

Article

Synthesis of the Hydrophobic Cationic Polyacrylamide (PADD) Initiated by Ultrasonic and Its Flocculation and Treatment of Coal Mine Wastewater

Xin Qi ¹, Junling Liu ^{2,*}, Cheng Wang ¹, Shiyao Li ^{3,*}, Xiang Li ⁴, Yicong Liang ⁵ and Khan Sarfaraz ⁶

¹ Yongchuan District Bureau of Planning and Natural Resources, Chongqing 402160, China; chyishin@hotmail.com (X.Q.); asdf16815@163.com (C.W.)

² Chongqing Huodao Technology Development co. LTD, Chongqing 401120, China

³ School of Water Conservancy and Architectural Engineering, Shihezi University, Shihezi 832003, China

⁴ School of Civil Engineering and Architecture, Chongqing University of Science and Technology, Chongqing 401331, China; lx33cqu@163.com

⁵ School of Civil and Transportation Engineering, Guangdong University of Technology, Guangzhou 510006, China; lyc219@mail2.gdut.edu.cn

⁶ Key Laboratory of the Three Gorges Reservoir Region's Eco-Environment, Ministry of Education, Chongqing University, Chongqing 400045, China; sfk.jadoon@yahoo.com

* Correspondence: liujljl@163.com (J.L.); Shiyao.Li@stu.shzu.edu.cn (S.L.)

Received: 1 November 2019; Accepted: 13 December 2019; Published: 2 January 2020



Abstract: In this study, a new type of hydrophobic cationic polyacrylamide P (AM-DMC-DABC) (PADD) was synthesized by ultrasonic (US)-initiated polymerization, which is used for the separation and removal of coal mine wastewater. The acrylamide (AM), methacryloyloxyethyl trimethyl ammonium chloride (DMC) and acryloyloxyethyl dimethylbenzyl ammonium chloride (DABC) were used as monomers to prepare. The factors that affecting the US initiated polymerization of PADD were analyzed. Fourier transform infrared spectroscopy (FT-IR), ¹H nuclear magnetic resonance (¹H NMR) and scanning electron microscopy (SEM) were used to characterize the chemical structure, thermal decomposition performance and surface morphology of the polymers. FT-IR and ¹H NMR results showed that PADD was successfully synthesized. In addition, irregular porous surface morphology of PADD were observed by SEM analysis. Under the optimum conditions (pH = 7.0, flocculant dosage = 16.0 mg/L), the excellent flocculation performance (turbidity removal rate (TR) = 98.8%), floc size $d_{50} = 513.467 \mu\text{m}$, fractal dimension (D_f) = 1.61, flocculation kinetics (K_{N0}) = $27.24 \times 10^{-3} \cdot \text{s}^{-1}$) was obtained by using high-efficiency flocculant PADD. Zeta potential analysis was used to further explore the possible flocculation mechanism of removal. The zeta potential and flocculation analytical results displayed that the flocculation removal process of coal mine wastewater mainly included hydrophobic effect, adsorption, bridging and charge neutralization, and electric patching when PADD was used. The PADD showed more excellent coal mine wastewater flocculation performance than PAD, commercial cationic polyacrylamide (CPAM) CCPAM and PAM. Thus PADD, with its good flocculation effect on coal mine wastewater under relatively wide pH range, had bright practical application value.

Keywords: coal mine wastewater; cationic polyacrylamide; ultrasonic initiation; flocculation; floc characteristics; turbidity removal

1. Introduction

With the development of social economy and the increase of population in China, the contradiction between supply and demand of water resources has become increasingly prominent. The shortage and pollution of water resources has seriously restricted the development of national economy and society, and also posed a potential threat to human health [1]. In the process of coal mining, a large quantity of coal mine wastewater is produced every year in China due to its considerable scale of coal production and consumption. Direct discharge of coal washing wastewater not only seriously pollutes the surrounding environment, but also causes great waste of water resources. In recent years, the environmental pollution caused by high turbidity coal mine wastewater has become the focus of discussion of the public and regulatory agencies [2]. Coal mine wastewater is a stable colloidal system with high concentration of suspended solids, fine particles, and strong negative charge on its surface, which is difficult to treat [3]. When these suspended solids enter the water in large quantities, the turbidity of the water body increases and the transmittance decreases, which affects the photosynthesis of aquatic organisms, inhibits their growth and reproduction, and hinders the self-purification of the water body [4]. The suspended solids in the wastewater can also block the gills of fish, causing suffocation and death of fish, and also causing diarrhea, which endangers human health. In addition, the sedimentable solids in the suspended solids in the wastewater are deposited at the bottom of the river, causing sediment accumulation and decay, and deteriorating the water quality [5]. Therefore, it is necessary to purify the high turbidity coal mine wastewater.

A variety of technologies have been used to remove high turbidity coal mine wastewater, including adsorption, concentration, membrane treatment, and flocculation [6–9]. Among them, flocculation technology has the characteristics of simple operation, high efficiency, and low cost, and environmentally-friendly [10]. It has attracted more and more attention in wastewater purification and separation [11]. This technology has been widely used in the separation and dehydration of solid/water systems. So far, a large number of flocculants with different functions have been developed for suspended matter removal, sludge dewatering, dye wastewater treatment and heavy metal wastewater treatment [12–14]. Cationic polyacrylamide (CPAM) is one of the most widely used flocculants for separating colloidal suspensions. Positively charged CPAM can completely neutralize negatively charged colloidal particles, so the stability of colloidal particles is destroyed [15]. Then the unstable colloidal particles are wrapped and connected to form large flocs under the action of CPAM adsorption and bridging, which can rapidly settle down, thus achieving the purpose of reducing turbidity and purifying water quality [16]. Therefore, it is very urgent and necessary to prepare a new and efficient CPAM flocculant for the separation and removal of suspended colloidal particles in coal mine wastewater.

At present, solution polymerization is the simplest and most widely used method to prepare CPAM. Solution polymerization can be initiated by heat, radiation, microwave radiation, ultraviolet light, and ultrasonic [17,18]. Ultrasonic-initiated polymerization has the advantages of low temperature, short polymerization time, and high reaction rate, which is an efficient way of achieving polymerization [19]. In addition, ultrasonic-initiated polymerization is not only simple to operate, but also does not cause secondary environmental pollution. It is an environmentally friendly initiation method and can be used as an efficient polymerization technology for the synthesis of CPAM. Acrylamide (AM), methacryloxyethyl trimethyl ammonium chloride (DMC), and hydrophobic acryloxyethyl dimethyl benzyl ammonium chloride (DABC) are considered to be common and safe synthetic monomers [20,21]. Moreover, DABC with hydrophobic groups (phenyl) can cause systems with unique rheological properties, resulting in the formation of transient networks and the increase of solution viscosity [22]. These associations enhance the interaction between hydrophobic groups and colloidal particles, which is beneficial to improve the adsorption bridging capacity and enhance the flocculation effect [23]. Therefore, in this study, the copolymer P (AM-DMC-DABC) (PADD) was prepared by ultrasonic-initiated polymerization using AM, DMC, and DABC as monomers to treat coal mine wastewater.

In this study, the objectives are: (1) Polymerization of novel terpolymer (PADD) initiated by ultrasonic with AM, DMC, and DABC as monomers; (2) investigation of the effect of single factor experimental conditions such as ultrasonic power, pH, initiator V-50 mass fraction, the mass ratio of AM:DMC:DABC on polymerization; (3) characterization of the chemical structure, morphology and thermal properties of polymer PADD by Fourier transform infrared spectroscopy (FT-IR), ^1H nuclear magnetic resonance spectroscopy (^1H NMR) and scanning electron microscopy (SEM); (4) discussion of the effects of pH value and dosage on flocculation performance were discussed. The flocculation performance was evaluated from the aspects of floc structure and morphological characteristics, such as floc size, floc fractal dimension, and flocculation kinetics; and (5) study of flocculation mechanism involved in flocculation process.

2. Materials and Methods

2.1. Materials

Industrial monomer acrylamide (AM) (98 wt%) was purchased from Jinjinle Chemical Co., Ltd. (Zhuhai, China). Methacryloxyethyl trimethyl ammonium chloride (DMC) (78 wt%) and methacryloxyethyl dimethyl benzyl ammonium chloride (DABC) (75 wt%) monomers were provided by J&K Technology Co., Ltd. (Beijing, China) and Dengfeng Enteng Biotechnology Co., Ltd. (Zhengzhou, China), respectively. 2,2-azodi (2-methylpropylimide) dihydrochloride (V-50) was obtained from Shanghai Adamas Reagent Co., Ltd. Nitrogen (purity > 99.9%) is supplied by Chongqing Tonghui Gas Co., Ltd. (Chongqing, China). Sodium hydroxide acetone and absolute ethanol were purchased from Chongqing Chuandong Chemical Co., Ltd. The experimental water is deionized water. Except DMC and DABC are industrial pure, the others are analytical pure. The Commercial CPAM, named as CCPAM, was purchased from Gongyi integrity purification equipment co. LTD, (Gongyi, China). Meanwhile, the CCPAM is copolymerized of AM and DMC. PAM (homopolymer of AM) and P(AM-DMC) shorted as PAD were synthesized in laboratory for characterization and comparative analysis.

2.2. Preparation of Polymers

The preparation circuit of PADD is shown in Figure 1 and the preparation process of PADD by ultrasonic-initiated polymerization is as follows.

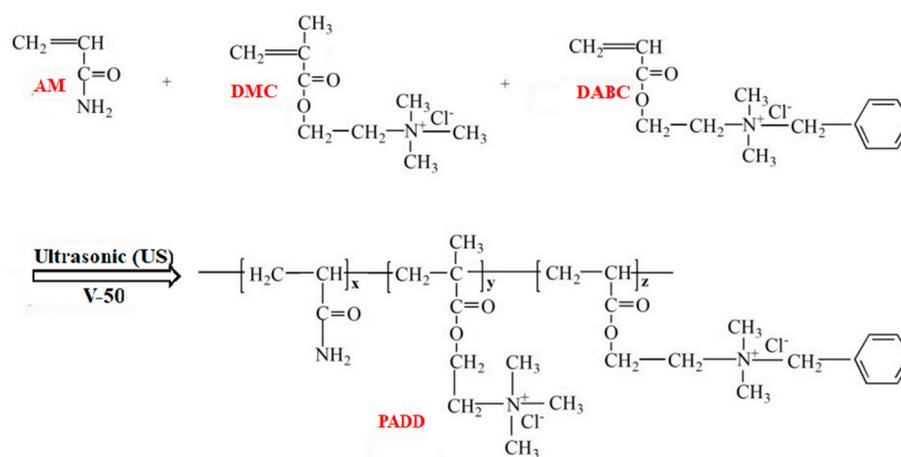


Figure 1. The scheme of polyacrylamide P (AM-DMC-DABC) copolymerization.

Firstly, a certain amount of AM, DMC, DABC, and deionized water were added to 150 mL quartz bottle, and the homogeneous solution was obtained by ultrasonic for 3 min. Secondly, 0.5 mol/L hydrochloric acid and sodium hydroxide were used to adjust the pH value of the above solution to a specific value. A predetermined amount of V-50 was added, and the solution was nitrogen-filled at

room temperature for 20 min, and the reaction flask was capped. The solution was ultrasonicated at 35 °C for 25–35 min on an ultrasonic instrument (frequency, 45 KHz, KQ 2200E, Kunshan Ultrasonic Instrument Co., Ltd., Kunshan, China). Alcohol and acetone were used to purify the product, and the purified product was dried in a vacuum oven at 80 °C for 12 h, and after appropriate grinding, a powdery product PADD was obtained. Meanwhile, the preparation steps of PAM and PAD are same as those of PADD.

2.3. Characterization of Polymers

The intrinsic viscosity the polymer is determined by Ubbelohde viscometer (Shanghai Shenyi Glass Instrument Co., Ltd., China) at 30 °C. The conversion of polymers was determined by gravimetric method [24]. In addition, the infrared absorption spectrum of the product was measured by the KBr tablet method using a Series II550 infrared and microscope of METTLER TOLEDO Instrument Co., Ltd. The ¹H NMR spectrum of the sample was determined by using the heavy water (D₂O) as a solvent and tetramethylsilane (TMS) as an internal standard on Avance-500 type nuclear magnetic resonance spectrometer from Bruker, Germany. The SEM of the sample was observed with a MIRA 3 LMU scanning electron microscope from TESCAN, Czech Republic, and its surface morphology was analyzed. The details for the polymer molecular weight (M_w) measurement was displayed in Text S1 in Supporting Information. Details of the polymers used in this study are recorded in Table 1.

Table 1. Flocculants used for characterization and flocculation test.

Flocculant	Molecular Weight (1×10^6 Da)	Cationic Degree (%)	Conversion Percent (%)
PADD	400	40.0	99.8
PAD	400	40.0	99.6
CCPAM	400	20.0	/
PAM	300	/	99.8

2.4. Analysis Method and Stirring Test

The flocculation experiment was carried out by six-unit agitator with preset program. And the physical and chemical properties of coal mine wastewater used in flocculation experiments are shown in Table 2.

Table 2. The properties of the coal mine wastewater used in the experiment.

pH	Density (g·mL ⁻¹)	Zeta Potential (mV)	Turbidity (NTU)	Average Size Distribution (d_{50} , μ m)	Color
7.47	1.169	-29.30	313.9	76.2	Gray and black

Each beaker is filled with 500 mL of coal mine wastewater. The initial pH of the wastewater sample is adjusted by HCl (0.5 mol/L) and NaOH (0.5 mol/L). The six-unit agitator was started, and then a certain amount of flocculant was added. Flocculation tests included rapid mixing (300 rpm 2 min), slow mixing (50 rpm, 10 min), and settling (20 min). The supernatant turbidity was measured using a 2100P turbidity meter (HACH, Loveland, CO, Shanghai, China). The floc size was determined by a laser diffractometer (Mavern 2000, Malvern, UK). The image analysis software (Image-Pro Plus, version 6.0, Media Cybernetic) is used to process the image, and the fractal dimension of the flocs is calculated. The calculation method is detailed in Text S2 in Supporting Information. The cationic character is determined by colloid titration. At the same time, the Zeta potential of the supernatant was recorded using a Zetasizer Nano ZS90 (Malvern Instruments Ltd., Malvern, UK). Besides, the method for the flocculation kinetics and (turbidity removal rate (TR) measurement is detailed in Text S3 and S4 in Supporting Information, respectively.

3. Results and Discussions

3.1. Effect of Single Factor Experimental Conditions on Polymerization

The effect of single factor experimental conditions on the molecular weight of polymers is shown in Figure 2.

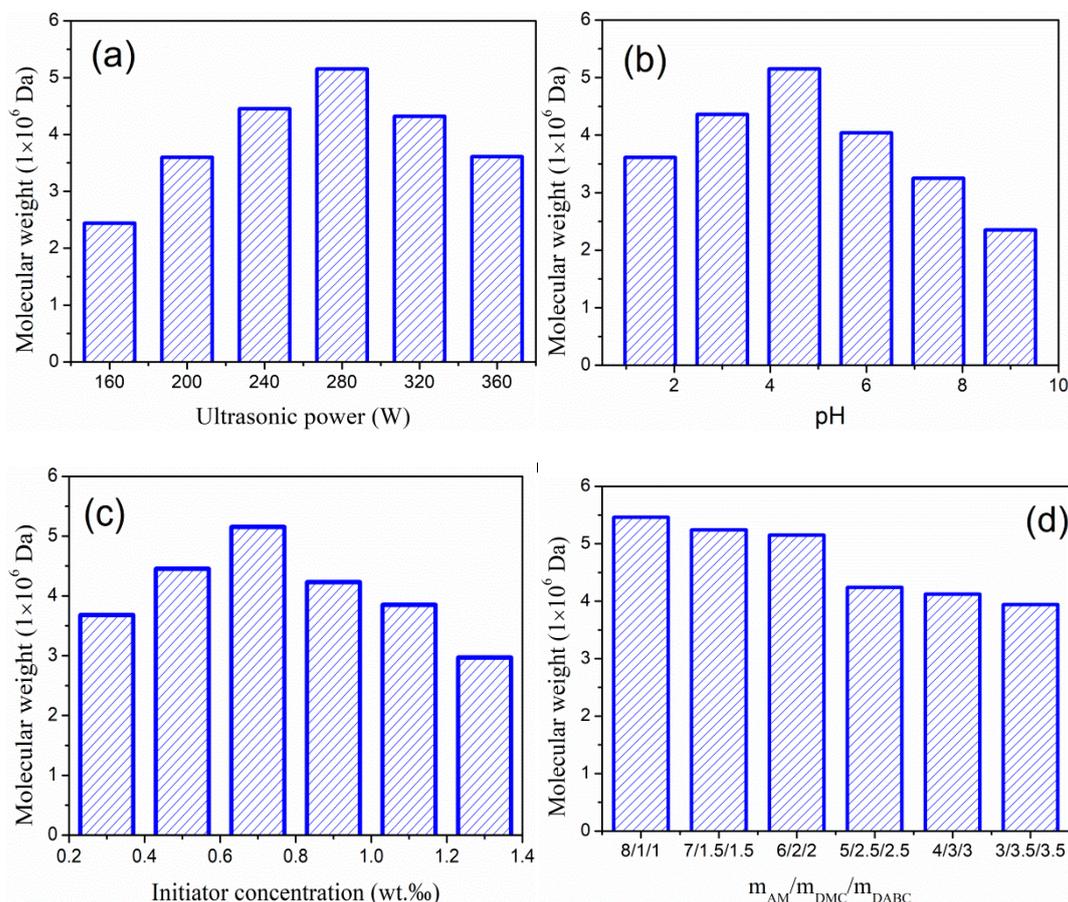


Figure 2. Effects of (a) ultrasonic power, (b) pH, (c) initiator concentration, and (d) monomer mass ratio on polymerization.

3.1.1. Effect of Ultrasonic Power on Polymerization

Figure 2a explores the effect of ultrasonic power on the molecular weight of PADD. The other experimental conditions were fixed as follows: total monomer mass fraction 30 wt%, ultrasonic irradiation 30 min, pH 4.5, initiator V-50 mass fraction 0.07 wt%, cationic monomer AM:DMC:DABC mass ratio 6:2:2. As can be seen from Figure 2a, the molecular weight of polymer increases first and then decreases with the increase of power from 160 W to 360 W. Increasing the power of ultrasonic at the beginning can produce more free radicals, promote the reaction and increase the molecular weight of PADD. However, the molecular weight of PADD decreases with the increase of ultrasonic power over 280 W. This is mainly due to the excessive power of ultrasonic, which will induce the initiator to split in a short time and produce excessive free radicals, and can result in severe collision of monomers. As a result, it accelerates chain transfer and chain termination, and leads to the reduction of molecular weight [19]. Meanwhile, with the continuously increasing power of ultrasonic, the excessive temperature produced locally by the “hole effect” of ultrasonic will cause the breakage and degradation of the polymer main chain. At this time, the molecular weight of the polymer will decrease. Based on the above experimental results, the optimal ultrasonic power is 280 W.

3.1.2. Effect of pH on Polymerization

Previous studies have shown that in the process of solution polymerization, the pH of the system has a certain effect on the molecular structure of the polymer [17]. Therefore, while fixing other reaction conditions unchanged, the effect of pH on the molecular weight of the PADD was also investigated. The results are shown in Figure 2b. It can be seen from Figure 2b that the pH of the reaction system has a great influence on the molecular weight of the polymer. When the pH is less than 4.5, the molecular weight of the product increases with the increasing of pH. The molecular weight of the product reaches its maximum in pH of 4.5. When the pH of the system is further increased, the molecular weight of the product decreases rapidly. When the pH of the system is low, the amide groups on AM molecule are prone to conduct imidization within or between molecules, which results in the crosslinking of the polymers in the system and hinders the chain growth reaction, and affects the molecular weight of the product [4]. When the pH of the reaction system is too high, the monomer AM is easy to hydrolyze to produce NH_3 , and the chain transfer reaction is accelerated, so the molecular weight of the product decreases accordingly [25,26]. Therefore, the optimum pH for the experiment is 4.5.

3.1.3. Effect of Initiator Concentration on Polymerization

As shown in Figure 2c, the effect of initiator concentration on the polymerization of PADD was investigated and other conditions remained unchanged. In the process of increasing initiator dosage, the molecular weight of polymer PADD increases first and then decreases. It obtains the highest molecular weight at the initiator concentration of 0.07 wt%. Firstly, the initiator will be cracked under the action of ultrasonic to form the initial free radical. In this condition, the monomer free radical is formed and becomes the active center for initiating the polymerization. When the dosage of initiator is low, the primary free radicals generated will be surrounded by other molecules, which is easy to form "cage effect". The free collision efficiency of monomers decreases to form fewer free radicals, which is not conducive to chain initiation reaction. As a result, a relative low molecular weight of PADD is got [27]. With the increasing concentration of initiator, primary free radicals will be generated, and the collision probability between them and monomers will be increased. The "cage effect" will be weakened and the initiation efficiency will be increased. The monomers will be transformed into polymers through chain growth reaction, which will increase the molecular weight of PADD. When the concentration of initiator is increased to 0.07 wt%, excessive primary and monomer free radicals will be produced, which makes radical polymerization more intense, resulting in an explosive polymerization. Thus, chain transfer and chain termination are likely to occur and the molecular weight of the product is greatly reduced. Therefore, the concentration of initiator is selected as 0.07 wt%.

3.1.4. Effect of Mass Ratio of Cationic Monomers on Polymerization

In the process of flocculation, besides the effect of adsorption bridging on the flocculation of CPAM, the effect of electric neutralization and patching is also important for flocculation. Figure 2d shows that the molecular weight of PADD decreases gradually with the mass fraction of cationic monomer (DMC + DABC). This is mainly because the activity of AM monomer is more active than that of DMC + DABC monomer, and the steric hindrance of AM monomer involved in the reaction is less than that of DMC + DABC monomer. When the content of AM monomer in solution is high, the reaction rate of AM monomer is faster, the initiation and growth of AM monomer chain can proceed smoothly, and the molecular weight of the product is higher. As the mass ratio of DMC to DABC increases, the activity of the reaction system decreases and the steric hindrance of the reaction become larger. In this condition, the energy barrier of the reaction system to be overcome is higher, and the chain growth is difficult, so the molecular weight of PADD is relatively low. When $m_{\text{AM}}:m_{\text{DMC}}:m_{\text{DABC}}$ is between 6:2:2 to 5:2.5:2.5, the molecular weight of the product decreases significantly. In the actual flocculation process, the content of cationic monomers must be sufficient, so that PADD has enough positive quaternary ammonium salt groups to neutralize and patch negatively charged colloidal particles. It is necessary to

select a suitable shell $m_{AM}:m_{DMC}:m_{DABC}$ mass ratio [28]. In addition, the appropriate DABC content in PADD is also beneficial to enhancing the flocculation effect. This is because that the existence of hydrophobic groups make the molecular chains easy to stretch and cross-link with adjacent molecular chains to form larger spatial network structure, which helps to improve the adsorption bridging effect of PADD [29]. Accordingly, the $m_{AM}:m_{DMC}:m_{DABC} = 6:2:2$ selected in this paper is appropriate. At this time, the molecular weight of the polymer can reach 5.15×10^6 Da, and it has good adsorption bridging and electric neutralization ability.

3.2. FTIR Spectral Analysis

The FT-IR spectra of PAM, PAD and PADD are studied in Figure 3. The stretching vibrations of $-NH_2$ and $C=O$ groups in AM were 3434 and 1665 cm^{-1} [3,30], respectively. The asymmetric stretching vibrations of $-CH_3$ and $-CH_2-$ groups were 2940 and 2842 cm^{-1} , respectively. The bending vibration of $-CH_2-$ in $-CH_2-N^+$ group in DMC is 1458 cm^{-1} , and the characteristic absorption peaks at 963 cm^{-1} correspond to the deformation vibration characteristic peaks of $N-H$ and $-N^+(CH_3)_3$ groups in DMC [24,31], respectively. In PADD, the absorption peaks at 773 and 702 cm^{-1} are the characteristic absorption peaks produced by the vibration of benzene skeleton in DABC molecule [32]. The characteristic absorption peaks of AM, DMC, and DABC all appeared in PADD, which indicated that the ternary copolymer PADD was prepared of AM, DMC, and DABC by ultrasonic initiation.

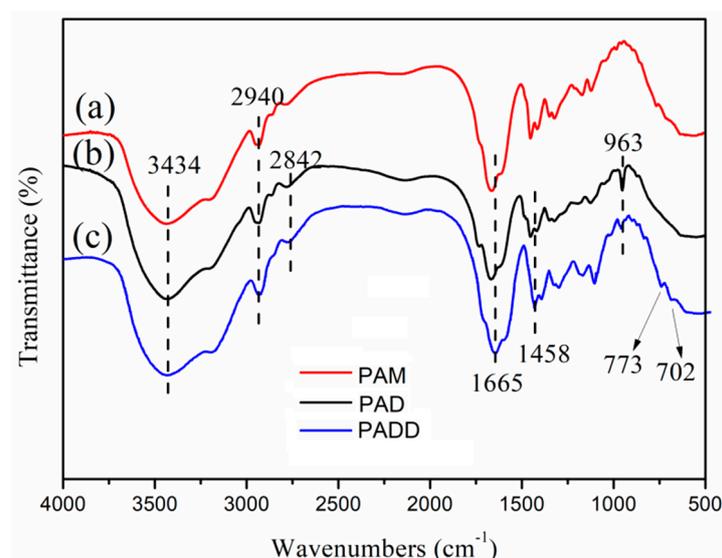


Figure 3. The FTIR of (a) PAM, (b) PAD, and (c) PADD.

3.3. 1H NMR Spectrum Analysis

Similar to FTIR spectra, the 1H NMR spectra of PAM, PAD and PADD were studied for further analysis of structural properties. The results are shown in Figure 4.

These polymers display the following resonance peaks. The resonance peaks of $-CH_2-$ (a) and $-CH-$ (b) protons at the polymer skeleton are observed at $\delta = 1.63$ ppm and $\delta = 2.19$ ppm, respectively [17,19]. The chemical shifts at $\delta = 1.158$ (H_c), $\delta = 4.49$ (H_d), $\delta = 3.77$ (H_e), and $\delta = 3.30$ (H_f) ppm correspond to $-CH_3$, $-O-CH_2-$, $-CH_2-N^+$, and $-N^+(CH_3)$ groups on the chain of cationic monomers DMC and DABC, respectively [27,28]. The sharp formant at $\delta = 4.80$ ppm is associated with the proton of solvent D_2O . Furthermore, the characteristic resonance peaks of DABC observed at $\delta = 4.49$ ppm (g) and $\delta = 7.54$ ppm (h) are attributed to protons in the $-CH_2-$ group attached to the phenyl group and protons of the phenyl group, respectively. The DABC characteristic peaks were observed in PADD rather than PAM and PAD [32]. Based on the above analysis results, it is proved that PADD is successfully synthesized by AM, DMC, and DABC.

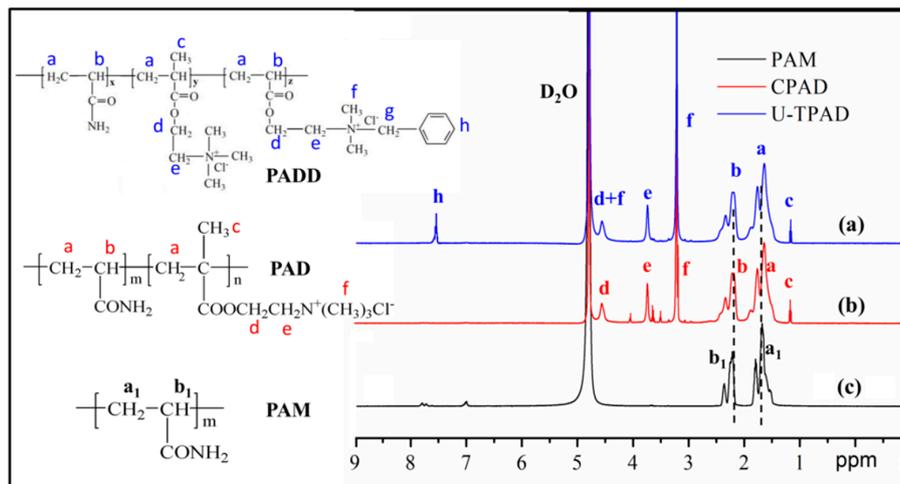


Figure 4. The ^1H nuclear magnetic resonance (^1H NMR) spectra of (a) PAM, (b) PAD, and (c) PADD.

3.4. SEM of Polymer

The SEM of the polymer is studied and the results are shown in Figure 5. The surface morphology of PAM, PAD, and PADD is very different in vision.

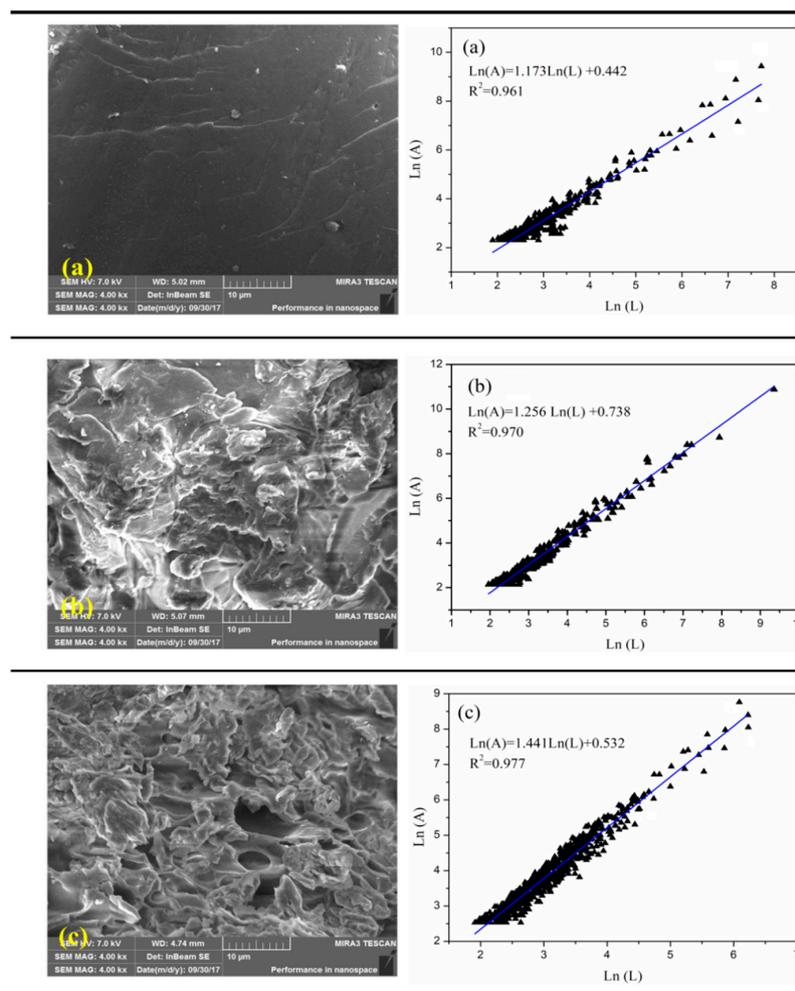


Figure 5. The SEM of (a) PAM, (b) PAD, and (c) PADD.

In Figure 5a, the surface of PAM is smooth, the structure is compact and the voids are few. This is mainly because the activity of AM is higher and homopolymerized of PAM with the lower polymerization activation energy. Thus, it is easier to generate a larger molecular weight, and the longer polymer chains are stacked and densely packed in space to possess a smooth and dense surface morphology [10]. However, when DMC grafted AM monomer, the surface morphology of PAD changed significantly. The PAD surface is rough uneven with few holes in Figure 5b. The introduction of DMC greatly increases the aperture and irregularity of PAD surface. The reason for this change is that the DAC is introduced into the AM chain, destroying the original structure of the PAM. In Figure 5c, it can be clearly seen that the surface of PADD is more disordered and irregular with many obvious holes. This is mainly due to the difference of physical and chemical properties between DMC, DABC, and AM, and the difference of molecular structure in space. After grafting DABC to PAD, the original ordered structure of PAD was destroyed, resulting in porous structure and rough surface morphology. In addition, the fractal dimension of the polymer surface is calculated by using Image-Pro Plus 6.0 software [33]. The results show that the fractal dimensions of PAM, PAD, and PADD are 1.173, 1.256, and 1.441, respectively. The surface fractal dimension of PADD is larger than that of PAM and PAD. PADD has higher hybrid and irregular surface morphology, which is conducive to contact with water molecules and maybe benefit for its solubility as well as improving the flocculation effect [22,25].

4. Flocculation Performance

4.1. The Influence of Flocculant Dosage on Flocculation

As shown in Figure 6, the effect of flocculant dosage on turbidity removal rate of coal mine wastewater was investigated.

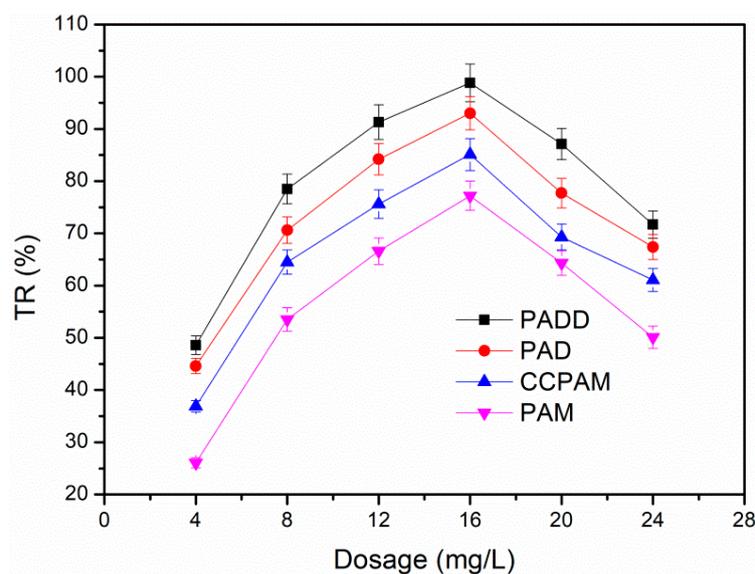


Figure 6. The effect of flocculant dosage on turbidity removal rate.

With the increase of flocculant dosage from 4 mg/L to 16 mg/L, the removal rate of coal mine wastewater reached the maximum. Appropriate amount of flocculant is necessary for coal mine wastewater flocculation. This is mainly due to the interaction of positively charged cationic flocculants with and negatively charged colloidal particles in coal mine wastewater, resulting in electrostatic attraction, adsorption and flocculation. Thus, it improves the turbidity removal rate of coal mine wastewater. However, when the dosage of flocculant increased further, the removal rate of coal mine wastewater turbidity showed a downward trend. This is mainly because the excessive cationic flocculant will encapsulate colloidal particles, and the vacant adsorption sites will be greatly reduced,

which is not conducive to the role of bridging. In addition, it can also reverse the electrical properties of colloidal particles and enhance the electric repulsion between them, resulting in poor flocculation effect of coal mine wastewater [34,35]. At the same time, among all flocculants, PADD has the best flocculation performance in flocculants. The order of flocculation effect was as follows: PADD (turbidity removal rate 98.8%) > PAD (turbidity removal rate: 93.0%) > CCPAM (turbidity removal rate: 85.1%) > PAM (turbidity removal rate: 77.2%). The above phenomena can be explained as that PADD, hydrophobically modified by introducing hydrophobic monomer (phenyl), The incorporation DABC will increase the associations between hydrophobic units which leads to the formation of transient networks and thus increasing the adsorption, capture and bridging effect [22]. Therefore, it has a more desirable flocculation performance than PAD. Compared with CCPAM, the cationic degree of PAD is higher, which is beneficial to enhance the ability of charge neutralization, electrostatic attraction and electrical patching, and thus enhancing the flocculation performance of polymers [20,36]. PAM with no cationic charge and low molecular weight shows an undesirable flocculation performance just depending on the bridging and adsorption effect.

4.2. The Effect of pH Value on Flocculation

The effect of pH on TR of coal mine wastewater was investigated when flocculant dosage was 16 mg/L, and the results were shown in Figure 7.

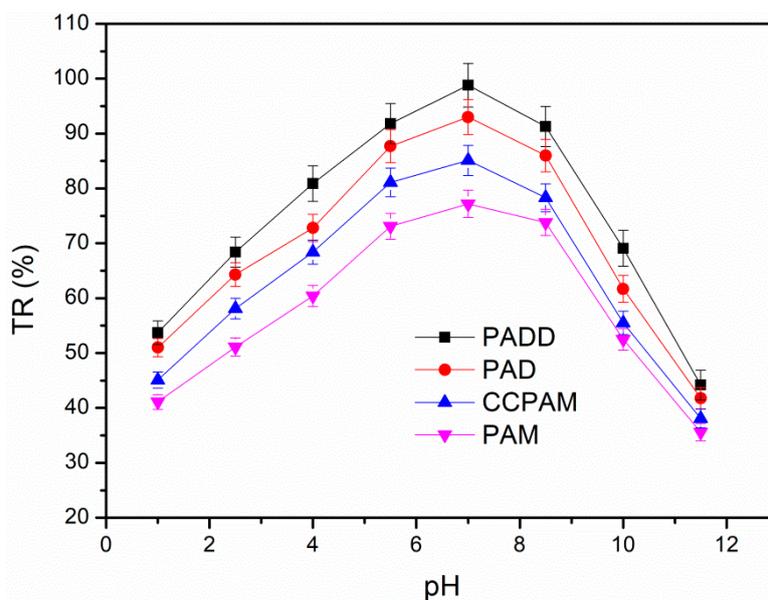


Figure 7. The influence of pH on turbidity removal rate (TR).

The flocculants displayed individual variation on flocculation performance under different pH values, which proved that pH played an important role for coal mine wastewater treatment. As the pH value gradually increased, the turbidity removal of coal mine wastewater first increased and then decreased. When the pH value was 7.0, the removal rate of the four flocculants reached the maximum value. The neutral condition (pH = 7.0) was more conducive to the removal, while the strong acid and alkali condition was not favorable for the coal mine wastewater flocculation. Excessive H^+ ions from a strong acid environment led to strong electrostatic repulsion between coal colloids, which prevented the growth of flocs and reduced the flocculation efficiency [30]. On the contrary, the turbidity removal rate efficiency of the coal mine wastewater was declined under the strong alkalinity condition, and the flocculant performance was also undesirable. On the one hand, the $-NH_2$ group of flocculants tended to hydrolyze under the strong alkalinity condition [4]. On the other hand, the colloid was wrapped by superfluous OH^- groups to become negatively charged groups. It will result in an electrostatic

repulsion between colloids. Consequently, the charge neutralization ability of flocculant reduced, and the TR of coal mine wastewater decreased. During the whole pH range, PADD displays the most excellent flocculation performance among these flocculants. Moreover, within the pH value range of 4.0–8.0, PADD had good performance on TR, indicating that it possessed more extensive application in the actual treatment process of high-turbidity polluted water.

4.3. Floc Characteristics and Flocculation Mechanism

4.3.1. Floc Dynamics Investigation

In order to study the effect of flocculant on turbidity removal of coal mine wastewater, flocculation kinetics analysis was carried out under the condition at dosage of 16 mg/L and pH of 7.0, and the result was showed in Figure 8.

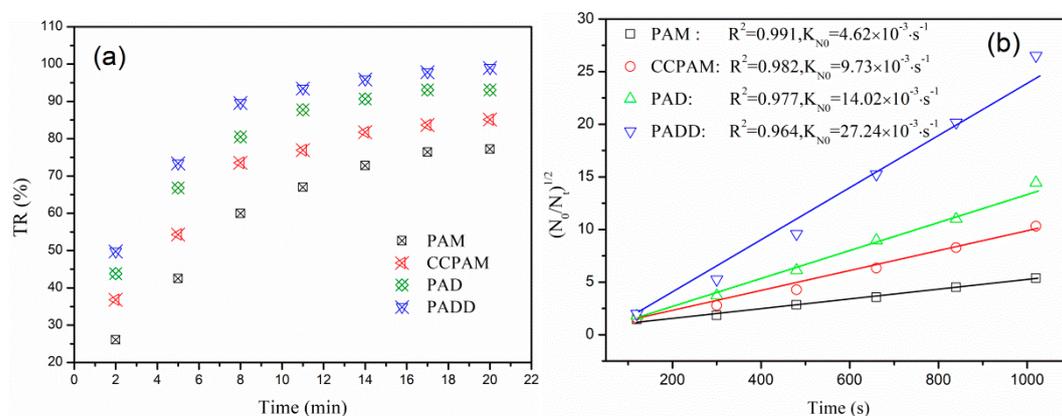


Figure 8. The effects of flocculation time on (a) turbidity removal rate of coal mine wastewater and (b) $(N_0/N_t)^{1/2}$.

As shown in Figure 8a, turbidity removal of coal mine wastewater with four flocculants increased rapidly at first, then increased slowly until it was stable. Clearly, among all flocculants, the coal mine wastewater turbidity removal rate of PADD increased at the fastest rate for the first 9 min. At the same time, the simulated curve slope (K_{N0}) of the four flocculants was fitted in Figure 8b and the values were arranged in the following order: PADD ($K_{N0} = 27.24 \times 10^{-3} \cdot s^{-1}$) > PAD ($K_{N0} = 14.02 \times 10^{-3} \cdot s^{-1}$) > CCPAM ($K_{N0} = 9.73 \times 10^{-3} \cdot s^{-1}$) > PAM ($K_{N0} = 4.62 \times 10^{-3} \cdot s^{-1}$). Among them, PADD has the highest slope value, indicating that PADD has the best flocculation effect. PADD has high cationic degree (40%) with strong charge neutralization ability, it can completely attract and neutralize negatively charged coal mine wastewater colloidal particles, resulting in the loss of colloidal stability. On the other hand, PADD has a high molecular weight (4.0×10^6 Da) with strong adsorption bridging effect. The molecular chain of the PADD will effectively intercept and wrap colloids to form a large flocculent structure [31]. In addition, hydrophobic phenyls in PADD polymer chains will lead to good extension of polymer chains, and more active sites of polymer chains are exposed. More effective molecular collision and flocculation occur between PADD polymer chain and colloidal particles of coal mine wastewater, which improves the flocculation effect of polymer.

4.3.2. Fractal Dimension and Size of Flocs

In Figure 9, the floc size d_{50} and D_f of the four coagulants at pH = 7.0 showed a trend of increasing first and then decreasing, and obtaining the maximum value at 16 mg/L. The D_f (1.61) and particle size ($d_{50} = 513.467 \mu\text{m}$) of PADD reached the maximum on this condition. The dosage can affect the structure characteristics of flocs by affecting the surface properties of colloids in coal mine wastewater. Only under the action of proper amount of flocculant, cationic groups on polymer chains can attract and

neutralize negatively charged colloidal particles completely by the action of electrostatic attraction [37]. The polymer molecular segments adsorbed with colloidal particles of coal mine are free to extend into the solution and collide with other colloidal particles under the action of adsorption bridges, and aggregate into flocs with large and dense structures [38]. However, due to the excessive dosage of flocculant, the electrostatic repulsion between colloidal particles in coal mine wastewater increases, making it difficult for colloidal particles to be captured and fixed by polymer molecular chains, and it is difficult to aggregate to form large and dense structures. Compared with the CCPAM and PAM, the particle size d_{50} and D_f of PADD and PAD becomes more larger, which indicates that cationic degree and molecular weight can affect the structure of the flocs. As higher cationic degree and molecular weight can significantly improve the ability of PADD and PAD to neutralize, patch, and adsorb bridges. Once PADD or PAD is added to coal mine wastewater, more negatively charged particles are neutralized and adsorbed on molecular chains, and they are entangled by shear stress caused by water agitation. The encapsulated flocs are continuously squeezed, and the voids in the encapsulated flocs are constantly crowded, and the structure becomes more and more compact, resulting in a larger and more compact floc structure [39–41]. Therefore, the particle size and D_f of the flocs subjected to PADD or PAD increased. The PADD and PAD have the same cationic degree and molecular weight, and therefore it is speculated that the difference of particle size d_{50} and D_f is derived from the hydrophobic phenyl group. It is indicated that the introduction of DABC in the flocculant is more useful to enhance its flocculation efficiency. A relatively low floc size and D_f is produced. For PAM, the flocculation performance just relies on the effect of bridging and adsorption rather than charge neutralization and electrical patching, and thereby the flocculation efficiency is discounted, and the lowest floc size and D_f are obtained [42].

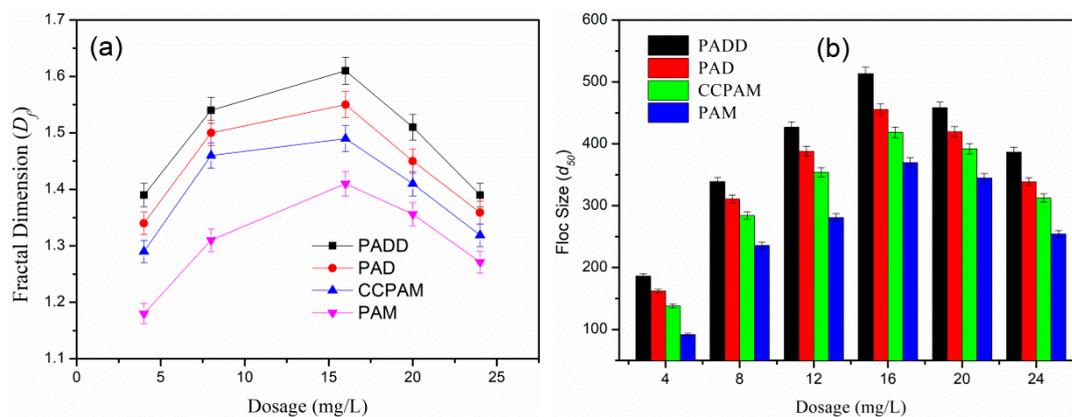


Figure 9. The floc (a) fractal dimension and (b) floc size.

4.3.3. Flocculation Mechanism

Zeta potential plays an important role in understanding the charge characteristics of colloids in coal mine wastewater. In order to understand the mechanism involved in flocculation process, zeta potential of supernatant after flocculation is analyzed at $pH = 7.0$. The results were shown In Figure 10. The initial zeta potential of wastewater is negative (-29.30 mV) before adding flocculant. Under these conditions, colloids in coal mine wastewater are very stable and difficult to remove under natural sedimentation. However, with the increase of flocculant dosage, zeta potential of coal mine wastewater changed to positive value. This phenomenon shows that cationic flocculants can greatly change the charge characteristics of colloids in coal mine wastewater, and then affect the flocculation performance. Compared with CCPAM, the relatively high cationic degree of PAD and PADD plays an important role in flocculation through charge neutralization and electric patching, and can neutralize negatively charged colloid of coal mine wastewater more effectively to improve the flocculation performance [30]. In addition to charge neutralization and electric patching, other flocculation mechanisms also play

a role in the flocculation process, which can be reflected by the following phenomenon. The PAM with a low molecular weight still shows a relatively unfavorable coal mine wastewater flocculation performance in Figures 6 and 7. It is proved that bridging and adsorption also play an important role in the flocculation process. Compared with PAM, CCPAM with a cationic degree of 20% and a higher molecular weight has a large floc size, D_f and large K_{N0} . It is manifested that the charge neutralization, electric patching, bridging and adsorption in CCPAM greatly improves the coal mine wastewater flocculation effect. PADD has a longer polymer chain and high cationic degree to neutralize, capture and adsorb colloids of coal mine wastewater through charge neutralization, bridging, and adsorption, which can form large and dense flocs with large floc size [43,44]. In this condition, flocs can be easily separated from the solution, and reduce the turbidity of coal mine wastewater [45]. The flocculation effect of PADD is better than that of PAD. The main reason is that the grafting of hydrophobic phenyl on PADD promotes the bridging enhancement, so PADD has larger floc size and D_f than PAD. As a result, the flocculation performance is better than PAD. In a word, the flocculation process has the function of charge neutralization, electric patching, the positive effect of hydrophobic phenyl group, adsorption bridging during the coal mine wastewater flocculation.

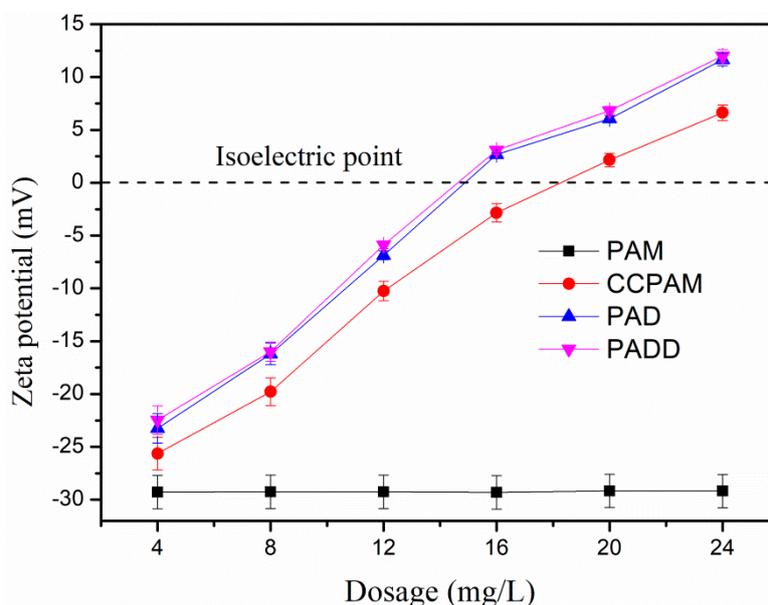


Figure 10. Zeta-potential for different flocculants.

5. Conclusions

In this study, the hydrophobic flocculant PADD was successfully synthesized through ultrasonic-initiated copolymerization technology by using AM, DMC, and DABC as synthetic monomers. The PADD was used in coal mine wastewater flocculation and treatment. The effect of single factor experimental conditions on the polymer molecular weight was investigated to have a better understanding of the ultrasonic-initiated copolymerization technology. The synthesized PADD was characterized, and the results indicated its successful preparation. The PADD had an irregular surface morphology, which was favorable for the flocculation performance improvement of coal mine wastewater. The PADD showed more excellent coal mine wastewater flocculation performance than PAD, CCPAM, and PAM. The hydrophobic effect, charging neutralization and electric patching, adsorption, and bridging of PADD play an important role in coal mine wastewater flocculation. These effects synergistically collaborate and contributed much to a large flocs size, a high fractal dimension and flocculation kinetic constant. Consequently, a better flocculation effect and higher turbidity removal rate of coal mine wastewater were obtained.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2227-9717/8/1/62/s1>.

Author Contributions: J.L. and S.L. designed the study and conducted parts of the experiments and data analysis, wrote the initial manuscript. X.Q. and K.S. helped to revise the manuscript. X.L. performed the characterization analyses. Y.L. completed the jar tests. C.W. performed the data curation. All authors have read and agreed to the published version of the manuscript.

Funding: The authors are grateful for the financial support provided by National Key Research and Development Program of China (No. 2017YFC040470002), Guangdong Provincial Natural Science Fund (No. 2017A030313321), the Chongqing Science and Technology Commission Project (Project No. cstc2018jcyjAX0699), the Scientific and Technological Research Program of Chongqing Municipal Education Commission (Grant No. KJQN201801515) the Fundamental Research Funds for the Central Universities, CHD (No. 300102289108), the Scientific and Technological Research Program of Chongqing Municipal Education Commission (No. KJQN201801515).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Li, X.; Zheng, H.L.; Wang, Y.L.; Sun, Y.J.; Xu, B.C.; Zhao, C.L. Fabricating an enhanced sterilization chitosan-based flocculants: Synthesis, characterization, evaluation of sterilization and flocculation. *Chem. Eng. J.* **2017**, *319*, 119–130. [CrossRef]
- Jenkins, M.; Tiwari, S.; Darby, J. Bacterial, viral and turbidity removal by intermittent slow sand filtration for household use in developing countries: Experimental investigation and modeling. *Water Res.* **2011**, *45*, 6227–6239. [CrossRef] [PubMed]
- Ma, J.Y.; Fu, K.; Jiang, L.Y.; Ding, L.; Guan, Q.Q.; Zhang, S.H.; Zhang, H.W.; Shi, J.; Fu, X. Flocculation performance of cationic polyacrylamide with high cationic degree in humic acid synthetic water treatment and effect of kaolin particles. *Sep. Purif. Technol.* **2017**, *181*, 201–212. [CrossRef]
- Feng, L.; Zheng, H.L.; Tang, X.M.; Zheng, X.Y.; Liu, S.; Sun, Q.; Wang, M.X. The investigation of the specific behavior of a cationic block structure and its excellent flocculation performance in high-turbidity water treatment. *RSC Adv.* **2018**, *8*, 15119–15133. [CrossRef]
- Hu, C.Y.; Lo, S.L.; Chang, C.L.; Chen, F.L.; Wu, Y.D.; Ma, J.L. Treatment of highly turbid water using chitosan and aluminum salts. *Sep. Purif. Technol.* **2013**, *104*, 322–326. [CrossRef]
- Liao, L.N.; Zhang, P. Preparation and Characterization of Polyaluminum Titanium Silicate and its Performance in the Treatment of Low-Turbidity Water. *Processes* **2018**, *6*, 125. [CrossRef]
- Prabhakar, S.; Ghosh, A.; Bindal, R.; Tewari, P. Outside skin tubular ultrafiltration membranes for separation of proteins and polysaccharides and removal of turbidity from seawater. *Desalin. Water Treat.* **2011**, *27*, 231–236. [CrossRef]
- Nkurunziza, T.; Nduwayezu, J.; Banadda, E.; Nhapi, I. The effect of turbidity levels and Moringa oleifera concentration on the effectiveness of coagulation in water treatment. *Water Sci. Technol.* **2009**, *59*, 1551–1558. [CrossRef]
- Khan, R.; Inam, M.; Akram, M.; Uddin, A.; Khan, S.; Yeom, I. Effect of Dissolved Organic Matter on Agglomeration and Removal of CuO Nanoparticles by Coagulation. *Processes* **2019**, *7*, 455. [CrossRef]
- Ma, J.Y.; Shi, J.; Ding, H.C.; Zhu, G.C.; Fu, K.; Fu, X. Synthesis of cationic polyacrylamide by low-pressure UV initiation for turbidity water flocculation. *Chem. Eng. J.* **2017**, *312*, 20–29. [CrossRef]
- Koley, S.; Prasad, S.; Bagchi, S.; Mallick, N. Development of a harvesting technique for large-scale microalgal harvesting for biodiesel production. *RSC Adv.* **2017**, *7*, 7227–7237. [CrossRef]
- Ma, J.Y.; Fu, X.; Xia, W.; Fu, K.; Liao, Y. Flocculation of a High-Turbidity Kaolin Suspension Using Hydrophobic Modified Quaternary Ammonium Salt Polyacrylamide. *Processes* **2019**, *7*, 108. [CrossRef]
- Moghaddam, S.; Moghaddam, M.; Arami, M. Coagulation/flocculation process for dye removal using sludge from water treatment plant: Optimization through response surface methodology. *J. Hazard. Mater.* **2010**, *175*, 651–657. [CrossRef] [PubMed]
- Hankins, N.; Lu, N.; Hilal, N. Enhanced removal of heavy metal ions bound to humic acid by polyelectrolyte flocculation. *Sep. Purif. Technol.* **2006**, *51*, 48–56. [CrossRef]
- Zhang, P.; Liao, L.N.; Zhu, G.C. Performance of PATC-PDMDAAC Composite Coagulants in Low-Temperature and Low-Turbidity Water Treatment. *Materials* **2019**, *12*, 2824. [CrossRef] [PubMed]
- Lou, T.; Wang, X.; Song, G.; Cui, G. Synthesis and flocculation performance of a chitosan-acrylamide-fulvic acid ternary copolymer. *Carbohydr. Polym.* **2017**, *170*, 182. [CrossRef]

17. Sun, Y.J.; Sun, W.Q.; Shah, K.; Chiang, P.C.; Zheng, H.L. Characterization and flocculation evaluation of a novel carboxylated chitosan modified flocculant by UV initiated polymerization. *Carbohydr. Polym.* **2019**, *208*, 213–220. [[CrossRef](#)]
18. Sun, Y.J.; Zhu, C.Y.; Sun, W.Q.; Xu, Y.H.; Xiao, X.F.; Zheng, H.L.; Wu, H.F.; Liu, C.Y. Plasma-initiated polymerization of chitosan-based CS-g-P(AM-DMDAAC) flocculant for the enhanced flocculation of low-algal-turbidity water. *Carbohydr. Polym.* **2017**, *164*, 222–232. [[CrossRef](#)]
19. Chen, L.; Liu, C.; Sun, Y.; Sun, W.; Xu, Y.; Zheng, H. Synthesis and Characterization of Ampholytic Flocculant CPCTS-g-P (CTA-DMDAAC) and Its Flocculation Properties for Microcystis Aeruginosa Removal. *Processes*. **2018**, *6*, 54. [[CrossRef](#)]
20. Zheng, H.L.; Sun, Y.J.; Guo, J.S.; Li, F.T.; Fan, W.; Liao, Y.; Guan, Q.Q. Characterization and Evaluation of Dewatering Properties of PADB, a Highly Efficient Cationic Flocculant. *Ind. Eng. Chem. Res.* **2014**, *53*, 2572–2582. [[CrossRef](#)]
21. Kotlyarevskaya, O.; Navrotskii, V.; Orlyanskaya, M.; Navrotskii, A.; Novakov, I. Flocculation Properties of Polyelectrolytes Based on 2- (N, N -Dimethyl- N -Benzylammonio) ethyl Methacrylate Chloride. *Russ. J. Appl. Chem.* **2004**, *77*, 622–628. [[CrossRef](#)]
22. Zheng, H.L.; Sun, Y.J.; Zhu, C.J.; Guo, J.S.; Zhao, C.; Liao, Y.; Guan, Q.Q. Uv-initiated polymerization of hydrophobically associating cationic flocculants: Synthesis, characterization, and dewatering properties. *Chem. Eng. J.* **2013**, *234*, 318–326. [[CrossRef](#)]
23. Zhu, G.C.; Liu, J.F.; Yin, J.; Li, Z.W.; Ren, B.Z.; Sun, Y.J.; Wan, P.; Liu, Y.S. Functionalized polyacrylamide by xanthate for Cr (VI) removal from aqueous solution. *Chem. Eng. J.* **2016**, *288*, 390–398. [[CrossRef](#)]
24. Feng, L.; Liu, S.; Zheng, H.L.; Liang, J.J.; Sun, Y.J.; Zhang, S.X.; Chen, X. Using ultrasonic (US)-initiated template copolymerization for preparation of an enhanced cationic polyacrylamide (CPAM) and its application in sludge dewatering. *Ultrason. Sonochem.* **2018**, *44*, 53–63. [[CrossRef](#)]
25. Feng, L.; Liu, J.Y.; Xu, C.; Lu, W.C.; Li, D.M.; Zhao, C.L.; Liu, B.Z.; Li, X.; Khan, S.; Zheng, H.L.; et al. Better understanding the polymerization kinetics of ultrasonic-Template method and new insight on sludge floc characteristics research. *Sci. Total Environ.* **2019**, *689*, 546–556. [[CrossRef](#)] [[PubMed](#)]
26. Lin, P.; Feng, J.; Zheng, H.; Yang, H.; Xu, J. Preparation of pH-sensitive polymer by thermal initiation polymerization and its application in fluorescence immunoassay. *Talanta* **2005**, *65*, 430–436. [[CrossRef](#)] [[PubMed](#)]
27. Khudyakov, I.; Turro, N. Cage Effect Dynamics under Photolysis of Photoinitiators. *Des. Monomers Polym.* **2010**, *13*, 487–496.
28. Ma, J.Y.; Shi, J.; Ding, L.; Zhang, H.W.; Zhou, S.; Wang, Q.J.; Fu, X.; Jiang, L.Y.; Fu, K. Removal of emulsified oil from water using hydrophobic modified cationic polyacrylamide flocculants synthesized from low-pressure UV initiation. *Sep. Purif. Technol.* **2018**, *197*, 407–417. [[CrossRef](#)]
29. Song, S.X. Experimental studies on hydrophobic flocculation of coal fines in aqueous solutions and flotation of flocculated coal. *Int. J. Oil Gas Coal Technol.* **2008**, *1*, 180–193. [[CrossRef](#)]
30. Zheng, H.L.; Feng, L.; Gao, B.Y.; Zhou, Y.; Zhang, S.X.; Xu, B.C. Effect of the cationic block structure on the characteristics of sludge flocs formed by charge neutralization and patching. *Materials* **2017**, *10*, 487.
31. Feng, L.; Zheng, H.L.; Wang, Y.L.; Zhang, S.X.; Xu, B.C. Ultrasonic-template technology inducing and regulating cationic microblocks in CPAM: Characterization, mechanism and sludge flocculation performance. *RSC Adv.* **2017**, *7*, 23444–23456. [[CrossRef](#)]
32. Liao, Y.; Zheng, H.; Qian, L.; Sun, Y.J.; Dai, L.; Xue, W.W. UV-Initiated Polymerization of Hydrophobically Associating Cationic Polyacrylamide Modified by a Surface-Active Monomer: A Comparative Study of Synthesis, Characterization, and Sludge Dewatering Performance. *Ind. Eng. Chem. Res.* **2014**, *53*, 11193–11203. [[CrossRef](#)]
33. Wang, M.X.; Feng, L.; Fan, X.W.; Li, D.M.; Qu, W.Q.; Jiang, S.X.; Li, S.X. Fabrication of Bifunctional Chitosan-Based Flocculants: Characterization, Assessment of Flocculation, and Sterilization Performance. *Materials* **2018**, *11*, 2009. [[CrossRef](#)] [[PubMed](#)]
34. Wu, Z.C.; Zhu, Y.; Huang, W.Y.; Zhang, C.W.; Li, T.; Zhang, Y.M.; Li, A.F. Evaluation of flocculation induced by pH increase for harvesting microalgae and reuse of flocculated medium. *Bioresour. Technol.* **2012**, *110*, 496–502. [[CrossRef](#)]
35. Suresha, P.R.; Manohar, V.B. Flocculation of kaolin from aqueous suspension using low dosages of acrylamide-based cationic flocculants. *J. Appl. Polym. Sci.* **2018**, *136*, 47286. [[CrossRef](#)]

36. Feng, L.; Zheng, H.L.; Gao, B.Y.; Zhao, C.L.; Zhang, S.X.; Chen, N. Enhancement of textile-dyeing sludge dewaterability using a novel cationic polyacrylamide: Role of cationic block structures. *RSC Adv.* **2017**, *7*, 11626–11635. [[CrossRef](#)]
37. Manognya, B.; James, S.B.; Christopher, B.F.; Mohammad, S.I. Impact of Natural Cationic Polymers on Charge and Clarification of Microalgae Suspensions. *Environ. Eng. Sci.* **2015**, *32*, 212–221.
38. Besra, L.; Sengupta, D.K.; Roy, S.K.; Ay, P. Influence of surfactants on flocculation and dewatering of kaolin suspensions by cationic polyacrylamide (PAM-C) flocculant. *Sep. Purif. Technol.* **2003**, *30*, 251–264. [[CrossRef](#)]
39. Son, M.; Hsu, T.J. Flocculation model of cohesive sediment using variable fractal dimension. *Environ. Fluid Mech.* **2008**, *8*, 55–71. [[CrossRef](#)]
40. Zhu, Z.; Peng, D.; Dou, J. Changes in the two-dimensional and perimeter-based fractal dimensions of kaolinite flocs during flocculation: A simple experimental study. *Water Sci. Technol.* **2018**, *77*, 861–870. [[CrossRef](#)]
41. Chung, H.; Ju, S.; Lee, D. Hydrodynamic drag force exerted on activated sludge floc at intermediate Reynolds number. *J. Colloid Interf. Sci.* **2003**, *263*, 498–505. [[CrossRef](#)]
42. Wu, J.; He, C. Experimental and modeling investigation of sewage solids sedimentation based on particle size distribution and fractal dimension. *Int. J. Environ. Sci. Technol.* **2009**, *7*, 37–46.
43. Huang, M.; Liu, Z.Z.; Li, A.M.; Hu, Y. Dual functionality of a graft starch flocculant: Flocculation and antibacterial performance. *J. Environ. Manag.* **2017**, *196*, 63–71. [[CrossRef](#)] [[PubMed](#)]
44. Li, R.H.; Gao, B.Y.; Huang, X.; Dong, H.Y.; Li, X.C.; Yue, Q.Y.; Qian, L. Compound bioflocculant and polyaluminum chloride in kaolin-humic acid coagulation: Factors influencing coagulation performance and floc characteristics. *Bioresour. Technol.* **2014**, *172*, 8–15. [[CrossRef](#)] [[PubMed](#)]
45. Ma, J.Y.; Xue, F.; Jiang, L.Y.; Zhu, G.C.; Shi, J. Magnetic flocculants synthesized by Fe₃O₄ coated with cationic polyacrylamide for high turbid water flocculation. *Environ. Sci. Pollut. Res.* **2018**, *25*, 25955–25966. [[CrossRef](#)] [[PubMed](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).