Synthesis, Characterization and Flocculation Performance of Cationic Polyacrylamide P(AM-DMD)

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Polymerization of acrylamide and dimethyl diallyl ammonium chloride P(AM-DMD) has been formed by using dimethyldiallylammonium chloride (DMDAAC) and acrylamide (AM) initiated by $(NH_4)_2S_2O_8$ under the condition of microwave. The effect of reaction variables such as microwave time, reactants ratio, dosage of EDTA, dosage of initiator and dosage of sodium benzoate were investigated and the product was detected and characterized by IR spectroscopy and electron microscope scanning. The IR characterization results showed that the synthesized product was a copolymer of acrylamide and dimethyldiallylammonium chloride, The SEM image were depicted that the surface morphology of P(AM-DMD) as an irregular surface with overlapping junctions. The results showed that the optimum conditions were the microwave time was 1.5 min, the reactants ratio(AM:DMD) was 2: 18,the dosage of EDTA was 8 mg, the dosage of initiator was 8 mg, the dosage of sodium benzoate was 4 mg. In addition, P(AM-DMD) had better flocculation efficiency than commercial PAC in turbidity and UV_{254} removing experiment, using the PAC and P(AM-DMD) had better effect than using single P(AM-DMD) and single PAC.

Keywords: Microwave, Residual turbidity, UV₂₅₄, Copolymers, Intrinsic viscosity.

INTRODUCTION

The provision of high-quality drinking water is a fundamental element of good public health[1]. With the over-exploitation of groundwater, the surface water has become the main source of water supplies in China. However, as the development of petroleum industry, chemical industry and synthetic drugs industry, there was more and more organic pollution in surface water[2]. Serious soil erosion also increased turbidity of the water body. which is a serious threat to human health. Therefore, there is a need for improving the treatment efficiency during the coagulation-flocculation process to solve this problem. At present, drinking water treatment processes mainly consist of coagulation, sedimentation and gravity filtration and coagulation is an essential process for the removal of various particulates and organic matter[3-5]. The coagulation was applied widely in water and waste water treatment and flocculating effect is mainly determined by the qualities and species of flocculants[6-8].

Cationic polyacrylamide is the most frequently applied traditional organic coagulant in the world[9,10]. Recently, organic polymer flocculants have been developed rapidly and become applied widely, especially in China, Japan and the United State. Among them, polymerization of acrylamide and dimethyl diallyl ammonium chloride P(AM-DMD) is one of the typical kinds and has become most widely applied. It has some advantages, such as the structural units of cationic is stable, the positive charge density on molecule chain is high, it could be applied to a wide range of pH and have better water solubility. And widely used in oil exploration, paper, textile, industrial wastewater treatment and sludge dewatering and other areas[11,12]. The polymerization method is mainly aqueous solution polymerization, suspension polymerization, inverse emulsion polymerization, precipitation polymerization and dispersion polymerization.

In this article, synthesis of the cationic polyacrylamide P(AM-DMD) was investigated using a new initiation system, microwave and initiator. The copolymer was synthesized by acrylamide and dimethyldiallylammonium chloride. The synthesis conditions such as microwave time, the reactants ratio(AM:DMD), the dosage of EDTA, the dosage of initiator $(NH_4)_2S_2O_8$ and the dosage of sodium benzoate were investigated to obtain optimal polymer with high intrinsic viscosity. The characterization was performed using infrared spectrometer and scanning electron microscope. Lastly, the turbidity and UV_{254} removal rate of the product and PAC on lake water were also studied.

EXPERIMENTAL

Analytical grade EDTA was purchased from Guangfu Science and Technology Development Co., Ltd; Analytical grade ammonium persulfate (APS), analytical grade urea and industrial grade dimethyl diallyl ammonium chloride (DMDAAC) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd; Industrial grade acrylamide (AM) was purchased from Chongqing Blue Clean Water Material Co., Ltd; Analytical grade sodium benzoate was purchased from Tianjin Damao Chemical Reagent. De-ionized water was used throughout the experiment and pH value of solution was adjusted using NaOH and HCl solution.

Instruments used in the experimental setup were as follows: Infrared spectrometer (Niclet 6700) supplied by Nicolet from American; UV-visible spectrophotometer (TU-1901) supplied by Beijing Purkinje General Instrument Co., Ltd; Scanning Electron Microscopy (JSM-6380LV) supplied by Japanese electronics company; ZR4-6 Jar Tester supplied by Zhongrun Water Industry Technology Development Co. Ltd. from Shenzhen, China.

Synthesis procedure of P(AM-DMD) and measurement of intrinsic viscosity: P(AM-DMD) was synthesized using two monomers AM and DMDAAC in an aqueous solution. The reaction was carried out under microwave radiation, a three-necked, round-bottom flask (250 mL) was used as the reaction vessel. The specific procedure is as follows. First, a give mass of AM and DMDAAC were added into a reaction vessel. Then, de-ionized water was added to make the monomer ratio reach 40 %. The mixture was stirred using a glass rod until the monomers dissolved completely. Next, the additives urea and EDTA were added to the vessel. Not adjust he initial pH value. Under the protection of nitrogen gas, the ammonium persulfate was added to the solution. After purging with nitrogen gas for 20 min, the reaction vessel was sealed and transferred to the microvave reaction device for several minutes and then transferred into a water bath.

Different weight of copolymer were dissolved in 50 mL de-ionized water, before adding 50 mL of 2 mol L^{-1} NaCl solution to make aqueous solution samples with different concentration. The flow time of the samples were measured by Ubbelohde viscosity meter and digital stopwatch. All the steps were according to GB 12005. 1-89.

Wastewater sample: The water samples were collected from a lake in Hunan University of Science and Technology. The chemical analysis of the water showed that the initial Turbidity and UV_{254} were 71.3 NTU and 9.42.

Trapping and removal of turbidity and UV_{254} with flocculants: A ZR 4-6 stirring machine ith six stirrers was used in this experiment. 100 mL of water sample was transferred into a beaker. Flocculants were dosed under medium stirring speed of 300 rpm for 2 min and the second stage was reduced to a slow stirring speed of 60 rpm for 6 min. After, quiescent settling of 15 min, samples were collected from 2 cm below the surface for measurement of turbidity and UV_{254}.

IR spectra: IR spectra of P(AM-DMD) was analyzed in the range of 4000-500 cm^{-1} with KBr as dispersant. The IR spectra is shown in Fig. 1. It was evident that the absorption peak at 3408.12 cm^{-1} correspond to -NH_2 stretching vibration for acrylamide, the asymmetric peaks nearby 2928.16 cm^{-1} attributable to the -CH_3 and -CH_2, the characteristic peak at 1655.51 cm^{-1} was -$CONH_2$ absorption peak, the 1450.03 cm^{-1} correspond to -CH_2-$N^+(CH_3)_3$ was bending vibration absorption peak, the asymmetric stretching vibration absorption peak at 1176.77 cm^{-1} was C-O-C in -$COOCH_2$- suggested that the synthesized product is a copolymer of AM and DMDAAC.

Electron microscope scanning: The SEM image of P(AM-DMD) are depicted in Fig. 2. It can been seen that the surface morphology of P(AM-DMD) as an irregular surface with overlapping junctions. As shown in Fig. 2, the surface structure of the product P(AM-DMD) was very rough with a large mushroom-shaped cross-cutting structure and possessed bigger specific surface area, which has a strong adsorption and bridging capabilities.
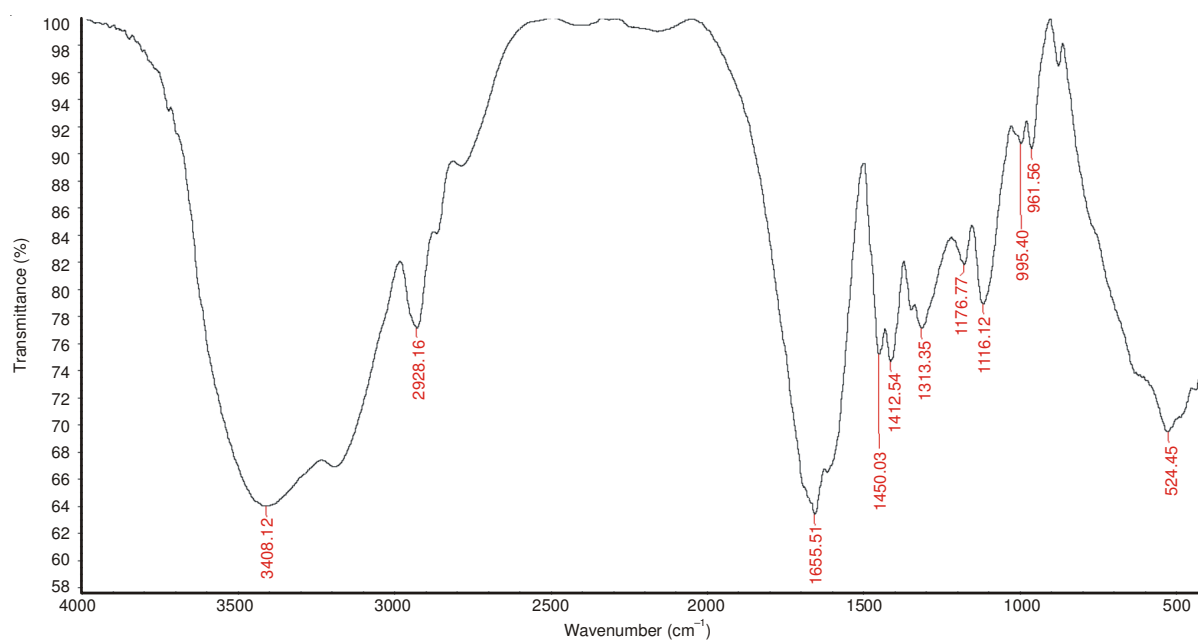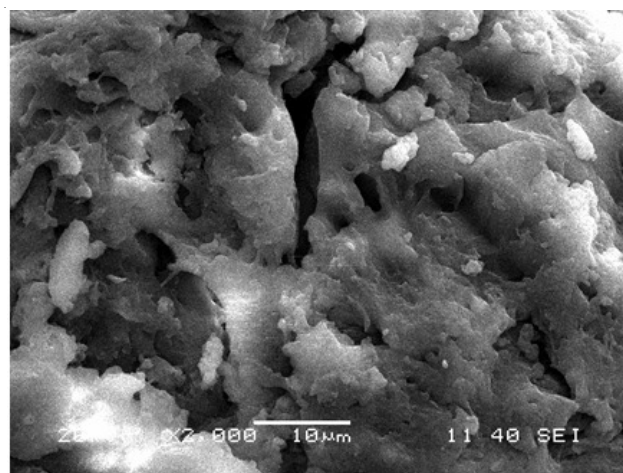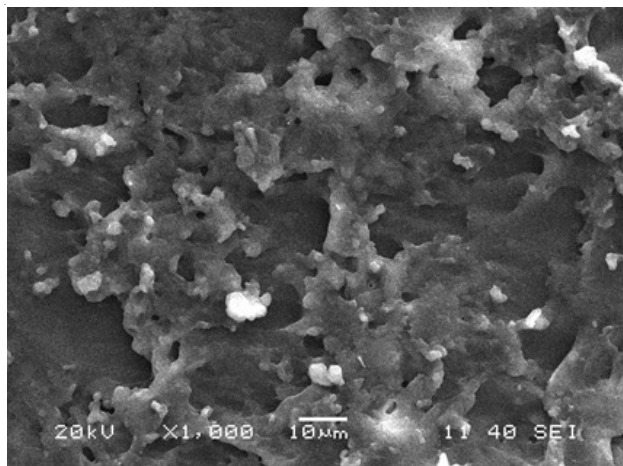

Fig. 1. Infrared spectrum of P(AM-DMD)

Fig. 2. SEM image of P(AM-DMD)

RESULTS AND DISCUSSION

Effect of microwave time on polymerization: When the other reaction variables were fixed, the effect of microwave time on the intrinsic viscosity was studied.

Fig. 3 shows that with the increased of the microwave time, the molecular weight of the product increased firstly and then decreased. And it could reach a maximum at the time of 1.5 min. That was because prolonging the microwave time could result in the growth of reaction temperature. When the
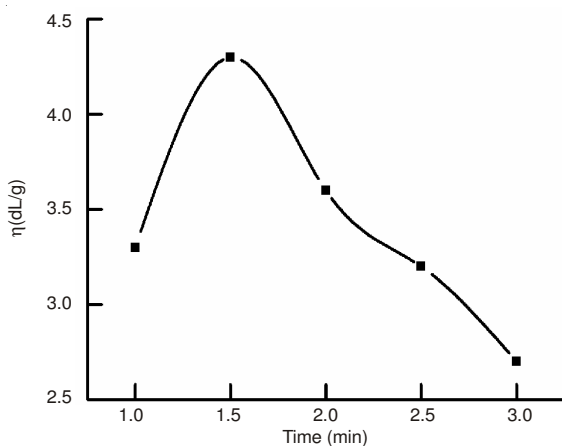

Fig. 3. Effect of microwave time on intrinsic viscosity

temperature was too low, the number of active radicals was small, the chains growth could not proceed smoothly, when continuing to extend the microwave time, the temperature could raise, which leaded to the increasing of active radicals, so the polymerization was complete and the molecular weight of the product increased. But when the active radicals achieved to a certain extent, it could cause the excessive growth rate and the heating rate was too large, leaded to the molecular weight decreases, so the optimum microwave time was 1.5 min.

Effect of reactants ratio on polymerization: When the other reaction variables were fixed, the effect of reactants ratio on the intrinsic viscosity was studied.

Fig. 4 shows that the optimum ratio of DMDAAC to AM was 2:18 and the molecular weight of the product was 4.6 dL/g. That because in the polymerization, AM activity was higher than DMDAAC activity, so the intrinsic viscosity of product would high with high content of AM. However, when there was too high content of AM, the polymerization rate increased, which leaded to the system generated lots of hot, owing to that, the copolymerization speeds up, molecular weight of the copolymer decreases down. When the content of DMDAAC was higher, increased the induction period and the time of appropriate polymerization temperature, the reaction can not proceed completely and the intrinsic viscosity of the product decreased, so the optimum ratio of monomer DMDAAC and AM was 2:18.
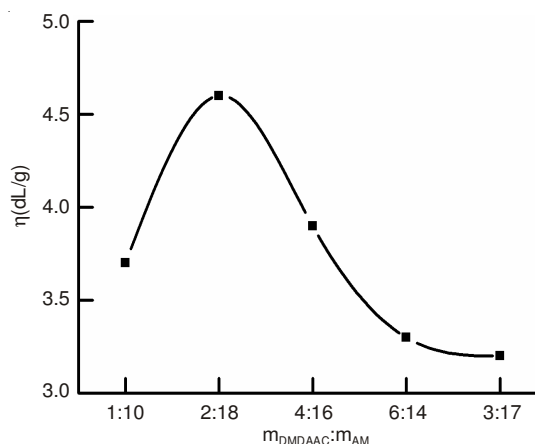

Fig. 4. Effect of reactants ratio on intrinsic viscosity

Effect of EDTA dosage on polymerization: When the other reaction variables were fixed, the effect of EDTA dosage on intrinsic viscosity was studied.

Fig. 5 shows that the intrinsic viscosity of polymers first increased and then decreased with the increased of the EDTA dosage. That because in the polymerization system, there was a small amount of impurities such as Cu^{2+} and Zn^{2+}, which have a negative impact on the reaction. When the EDTA dosage was 0.04 %, the intrinsic viscosity of the product could reach the maximum at 4.83 dL/g. However, when increased the dosage of EDTA in the reaction system, the intrinsic viscosity of the copolymer would drop, that because EDTA could act as a chain transfer agent in the polymerization, so if the EDTA insufficient, it could not complex all the metal ions in the system and if the EDTA exceed, the intrinsic viscosity of the
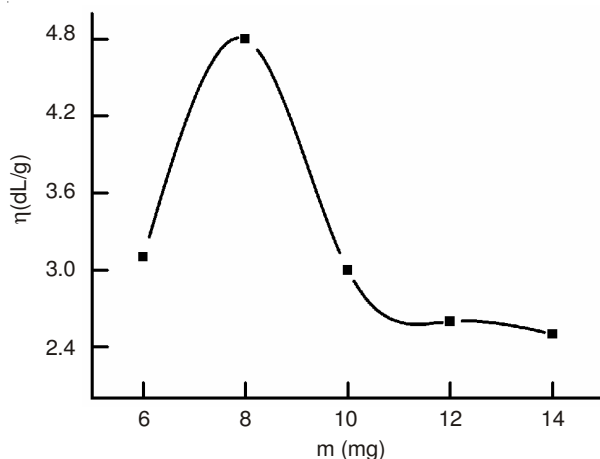
Fig. 5. Effect of EDTA dosage on intrinsic viscosity

product would be decreased, so the optimum dosage of EDTA was 0.004 %.

Effect of initiator dosage on polymerization: When the other reaction variables were fixed, the effect of dosage of initiator on the intrinsic viscosity was studied.

Fig. 6 shows that the intrinsic viscosity of polymers first increased and then decreased with the increased of the dosage of initiator. The reason may be that when the initiator concentration was low, the number of active radicals was small, so that the product of intrinsic viscosity value was low. When the initiator dosage increased, there were lots of active radicals, so the intrinsic viscosity of the product increased. But when the initiator exceeded, resulting in the number of active radicals too much and the system temperature raising fast, the reaction heat was not easy to emit, which resulting in the fracture of molecular chain of polymer.
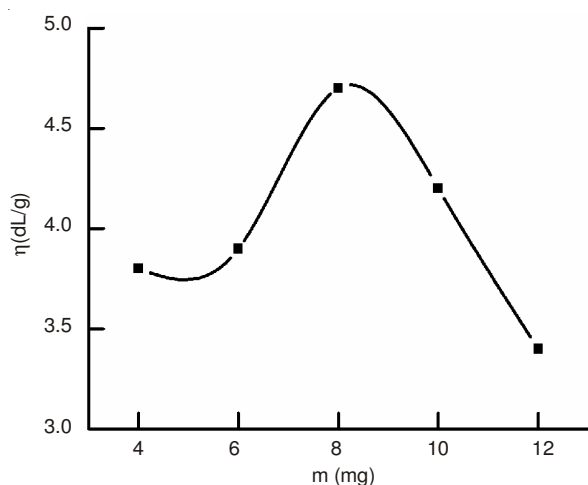

Fig. 6. Effect of initiator dosage on intrinsic viscosity

Effect of sodium benzoate dosage on polymerization: When the other reaction variables were fixed, the effect of sodium benzoate dosage on intrinsic viscosity was studied.

Fig. 7 shows that as the increased of sodium benzoate dosage, the intrinsic viscosity of the product decreased. The reason may be that sodium benzoate was a kind of chain transfer agent, which could play a role in eliminating free radicals and inhibit the progress of the polymerization reaction and leaded to decrease the intrinsic viscosity of product.
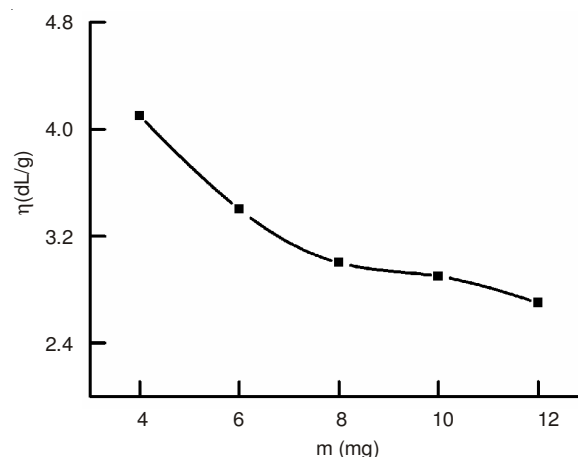

Fig. 7. Effect of sodium benzoate dosage on intrinsic viscosity

Application of P(AM-DMD) for removing turbidity and UV$_{254}$: P(AM-DMD) product synthesized under the optimum conditions was used in the flocculation of the water. The optimum conditions for the flocculation process investigated in this study were the dosage of flocculants and settling time.

Effect of the single flocculant on removal rate: The purpose of this experiment was to investigate the effect of P(AM-DMD) and PAC dosage on the residual turbidity and UV254 removal efficiency with an initial turbidity was 71.3 and the UV$_{254}$ was 9.42 cm^{-1}. The dosage of P(AM-DMD) was range from 1 to 6 mg/L and the dosage of PAC was range from 1 to 11 mg/L, not adjust the pH value.

Fig. 8A shows that the residual turbidity by using P(AM-DMD) changed from a high value of 71.3 NTU to its minimum of 7.2 NTU at 6.0 mg/L and the UV$_{254}$ removal rate increased from 37.5 % at 1 mg/L to its maximum 75.3 % at 6.0 mg/L, Fig. 8B shows that the residual turbidity by using PAC changed from a high value of 71.3 NTU to its minimum of 0.2 NTU at 9 and 10 mg/L and the UV$_{254}$ removal rate increased from 7.3 % at 1 mg/L to its maximum 31.2 % at 11 mg/L. That was because the mechanism of the NTU and UV$_{254}$ removal in water using P(AM-DMD) was charge neutralization and adequate bridging. The water had the negative charge, the polymer P(AM-DMD) and PAC had the positive charge, increased the dosage of polymer, the positive charge increased, in the result of enhanced the ability of charge neutralization. At low dosage, there were insufficient polymers to form adequate bridging links among particles and less positive charge and with sufficient polymers, the polymers could play a good role in bridging very well. The organic polymer had better efficiency than inorganic polymer, that because it has long molecular chain.

Effect of the composite flocculant on removal rate: The purpose of this experiment was to investigate the effect of P(AM-DMD) dosage whether could improve coagulation efficiency of PAC on the residual turbidity and UV$_{254}$ removal efficiency with an initial turbidity was 71.3 and the UV$_{254}$ was 9.42 cm^{-1}. The dosage of P(AM-DMD) was range from 0 to 1.4 mg/L and the dosage of PAC was 3 mg/L, not adjust the pH value.

Fig. 9 shows that the residual turbidity by using PAC and P(AM-DMD) changed from a high value of 71.3 NTU to its minimum of 0.3 NTU at 1 mg/L and the UV$_{254}$ removal rate
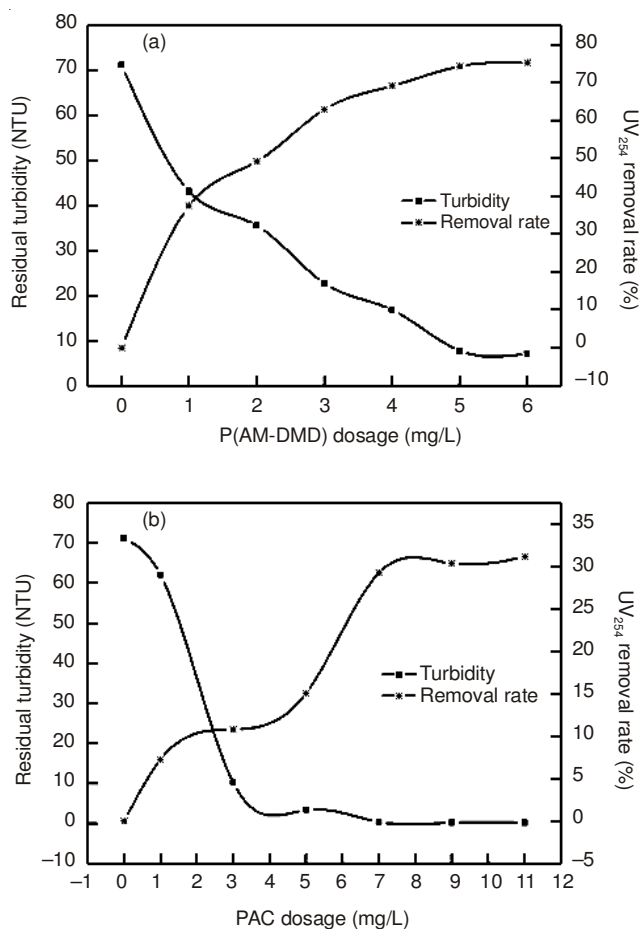
Fig. 8. Effect of single flocculant on turbidity and UV_{254} removal efficiency
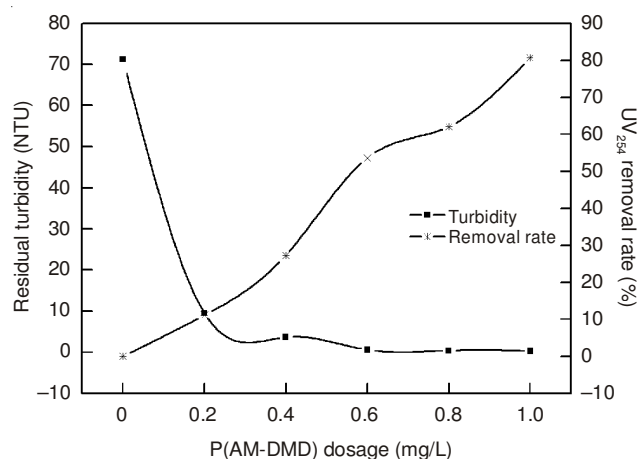

Fig. 9. Effect of composite flocculant on turbidity and UV_{254} removal efficiency

increased from 11.1 % at 0.2 mg/L to its maximum 80.7 % at 1 mg/L and then decreased. That because exceed the optimal dosage, there was no longer enough bare particle surface available for the attachment of segments and therefore particles became destabilized.

Conclusion

In this study, polydimethyl acrylamide diallyl ammonium chloride copolymer P(AM-DMD) has been formed by using dimethyl diallyl ammonium chloride (DMDAAC) and acrylamide (AM) initiated by $(NH_4)_2S_2O_8$ under the condition of microwave. During the reaction, the most predominant factors which effect on the intrinsic viscosity of polymer were investigated. The optimum conditions were the microwave time was 1.5 min, the reactants ratio (AM:DMD) was 2:18, the dosage of EDTA was 8 mg, the dosage of initiator was 8 mg, the dosage of sodium benzoate was 4 mg. The product was detected and characterized with IR spectroscopy and electron microscope scanning. The IR characterization results showed that the synthesized product is a copolymer of AM and DMDAAC. The SEM images were depicted that the surface morphology of P(AM-DMD) as an irregular surface with overlapping junctions which has a strong adsorption and bridging capabilities. By using the single P(AM-DMD) and single PAC and both using the P(AM-DMD) and PAC for removing the turbidity and UV_{254} has been investigated. During the experiments, when using the single P(AM-DMD), the lowest residual turbidity was 7.2 and the maximum UV_{254} removal rate was 75.3 % at the dosage of 6 mg/L. Using the single PAC, the lowest residual turbidity was 0.2 and the maximum UV_{254} removal rate was 31.2 % at the dosage of 11 mg/L. Using the PAC and P(AM-DMD), the lowest residual turbidity was 0.3 and the maximum UV_{254} removal rate was 80.7 % at the dosage of PAC was 3 mg/L and the dosage of P(AM-DMD) was 1 mg/L. The P(AM-DMD) could improve coagulation efficiency of PAC on the residual turbidity and UV_{254} removal efficiency

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