Article

Production of Cationic Polyacrylamide Flocculant P(AM–DMDAAC) by Microwave Assisted Synthesis, its Characterization and Flocculation Perfomance

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Abstract: A composite flocculant P(AM–DMDAAC) was synthesized by the copolymerization of acrylamide (AM) and dimethyl diallyl ammonium chloride (DMDAAC). Using microwave (MV) assistance with ammonium persulfate as initiator, the synthesis provided short reaction time and better solubility product. Nuclear magnetic resonance spectroscopy (1H NMR and 13C NMR), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and differential thermal analysis-thermo gravimetric analyzer (DTA-TGA) were used to determine the structure and morphology of P(AM–DMDAAC). Parameters affecting the intrinsic viscosity ([η]) of P(AM–DMDAAC), such as microwave time, mass ratio of DMDAAC to AM, initiator ammonium persulfatedosage, sodium benzoate dosage, bath time, reaction temperature and pH value were examined. Results showed that the optimum synthesis conditions were microwave time 1.5 min, m(DMDAAC): m(AM) is 4:16, 0.5 wt‰ initiator, 0.4 wt‰ EDTA, 0.3 wt‰ sodium benzoate, 2 wt‰ urea, 4 h bath time, 4.0h reaction time and pH 2. To study the removal of phenol by P(AM–DMDAAC), the influence of flocculant dose, pH value and the stirring speed were investigated, with optimization providing 99.8 % removal.

Keywords: acrylamide; microwave assistance; intrinsic viscosity; flocculant; phenol removal

1. Introduction

Among the many different pollutants in aquatic ecosystems, phenol is a common toxic organic compound [1-2]. The toxicity effects of phenol include protein coagulation which could cause the tissue damage and necrosis in the body, and at low concentrations can denature proteins [3]. The presence of phenol in industrial wastewater is of concern, due to their wide utilization in different industries, such as petroleum refining [4-5], resin and plastic production [6], leather and textile manufacturing, chemical and petrochemical plants, coke ovens, foundry operations, pulp and paper plants, rubber reclamation plants, pharmaceutics and agro-industrial operations [7]. The waste water from these processes can be treated by a number of physicochemical methods: adsorption, solvent extraction, wet oxidation, heterogeneous photo catalysis, biological treatments, and advanced oxidation [8-12]. H owever, the routinely available methods suffer from serious drawbacks including high cost and the formation of hazardous byproducts requiring management and disposal. As an alternative, flocculation is environmental friendly and cost effective strategy, and is an increasingly important process in pollution control [13-15]. Flocculation is usually the one of the steps in water treatment, and the final flocculation efficiency determines the kind of flocculant used [16-18]. Consequently,

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priorities for flocculant and coagulation performance include high efficiency, low cost, and low environmental impact [19-22].

Currently, many organic flocculants are available which include both synthetic and natural flocculants, such as cationic polyacrylamides (CPAM), anionic polyacrylamides, chitosan and its derivatives, starch and its derivatives [23-25]. Specifically, CPAM are the subject of increased attention because of their high efficiency in the purification of drinking water and waste water. The CPAM family of flocculants are acrylamide based and acrylamide is reactive monomer in free radical polymerization with extremely good water solubility and is one of the most cost-effective monomers. They are typical of organic flocculants with electropositive properties consistent with the presence of acryloyl oxygen ethyl trimethyl ammonium chloride (DAC), methyl acryloyl oxygen ethyl trimethyl ammonium chloride (DMC) and Dimethyl diallyl ammonium chloride (DMDAAC) functional groups. The conventional methods of synthesis of CPAM use a free radical initiator to generate free radical sites on the backbone polymer, with the reaction of aqueous polymerization initiated by a number of methods including direct heat, x-rays, microwave (MV), and ultraviolet radiation. Compared with other methods, MV-initiation has many advantages, such as short reaction time, low dosage of initiator and low reaction temperature. When using MV- initiation, there are two types method has been used, the microwave initiated synthesis(no chemical initiator) and microwave assisted synthesis(low dosage of initiator).

This study aimed to investigate the possibility of synthesizing P(AM–DMDAAC) flocculant by MV assisted initiated polymerization with AM and DMDAAC as monomers. The synthesis conditions such as microwave time, mass ratio of DMDAAC to AM, dose of ammonium persulfate, EDTA, sodium benzoate, urea, water bath time, reaction temperature and pH value were investigated to obtain optimal polymer with high intrinsic viscosity. In order to study the structural characteristics, nuclear magnetic resonance (1H NMR and 13C NMR) spectroscopy, fourier-transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM) and differential thermal analysis-thermo gravimetric analyzer (DTA-TGA) were used. Finally, the flocculation performance of P(AM–DMDAAC) was evaluated by its efficiency at removing phenol in a synthetic water sample, under varying. P(AM–DMDAAC) dose, different pH, and stirring speed .

2. Materials and Methods

2.1. Materials

Analytical grade EDTA and phenol were purchased from Guangfu Science and Technology Development Co., Ltd; Analytical grade ammonium persulfate, analytical grade urea, analytical grade AM and industrial grade dimethyl diallyl ammonium chloride (DMDAAC) were purchased from Tianjin Kermel Chemical Reagent 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.

2.2. Synthesis of P(AM–DMDAAC)

The P(AM–DMDAAC) was prepared using AM and DMDAAC as reactive monomer in an aqueous solution. The reaction was carried out under MV irradiation, and the specific procedure is as follows. First, a predetermined quantity of AM and DMDAAC were added into a reaction vessel. Then, deionized water was subsequently added to reach a monomer mass

ratio of 30%. The mixture was stirred using a glass rod until the monomers dissolved completely. Next, the additives EDTA, sodium benzoate and urea were added to the vessel. Not adjust the pH value, the aqueous solution was purged with pure N 2 at room temperature for 30 min to remove oxygen, and MV-initiator sodium benzoate was added to the vessel. The reaction vessel was introduced into the WMX-III-A Microwave reactor (Shaoguan KELI Experiment instrument Co., ltd., Shaoguan, China) at 20 W for 1.5 min. Then transferred into a water bath and dried in a vacuum oven at 80 °C.

2.3. Flocculation Test

A ZR 4-6 stirring machine (Shenzhen Zhongran Water Industry Technology Development Co., Ltd., Shenzhen, China) with six stirrers was used in this experiment. A 200 mL aliquot of simulated wastewater was transferred into a beaker. Flocculants were dosed under medium stirring speed of 250 r/min for 4 min, and then changed to the speed of 80 r/min for 10 minutes. After, settling of 30 minutes, samples were collected from 2 cm below the surface for measurement using UV-Vis and phenol concentration determined to calculate the removal rate.

2.4. Characterization of P(AM–DMDAAC)

The intrinsic viscosity η of the polymer, expressed in deciliters per gram (dL/g), was measured in a 1.0 mol/L NaCl solution with an Ubbelohde capillary viscometer (Shanghai Shenyi Glass Instrument Co. Ltd., China) at 30 ± 0.05 °C. The value of η was determined by one point method according to the Solomon−Ciuta formula. The 1H NMR spectrum and 13C NMR spectra were obtained with an AVANCE 500 nuclear magnetic resonance spectrometer (BRUKER Company, Germany), with D2O solvent. FTIR spectra were recorded by using Fourier Transformed Infra Red (FT-IR) Spectrophotometer (Nicolet 6700, Nicolet instrument Company, USA) with KBr pellets, and polymer morphology was examined by using the scanning electron microscope (SEM) (JSM-6380LV, JEOL Company, Japan). The thermal gravimetric analysis (TGA) was conducted at a heating rate of 10 °C·min−1 under nitrogen flow of 20 mL·min−1 over a temperature range from room temperature up to 600 °C on a DTG-60H synchronal thermal analyzer (SHIMADZU, Japan), in order to investigate the thermal stability of the copolymer. The concentration of phenol was examined by using UV-Vis spectrophotometer (TU-1910, Beijing Purkinje General Instrument Co., Ltd, China)

3. Results

3.1. Synthesis of P(AM–DMDAAC)

Because the intrinsic viscosity is a major determinant in controlling P(AM-DMDAAC) performance [26], the effectiveness of P(AM-DMDAAC) prepared in this study was assessed using intrinsic viscosity. Parameters affecting the intrinsic viscosity such as microwave time, mass ratio, dose of ammonium persulfate; EDTA, sodium benzoate, urea, bath time, temperature and pH, were examined.

3.1.1. Effect of the microwave time on intrinsic viscosity

Microwave power is one of the most important factors that affect the properties of polymer synthesis. Particularly excessive microwave power may cause a fast polymerization, the temperature of the system to increase quickly, and the heat of polymerization is not easy to dissipate. Microwave power was fixed at 20 W to minimize these effects. The impact of microwave time on the intrinsic viscosity of the polymer was investigated. As shown in Figure 1, the intrinsic viscosity of the polymer exhibits a peak at 1.5 minutes and the intrinsic viscosity of the polymer

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reaches a maximum of 4.20 dL/g. For low microwave timeit was difficult to provide sufficient temperature and the microwave effect in the reaction system, which meant the polymerization chain reaction was not established, at longer MV time, the reaction rate increases until an optimum and degrades due to the collision probability between free radicals, and at the same time the chain reaction becomes easily terminated, which leads the decrease intrinsic viscosity of the P(AM–DMDAAC). Therefore, the optimum microwave time was identified as 1.5 min.

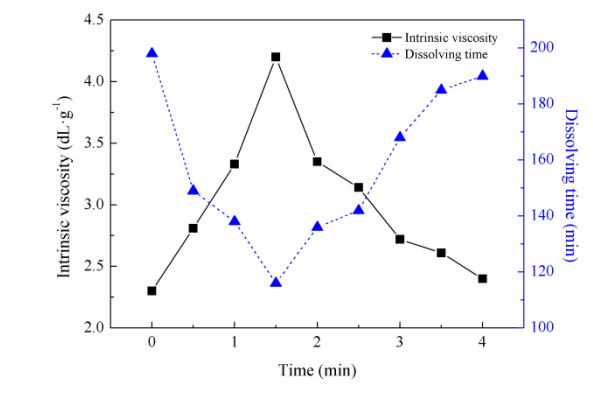

Figure 1. Effect of microwave time on intrinsic viscosity

3.1.2. Effects of the monomer quality ratio on intrinsic viscosity

The effects of the mass ratio of DMDAAC to AM on the intrinsic viscosity of P(AM–DMDAAC) was explored. As shown in Figure 2, the intrinsic viscosity of the polymer decreased with the increasing proportion DMDAAC monomer. When m(DMDAAC): m(AM) was 2:18, the intrinsic viscosity of the polymer reached the maximum of 4.21 dL/g. This is due to the chemical reactivity of cationic monomer DMDAAC being lower than the chemical reactivity of AM. When the initiator used was ammonium persulfate, the chemical reactivity ratios of the DMDAAC monomer to the AM monomer were γDMDAAC = 0.58 and γAM = 6.7, respectively, which means that the activity of the monomer AM was higher than that of DMDAAC monomer. The higher the proportion of DMDAAC monomer, the longer the time required to reach the polymerization temperature leading to incomplete monomer polymerization. So the intrinsic viscosity of the polymer decreased with the increased proportion of the DMDAAC monomer. The cationic degree was also an important factor influencing choice of polymer, in general the higher the degree of cationic, the better the water treatment effect. Therefore, the optimum m(DMDAAC): m(AM) was 4:16.

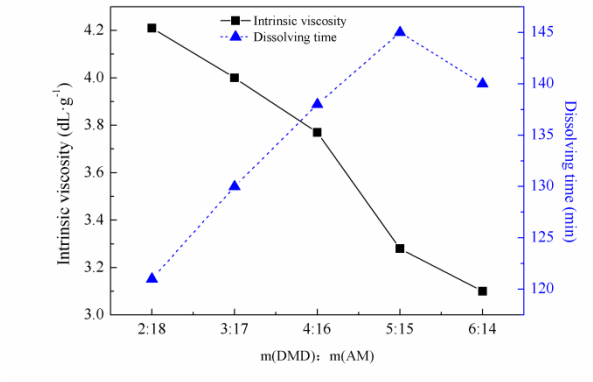

Figure 2. Effect of monomer quality ratio on intrinsic viscosity

3.1.3. Effect of ammonium persulfate dose on intrinsic viscosity

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The effects of the dosage of ammonium persulfate on the intrinsic viscosity of P(AM–DMDAAC) was explored. As shown in Figure 3, the intrinsic viscosity of the polymer exhibits an optimal point with the increasing proportion of ammonium persulfate. When the proportion of the initiator ammonium persulfatewas 0.5‰ (w/v), the intrinsic viscosity of the polymer reached the maximum of 4.80 dL/g. When the proportion of the initiator was lower, the concentration of free radicals and the reaction point were low, so the chain reaction was difficult to initiate and sustain and the intrinsic viscosity of polymer was lower. With the increasing proportion of the initiator, the concentration free radicals and the number of the reaction centers increased, which lead to the reaction rate and the intrinsic viscosity of polymer being higher. However, when the initiator proportion was too high, the excessive number of free radicals the higher the probability of collision and chain termination. Moreover, a fast reaction rate may also lead a sudden rise in temperature with a high susceptibility of implosion and a lower intrinsic viscosity of the polymer. Therefore, the optimum initiator ammonium persulfatedose was 0.5‰ (w/v).

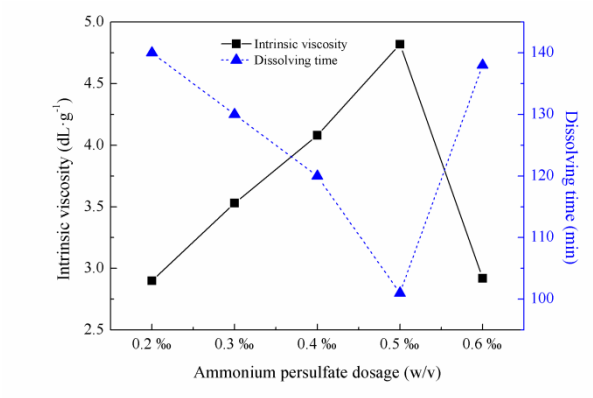

Figure 3. Effect of ammonium persulfate dose on intrinsic viscosity

3.1.4. Effect of EDTA dose on intrinsic viscosity

The industry grade AM monomer can contain metal ions, such as Cu2+ and Fe2+ which could consume primary radicals during reaction. These metal ions may hinder chain propagation and increase the induction period. The presence of EDTA to a complex with Cu2+ and Fe2+, would eliminate their influence on the reaction and increasing the intrinsic viscosity of the polymer. The effects of the proportion of EDTA on the intrinsic viscosity of P(AM–DMDAAC) was explored with all other conditions given. As shown in Figure 4, the intrinsic viscosity of the polymer showed a similar optimum with the increasing proportion of the EDTA. When the proportion of EDTA was 0.4 ‰ (w/v), the intrinsic viscosity of the polymer reached the maximum of 4.7 dL/g. When the proportion of the EDTA was low, metal ions in the reaction system, such as Cu2+, Fe2+, etc., were in excess so the polymerization reaction was also be hindered by the metal ions. Conversely, when the proportion of the EDTA was high, the probability of chain transfer reaction increased, which does not enhance the intrinsic viscosity and the optimum dose of EDTA was 0.4 ‰ (w/v).

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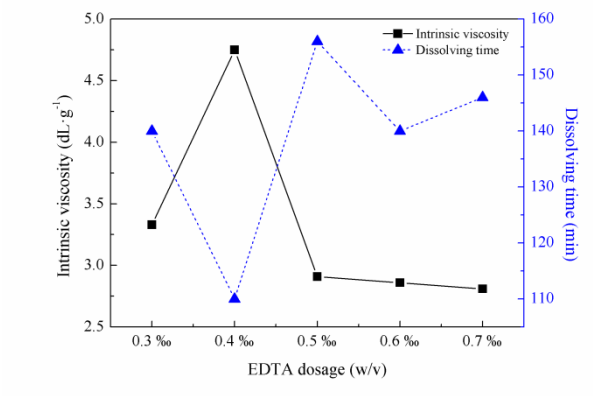

Figure 4. Effect of EDTA dose on intrinsic viscosity

3.1.5. Effect of sodium benzoate on intrinsic viscosity

Sodium benzoate is a kind of chain transfer agent which could effectively prevent the polymer from being cross-linked and ensure growth of the chain length. The effects of the sodium benzoate on the intrinsic viscosity of P(AM–DMDAAC) were explored with all other conditions given. As shown in Figure 5, the intrinsic viscosity of the polymer exhibited an optimal when the proportion of the sodium benzoate was 0.3 ‰ (w/v) andreached the maximum of 3.54 dL/g. When the proportion of sodium benzoate was low and it was insufficient to consume excess free radicals or to prevent the reaction system from being cross-linked, so the intrinsic viscosity of the polymer was lowered. Conversely, when the proportion of sodium benzoate was high, which could lead parts of the free radicals in the reaction system was completely consumed, thus hindering the chain growth in the polymerization reaction and lowering the intrinsic viscosity of the polymer.

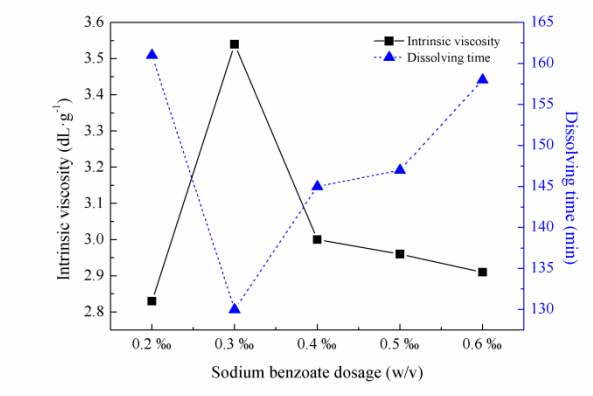

Figure 5. Effect of sodium benzoate on intrinsic viscosity

3.1.6. Effect of urea dose on intrinsic viscosity

As shown in Figure 6, the effects of the consumption of the urea on the intrinsic viscosity and solubility of P(AM–DMDAAC) showed optimal conditions with increasing urea. When the addition

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of urea was 2 ‰ (w/v), the intrinsic viscosity of the polymer reaches the maximum of 3.1 dL/g, as the lower dose of urea assists the reducing agent, which is involved the redox reaction and favors chain growth. Thus, the intrinsic viscosity of the polymer increases. When the urea dose is high, chain transfer occur, hindering the chain growth and reducing the intrinsic viscosity of the polymer. When the using of urea increased from 1 ‰ to 2 ‰, the dissolution time reduces from 149 min to 99 min.

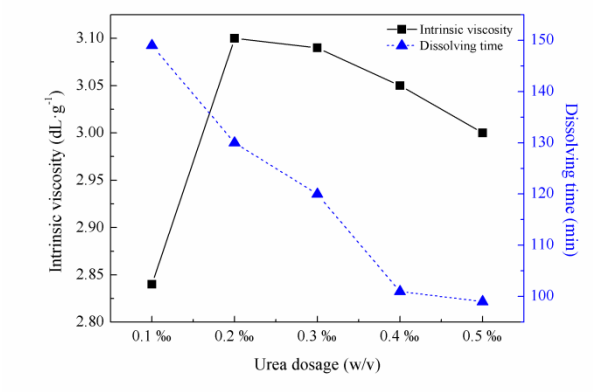

Figure 6. Effect of urea dose on intrinsic viscosity

3.1.7. Effect of bath time on intrinsic viscosity

The intrinsic viscosity of the polymer increased with water bath time, but the growth reached a plateau after extending it as showed in Figure 7. The reason was that when the water bath time is short, the polymerization reaction was incomplete and chain propagation was restrained. Thus, the intrinsic viscosity of the polymer was low. As the time in the water bath increases after 4 h, the intrinsic viscosity of the polymer increased slightly but whilst the degree of chemical reaction was high the continual extension of the reaction time not have any great effect on the intrinsic viscosity of the polymer. Therefore, the optimal water bath time was identified as 4 h.

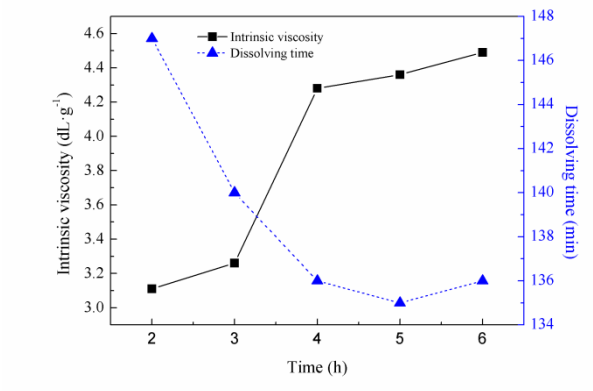

Figure 7. Effect of bath time on intrinsic viscosity

3.1.8. Effect of reaction temperature on intrinsic viscosity

The intrinsic viscosity of the polymer exhibited reached a plateau with the increasing reaction system temperature as shown in Figure 8. When the water bath temperature was 40 °C, the intrinsic viscosity of polymer reached the maximum of 4.3 dL/g, that because both the initiator and the activity of the monomer increased with the increased of reaction system temperature.The activity and the number of monomer free radicals in the reaction system increased accordingly, which was conducive to the polymerization reaction. When the temperature was too high, the polymerization reaction became increasingly intense, causing the free radicals of the monomer to cross-link and poison the polymerization reaction. Therefore, the optimal water bath temperature was 40 °C.

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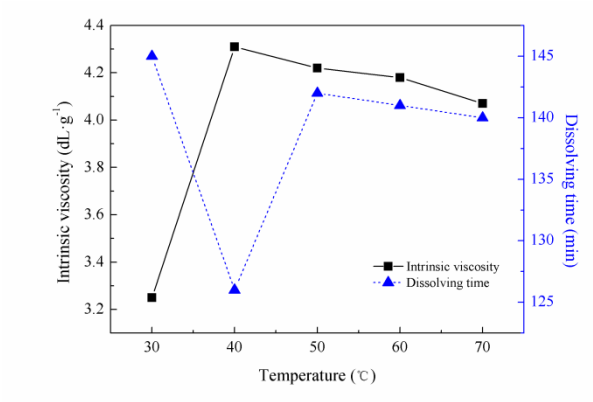
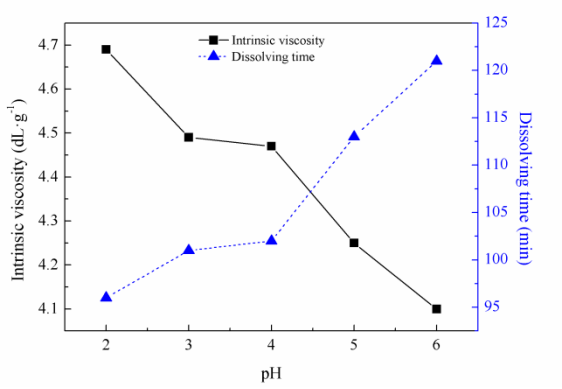


228 **Figure 8.** Effect of reaction temperature on intrinsic viscosity

229 3.1.9. Effect of pH value on intrinsic viscosity

230 As shown in Figure 9, the intrinsic viscosity of the polymer decreased with an increase in pH
231 value. When the pH value was 2.0, the intrinsic viscosity of the polymer reached the maximum of 4.7
232 dL/g, that because the pH value significantly affected the initiator ammonium persulfate to
233 counteract the speed in the polymerization reaction process. When the pH value increased, the
234 half-life period of ammonium persulfate becomes shorter with higher initiation rate and
235 temperature. The reaction heat accumulated in the reaction system, molecular chains break, and the
236 intrinsic viscosity decreased. Therefore, the optimal pH value was 2.



237 **Figure 9.** Effect of pH value on intrinsic viscosity

238 *3.2. Characterization*

239 3.2.1. SEM of P(AM–DMDAAC)

240 The Figure 10 illustrates the SEM images of P(AM–DMDAAC) and commercial PAM, thus two
241 different surface morphology were observed. It could been seen that the structure of P(AM–
242 DMDAAC) was very rough with a large mushroom-shaped cross-cutting structure rather than
243 commercial PAM, and possessed bigger specific surface area, which has a strong adsorption and
244 bridging capabilities.

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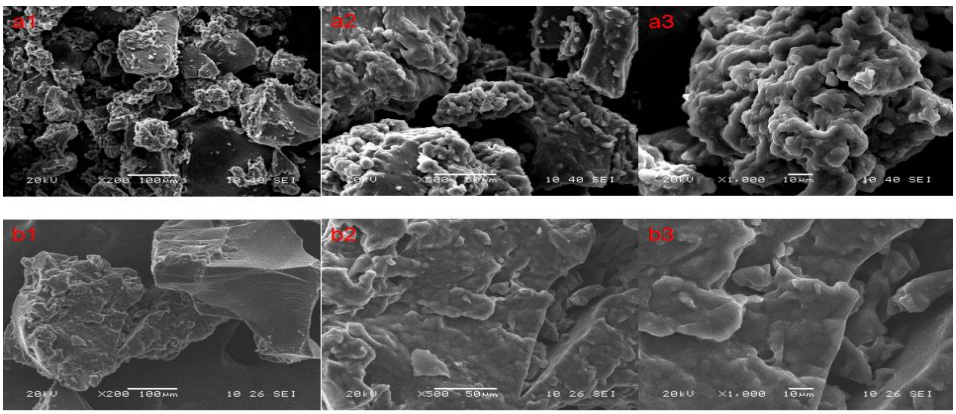

Figure 10. (a) SEM pictures of P(AM–DMDAAC); (b) SEM pictures of PAM

3.2.2. Infrared spectrum of P(AM–DMDAAC)

In Figure 11, the absorption peak at 3415.24 cm-1 is the of –NH2 stretching/vibration in the AM monomer, at 2932.22 cm-1 is the asymmetric absorption peak of –CH3 in the DMDAAC monomer, at 1654.09 cm-1 is the characteristic absorption peak of C=O in –CONH2, at 1449.46 cm-1 is the stretching vibration absorption peak of (–CH2–N+(CH3)3, and at 962.91 cm-1 is the absorption peak of N+R4, confirming the synthetic polymer is a copolymer of AM and DMDAAC.

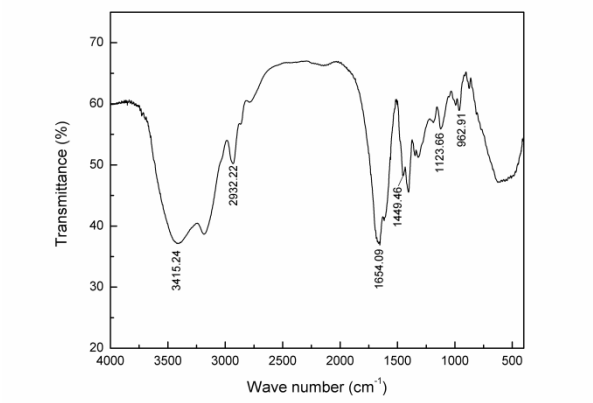

Figure 11. Infrared spectrum of P(AM–DMDAAC)

3.2.3. ^{1}H-NMR and ^{13}C-NMR spectra of P(AM–DMDAAC)

As shown in Figure 12, the characteristic peak resonance of –CH2– appears with the chemical shift at 3.572 ppm in acrylamide; the double-humped characteristic resonance of –CH3– appears with the chemical shift at 3.394 ppm; and the peak resonance of –NH2 appears with the chemical shift above 5 ppm. In the cationic units of the main chain, the characteristic peak of –CH2– successively appears with the chemical shift at 1.276 ppm and 1.396 ppm, and the characteristic peak of –CH– successively appears with the chemical shift at 1.818 ppm and 1.976 ppm. In Figure 13, the peak with the chemical shift at 179.42 ppm belongs to a characteristic peak resonance of C=O in –CONH2 and that of 41.6 ppm belongs to the characteristic peak resonance of –CH2 (–CH–).

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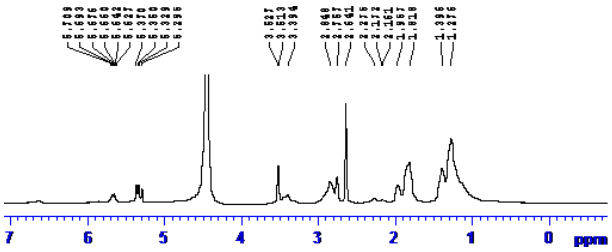


Figure 12. 1H-NMR of P(AM–DMDAAC)

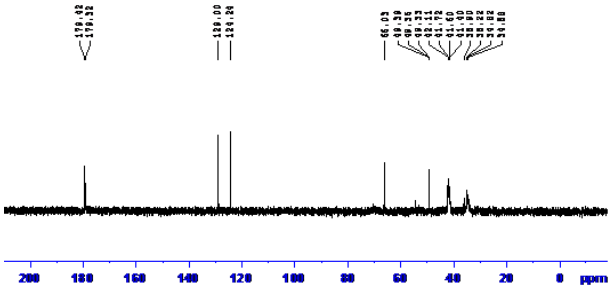


Figure 13. ^{13}C-NMR of P(AM–DMDAAC)

3.2.4. DTA-TGA of P(AM–DMDAAC)

The thermal stability of the P(AM–DMDAAC) polymer was performed on a DTG-60H synchronal thermal analyzer. The thermal gravimetric curve of P(AM–DMDAAC) was shown in Figure 14, with the increase of temperature, DSC curve appeared two endothermic peak, when temperature is 30 ℃~ 200 ℃ due to the evaporation of P(AM–DMDAAC) absorbed the first endothermic peak; when the temperature is 200 ℃~ 350 ℃ due to the P(AM–DMDAAC) oxidation/decomposition to give the second endothermic peak. The TGA curves shows that with the increase in temperature, there three points at which mass changes. 30 ℃~ 200 ℃with weight loss about 7.28 %, due to the evaporation of absorbed by P(AM–DMDAAC). 200 ℃~ 350 ℃with weight loss about 24.78 %, due to the amide imide reaction and quaternary ammonium base on the methyl group and hydrogen chloride loss. 350 ℃~ 600 ℃with weight loss about 47.09 %, the P(AM–DMDAAC) due to main chain rupture and full decomposition of the polymer. Therefore, DTA and TGA curves show that microwave assisted preparation of P(AM–DMDAAC) in normal temperature condition is extremely stable, decomposition will not occur under normal operating conditions.

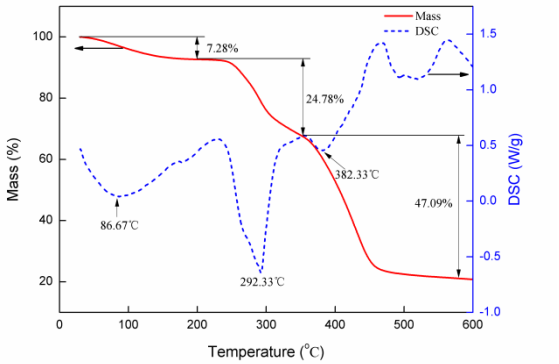
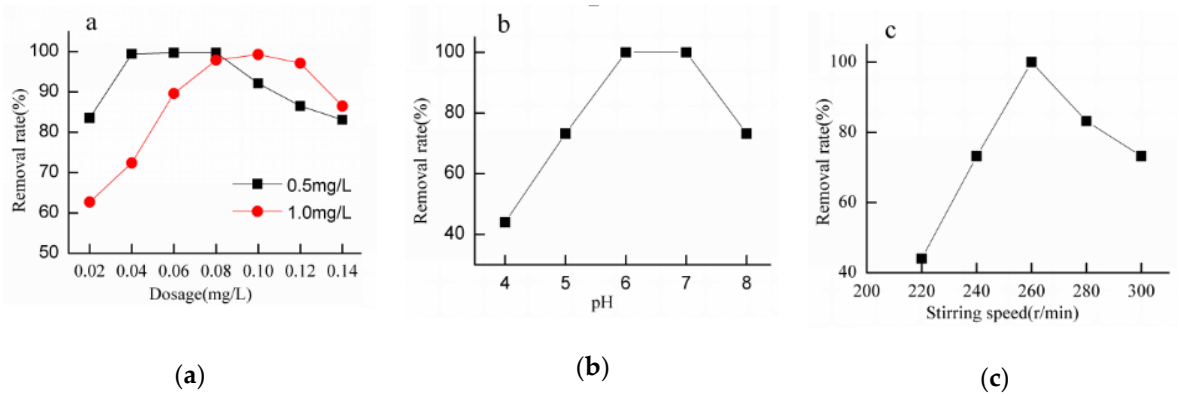


Figure 14. DSC-TGA of P(AM–DMDAAC)

3.3. Validation of the Effectiveness of P(AM–DMDAAC) to remove phenol

In this experiment, the effect of P(AM–DMDAAC) dose on the efficiency of phenol removal was investigated with the initial phenol concentrations of 0.5 mg/L and 1.0 mg/L. The dose of P(AM–DMDAAC) range from 0.02 mg/L to 0.10 mg/L, without adjusting the pH value. The effect of pH value on phenol removal efficiency was investigated with the initial phenol concentration of 0.50 mg/L and the pH value range between 4.0 and 8.0, with the effect of stirring speed on phenol removal efficiency investigated with the initial phenol concentration was 0.50 mg/L and the stirring speed range from 220 r/min to 300 r/min.



(**a**) (**b**) (**c**)

Figure 15. a. Effect of dose on removal rate , b. Effect of pH on removal rate, c. Effect of fast stirring speed on removal rate

Figure 15a shows that the removal efficiency of phenol by P(AM-DMDAAC) was good . The phenol removal rate changed from a reasonable value of 83.5 % at 0.02 mg/L P(AM–DMDAAC) to its maximum of 99.7% at 0.06 mg/L and subsequently removal efficiency reduces as the P(AM–DMDAAC) dose increased with the starting concentration was 0.5 mg/L w/v phenol. At the higher starting concentration (1.0 mg/L) removal rate changed from 62.7 % at 0.02 mg/L P(AM–DMDAAC) to its maximum of 99.3% at 0.10 mg/L before reducing as before. The explanation of this was that when P(AM–DMDAAC) was in excess, the positive charge on the flocs increased, andrepulsion interaction among flocs was enhanced and so flocs were restabilized and dispersed in treated samples. This is because the mechanism of phenol removal in water using P(AM–DMDAAC) is mainly by charge neutralization. When increasing the P(AM–DMDAAC)the positive charge density in the water body increases and the probability for P(AM–DMDAAC) and phenol contact with each other increases. When the optimum dose is exceeded, the positive charges carried by flocculant repeled each other, consequently affecting the removal rate.

The removal of phenol from the water body using P(AM–DMDAAC) showed an optimum with pH (Figure 15b) with the removal efficiency of phenol increasing from a low value of 44.0 % at pH

4.0 to its maximum of 99.8 % at pH 7.0 and then decreasing to 73.2 % at pH 8.0. This is due to neutralization of positive charges carried by the P(AM–DMDAAC) by OH-.

The effect of stirring speed (Figure15c) provided an optimal condition with removal efficiency of phenol changing from 44.0 % at 220 r/min to its maximum of 99.8 % at 280 r/min and subsequently decreasing to 73.2 % at 300 r/min. This may be explained by the sudden increase in the stirring speed increasing the probability of collision between the P(AM–DMDAAC) and phenol molecules producing better flocculation. As speed increased, theformed floc structure is destroyed by turbulence and collision.

4. Conclusions

A polymeric P(AM–DMDAAC) has been synthesised by acrylamide and dimethyl diallyl ammonium chloride through microwave assisted radiation. Several parameters affecting the performance were investigated. FTIR, 1H NMR and 13C NMR revealed the structural characteristics of the P(AM–DMDAAC) which indicated that the synthesis of polymer by MV assisted radiation was Effective. SEM images provided the apparent morphology of the polymer, which indicated it had a good adsorption and bridging ability rather than commercial PAM. DTA and TGA results showed P(AM–DMDAAC) in normal temperature condition is extremely stable. And it was found that the reaction rate is faster, and the solubility of the P(AM–DMDAAC) is better. In the removal of phenol experiments, the results exhibited well performance.

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