated by the thermal gravimetric analysis (TGA), which was carried out on a TA SDT Q600 synchronal thermal analyzer. The thermal gravimetric curve of P(AM-DMDAAC-BA) copolymer was shown in Fig. 4.

As shown in Fig. 4, the TGA diagram of the P(AM-DMDAAC-BA) copolymer showed three steps for the weight loss. The first one occurred in the range of 30–200 °C (weight loss was about 8.83% of the total weight), corresponding to the evaporation of intra and intermolecular moisture [23–25]. The copolymer contained a large number of strong hydrophilic groups which could induce the sample to combine with water molecules. The second one occurred in the range of 200–300 °C (weight loss was about 18.63% of the total weight), corresponding to the imine reaction of the amide group and the thermal decomposition of hydrophobic side chain [12,23]. And the third one occurred in the range of beyond 300 °C (weight loss was about 53.47% of the total weight). At about 450 °C, the copolymer decomposed completely. This part of weightlessness was due to the thermal decomposition of the copolymer backbone. When the temperature exceeded 450 °C, the thermal gravimetric curve went to mild and no longer changed. The residual weight was only 20% of the initial weight of the test sample.

As could be seen in the thermal gravimetric curve of the copolymer in Fig. 4, there was an obvious peak of heat absorption, corresponding to the imine reaction of the amide group and the thermal decomposition of hydrophobic side chain. The

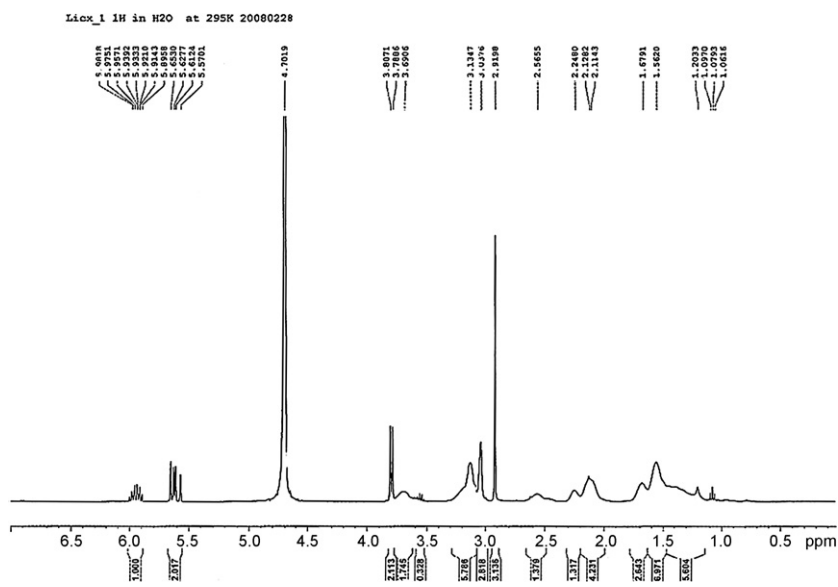


Fig. 2. NMR ^1H spectrum of P(AM-DMDAAC-BA) copolymer.

glass-transition temperature and decomposition temperature of P(AM-DMDAAC-BA) was 269.15 °C and 293.08 °C, respectively. The enthalpy value of the heat-absorption peak was 336.0 J/g.

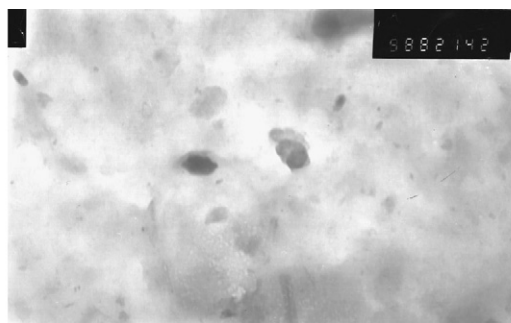
Results of TGA analysis indicated that the copolymer had favorable thermal stability.

3.2. Effect of P(AM-DMDAAC-BA) dosage on its degrading efficiency

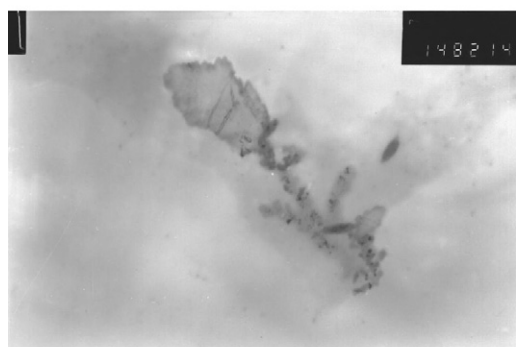
Fig. 5 showed the effect of P(AM-DMDAAC-BA) dosage on the oil removal efficiency for oily wastewater treatment. It can be seen from Fig. 5 that oil removal efficiency increased along with the flocculant dosage.

Oil removal efficiency reached 89.6% at the flocculant dosage of 30 mg/L and it was maximized to 93.3% at the flocculant dosage of 50 mg/L. The phenomenon could be explained as follows.

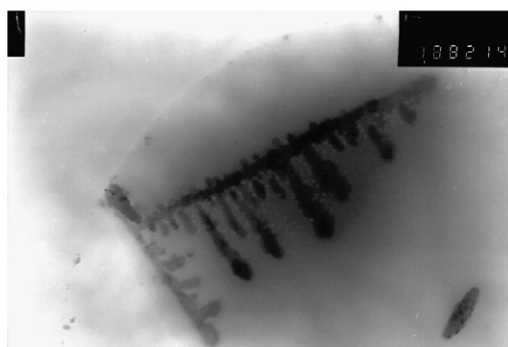
As cationic organic polymer, P(AM-DMDAAC-BA) had its intrinsic cationic groups, which had a high positive charge and are therefore more effective in neutralizing the negative charge on suspended colloid particles and natural organic materials during the coagulation process of oily wastewater [26]. In addition, the adsorption bridging effect of organic macromolecules among the flocs would be enhanced due to the long molecule chain and the hydrophobic groups. The small flocs formed by coagulation could be built up into larger agglomerates by flocculation with



(a) BA=0.5% (×14000)



(b) BA=1.0% (×14000)



(c) BA=2.0% (×14000)

Fig. 3. TEM pictures of P(AM-DMDAAC-BA) with different hydrophobic monomer content.

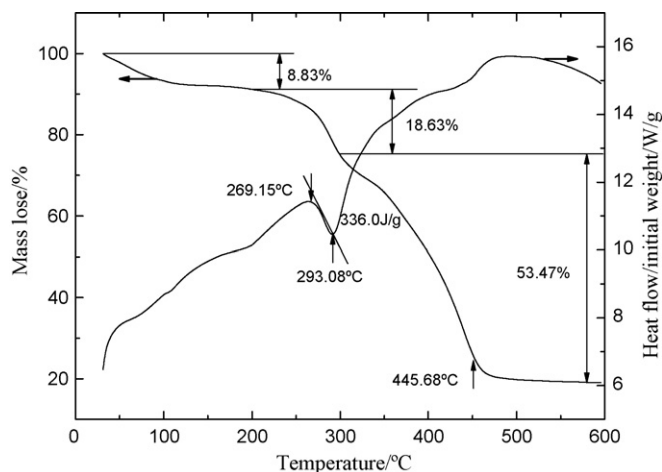


Fig. 4. Thermal gravimetric curve of P(AM-DMDAAC-BA) copolymer.

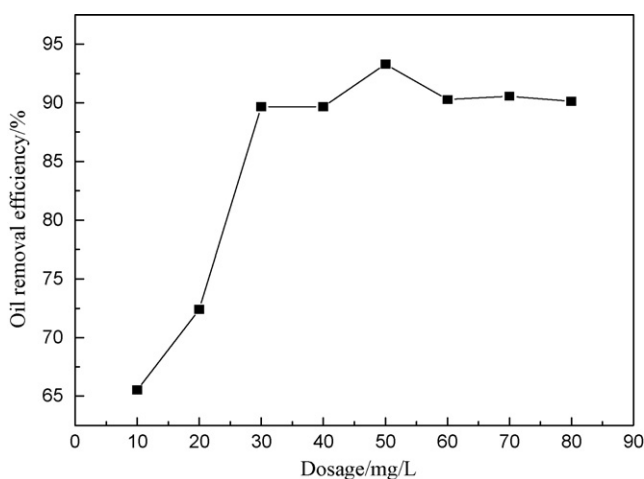


Fig. 5. Effect of P(AM-DMDAAC-BA) dosage on oil removal efficiency.

the copolymer, with the larger particles formed in this way giving accelerated rates of sedimentation [21]. With these performances, P(AM-DMDAAC-BA) was thought to be effective in the removal of the oiliness in the wastewater. While the flocculant dosage increased to some extent, the oil removal efficiency decreased and restabilization took place. The reason was that the number of cationic groups increased obviously and surface of the colloid particles would be positively charged, which was directly related to the repulsion between the added polymer molecules and the polymer chains that already adsorbed on the colloid and particle surface [26].

Flocculation experiments of oily wastewater indicated that the degreasing effect of P(AM-DMDAAC-BA) optimized at the dosage of 50 mg/L, which is a comparatively higher dosage. In order to reduce the operating cost and ensure the treatment efficiency simultaneously, it was very essential to make use of P(AM-DMDAAC-BA) together with some other cheap natural macromolecule flocculant aids or some inorganic flocculants.

3.3. Synergistic effect of P(AM-DMDAAC-BA) with natural macromolecule flocculant aid

In this part, soluble starch, a common and cheap natural macromolecule coagulant aid, was utilized together with the P(AM-DMDAAC-BA) flocculant. The optimum dosing mode of the two chemicals during the oily wastewater treatment was searched

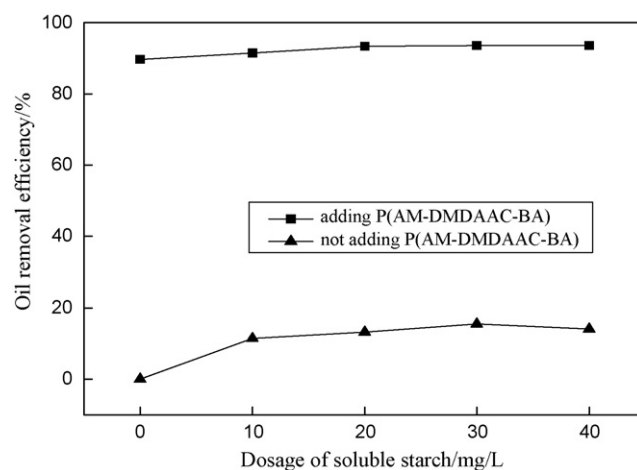


Fig. 6. Effect of starch dosage on oil removal efficiency.

according to the degreasing efficiency under different reagent combinations.

3.3.1. Effect of starch dosage on oil removal efficiency

In order to reduce the treating cost efficiently, the flocculant aid was added at the P(AM-DMDAAC-BA) dosage of 30 mg/L. The effectiveness of oily wastewater removal by soluble starch in the absence and presence of P(AM-DMDAAC-BA) measured in term of oil removal efficiency was shown in Fig. 6.

It was found from Fig. 6 that the solo-use of soluble starch showed little effect on the coagulation process of oily wastewater. The oil removal efficiency could reach only about 15% along with the increase of the soluble starch dosage. Results of Fig. 5 showed that the oil removal efficiency of P(AM-DMDAAC-BA) was 89.6% when its dosage was 30 mg/L. However, as the results shown in Fig. 6, when the dosage of the organic flocculant was 30 mg/L, the oil removal efficiency increased slightly along with the increase of the soluble starch dosage and the oil removal efficiency could reach 93.4% when the dosage was 20 mg/L. Increasing the starch dosage beyond this value did not improve oil removal efficiency any further.

So, addition of soluble starch was useful to the enhancement of degreasing efficiency and its dosage could be determined at 20 mg/L.

3.3.2. Effect of P(AM-DMDAAC-BA) dosage on oil removal efficiency at starch dosage of 20 mg/L

The effect of P(AM-DMDAAC-BA) dosage on oil removal efficiency when P(AM-DMDAAC-BA) was added together with soluble starch was investigated at the flocculant aid dosage of 20 mg/L. The oil removal efficiency by P(AM-DMDAAC-BA) flocculant in the absence and presence of soluble starch measured in term of oil removal efficiency was shown in Fig. 7.

As shown in Fig. 7, when the starch dosage was 20 mg/L, the oil removal efficiency was enhanced significantly along with the increase of P(AM-DMDAAC-BA) dosage. The oil removal efficiency could reach 93.4% at P(AM-DMDAAC-BA) dosage of 30 mg/L. Increasing the P(AM-DMDAAC-BA) dosage beyond this value did not improve oil removal efficiency any further.

The results mentioned above mean that the addition of flocculant aid soluble starch was able to decrease P(AM-DMDAAC-BA) dosage from 50 mg/L to 30 mg/L. Moreover, the oil removal efficiency was a little higher than that under the solo-addition of P(AM-DMDAAC-BA). This observation indicated that adding soluble starch could lower the operating cost significantly while ensure

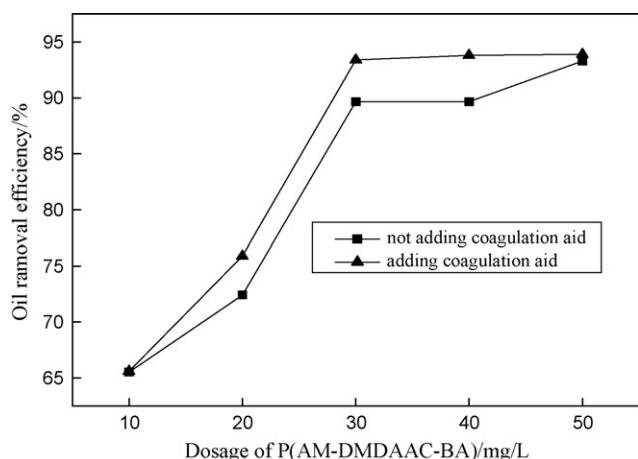


Fig. 7. Effect of P(AM-DMDAAC-BA) dosage on oil removal efficiency.

Table 1

Effect of dosing mode of the two chemicals on oil removal efficiency.

Dosing sequence of the two chemicals	Oil removal efficiency (%)
Adding $Al_2(SO_4)_3$ prior to P(AM-DMDAAC-BA)	98.2
Adding $Al_2(SO_4)_3$ simultaneously with P(AM-DMDAAC-BA)	96.6
Adding $Al_2(SO_4)_3$ posterior to P(AM-DMDAAC-BA)	95.7

the degreasing effect of the organic flocculant, owing to the low cost of soluble starch.

3.4. Synergistic effect of P(AM-DMDAAC-BA) with $Al_2(SO_4)_3$

The benefits arising from polymer use were several. On the one hand, the rate of separating the solid and water phases would be increased, owing to larger agglomerate sizes. On the other hand, the sludge volume after coagulation would be dramatically decreased to as low as a third of what would otherwise be obtained [11]. But many problems appearing in synthesis and performance limited their usage, including the high operating cost during the wastewater treatment [12]. Therefore, for overcoming the aforementioned difficulties and maximizing the coagulation efficiency, it was necessary to combine a cationic inorganic coagulant with the organic polymer, so as to utilize the effective properties of both components [3,23,27].

In this paper, P(AM-DMDAAC-BA) was used together with $Al_2(SO_4)_3$ to investigate the synergistic effect between them and the effect of their dosing sequences on oil removal efficiency.

3.4.1. Effect of dosing sequence of the chemicals on oil removal efficiency

Different dosing modes of the two chemicals were tested in order to search for the optimal dosing method for the treatment of oily wastewater at $Al_2(SO_4)_3$ dosage of 100 mg/L and P(AM-DMDAAC-BA) dosage of 10 mg/L. The effectiveness of oily wastewater removal by P(AM-DMDAAC-BA) and $Al_2(SO_4)_3$ measured in term of oil removal efficiency was shown in Table 1.

As indicated in Table 1, the degreasing effect of the various dosing modes varies according to the following order: adding $Al_2(SO_4)_3$ first > adding the two chemicals simultaneously > adding P(AM-DMDAAC-BA) first. The reason was due to the difference between their mechanisms of action. The charge neutralization of inorganic coagulants predominated, compared with the adsorption bridging effect of organic flocculants. When P(AM-DMDAAC-BA) was added prior to $Al_2(SO_4)_3$, due to the predominant bridging effect existing in the flocculation process of organic copolymer, par-

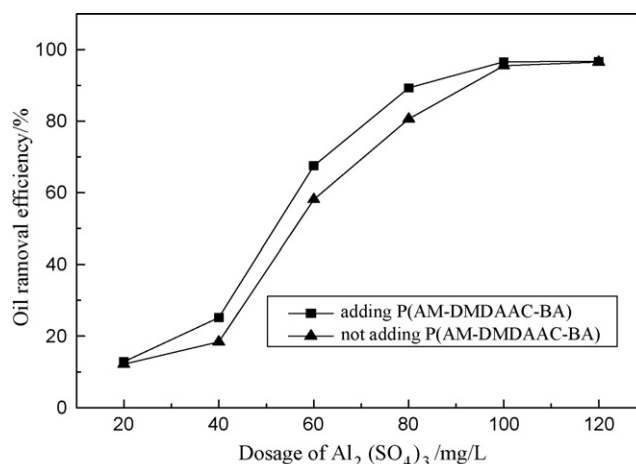


Fig. 8. Effect of $Al_2(SO_4)_3$ dosage on oil removal efficiency.

tial colloids and oil droplets were not neutralized and their polarity was still powerful [26]. As a consequence, these materials could not be easily adsorbed or wrapped up by organic macromolecule flocculants, inducing the lower oil removal efficiency.

On the contrary, when $Al_2(SO_4)_3$ was added first, the zeta potential of the colloids in wastewater decreased markedly and the repulsion among the particles was weakened due to the charge neutralization and the electric double layer compressing effect of Al^{3+} . In this way, in the flocculation stage, it is feasible for the great numbers of small flocs formed by the prior coagulation to increase their nucleation rate and to be built up into larger agglomerates by flocculation with the copolymer. Consequently, suspension of great number of larger floccules was enhanced, and subsequently, removal of larger amount of organic matter was achieved due to the availability of larger surface area on which adsorption of the organic matter took place [28]. Finally, accelerated rates of sedimentation and strong immeshing effect were achieved, in turn strengthening the more effective degreasing performance than other dosing modes during the treatment of oily wastewater.

3.4.2. Effect of $Al_2(SO_4)_3$ dosage on oil removal efficiency

The effect of $Al_2(SO_4)_3$ dosage on oil removal efficiency when it was used together with 10 mg/L of P(AM-DMDAAC-BA) was investigated and the coagulation performance of $Al_2(SO_4)_3$ in the absence and presence of P(AM-DMDAAC-BA) measured in term of oil removal efficiency was shown in Fig. 8. During the experiment, $Al_2(SO_4)_3$ was added prior to P(AM-DMDAAC-BA).

It was found that when $Al_2(SO_4)_3$ dosage was lower than 80 mg/L, the oil removal efficiency increased gradually with increasing $Al_2(SO_4)_3$ dosage in the absence and presence of P(AM-DMDAAC-BA). While this trend became less obvious and the oil removal efficiency ascended very slowly beyond the $Al_2(SO_4)_3$ dosage of 80 mg/L. About 95% of oil removal efficiency was observed when $Al_2(SO_4)_3$ dosage was above 100 mg/L.

As observed from the coagulation experiments, using $Al_2(SO_4)_3$ only, the generated flocs were fluffy and sludge volume was comparatively large, indicating the disadvantages of inorganic coagulants. On the contrary, the synergistic effect of P(AM-DMDAAC-BA) and $Al_2(SO_4)_3$ showed a higher oil removal efficiency than that under the solo-use of $Al_2(SO_4)_3$ in all experiments. Moreover, visual observation of floc size showed dense and robust flocs formed for the oily wastewater flocculated with the use of P(AM-DMDAAC-BA) and $Al_2(SO_4)_3$, which in turn result in accelerated floc settling rate and decreased sludge volume. Previous studies for synthetic dye wastewater treatment showed a similar result [29].

This observation indicated that the synergistic effect of P(AM-DMDAAC-BA) and $Al_2(SO_4)_3$ concentrated their advantages, so as to enhance the condensation effect and oil removal efficiency and to reduce the operating costs simultaneously.

4. Conclusions

The synthesis and characterization of hydrophobically associating cationic polyacrylamide P(AM-DMDAAC-BA) for oily wastewater treatment had been investigated. The main conclusions from this work were listed as the following:

- (1) 1H NMR spectrum proved the formation of the hydrophobically associating cationic copolymers. Results of TEM showed that adsorption bridging property of P(AM-DMDAAC-BA) was significantly strengthened along with the increase of hydrophobic group content in the copolymer, which would result in a considerable flocculation performance during wastewater treatment. Results of TGA analysis indicated that the copolymer had favorable thermal stability.
- (2) The dosage of P(AM-DMDAAC-BA) influenced its deoiling performance obviously during the oily wastewater treatment and the oil removal efficiency of P(AM-DMDAAC-BA) could reach 93.4% at dosage of 50 mg/L.
- (3) P(AM-DMDAAC-BA) had significant synergistic effect with soluble starch which is one kind of natural macromolecule coagulant aid. The dosage of P(AM-DMDAAC-BA) could be reduced obviously during the synergistic effect of P(AM-DMDAAC-BA) and soluble starch and it was beneficial to decrease the operating cost of large-scale industrial application.
- (4) P(AM-DMDAAC-BA) also had significant synergistic effect with $Al_2(SO_4)_3$. The favorable deoiling performance could be achieved at low dosage of P(AM-DMDAAC-BA) and it was also beneficial to decrease the operating cost of large-scale industrial application. In addition, the settling velocity of the flocs could be enhanced and the sludge volume could be diminished when using P(AM-DMDAAC-BA) and $Al_2(SO_4)_3$ together.
- (5) When P(AM-DMDAAC-BA) was used together with $Al_2(SO_4)_3$, the oil removal efficiency under the dosing mode of adding $Al_2(SO_4)_3$ prior to P(AM-DMDAAC-BA) was higher than those under other dosing modes.

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