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Preparation of a cationic polyacrylamide (CPAM) and its flocculation performance in the environmental estrogen removal and separation

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ABSTRACT

In this study, a new cationic polyacrylamide (CPAM) with different cationic degree was developed for the 17β-estradiol (E2) environmental estrogen removal. This new flocculant (PAA) was copolymerized byacrylamide (AM) and acryloyloxyethyl dimethylbenzyl ammonium chloride (AODBAC) using ultrasonic-initiated polymerization technique. The structure, morphology and thermal decomposition property of the prepared copolymer were analyzed through instrumental analyses such as Fourier transform infrared spectroscopy (FT-IR), ^{1}H nuclear magnetic resonance spectroscopy (^{1}HNMR), scanning electron microscopy (SEM) and thermogravimetry/differential scanning calorimetry (TG/DSC). The results showed that PAA was successfully synthesized. Meanwhile, it was demonstrated that PAA had a rough surface area with many holes and a favorable thermal stability. The E2 flocculation results demonstrated that the optimal flocculation conditions was at a cationic degree of 40%, pH = 7, stirring speed of 120 rpm, stirring time of 10 min, sedimentation time of 30 min and E2 initial concentration of 0.6 mg/L. In this condition, an excellent E2 flocculation performance (E2 removal rate: 92.3%, floc size: 22.1 μm) was obtained for PAA-3. During the E2 flocculation process, the charge neutralization was the main effect in both neutral (pH = 7) and acidic (pH = 4) conditions, but the adsorption was the dominant effect in alkaline (pH = 10) condition.

Keywords: Environmental estrogens; Ultrasonic copolymerization; Characterization; Flocculation; Cationic polyacrylamide; Water treatment

1. Introduction

The environmental estrogen (EEs), an important group of endocrine disrupting chemicals (EDCs), has raised substantial concerns among both the public and regulatory agencies because EEs may affect the water quality and pose potential threat to wildlife and human health [1]. It is well established that the EEs showing the structural and functional similarity with entogenous estrogen will result in a series of risks and damages such as endocrine disorder, sex reversal like feminization of male fish, dysontogenesis, distortion and species extinction even at a trace level [2]. EEs, including natural steroids (estrone (E1), 17β-estradiol (E2), estriol (E3)) and synthetic chemicals (17α-ethinyl estradiol) (EE2), bisphenol A (BPA) and 4-nonylphenol (NP)) was mainly derived from the release of pharmaceutical industries, wastewater treatment plants (WWTPs) and plastic industries, and it has been widely detected indifferent environmental matrixes (surface water, soil, and atmosphere) around the world [3]. It has become a great challenge for water treatment facilities to remove EEs, and therefore the research and developing of an efficient and reliable EEs treatment method is crucial and necessary.

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Various technologies and methods, including advanced oxidation processes [4], biodegradation, activated carbon (AC) adsorption [5], aquatic plants treatment [6], flocculation [7] and membrane treatment [8] have been developed to remove EEs. Among them, flocculation is regarded as an important technology in polluted water purification because of its unique properties such as facile operation, high efficiency and low cost [9]. Meanwhile, flocculation is environment friendly and it has been widely and successfully used in solid-liquid separation, organic matter removal, heavy metal removal and sludge dewatering [10–12]. However, the research focusing on removal EEs by flocculation is limited and the mechanism involved in the flocculation process is not well known.

As the core part of flocculation, charge neutralization, bridging and adsorption play an important role in the removal of contaminative substance [13]. The negatively charged pollutant is neutralized completely by the cationic flocculant and combined tightly under the effect of charge neutralization. Then, the neutralized pollutant is adsorbed by the flocculant polymer chain and aggregate together to form large flocs under the effect of bridging and sweeping [14]. Besides, the flocculant has some characteristic chemical group such as $–NH_2$, $–N^+–(CH_3)_3$ and$–SO_3^-$ which will form a chemical bond between the flocculant and pollutant, and thus the removal of contaminative substance becomes more facile and efficient. Therefore, it is so urgent to synthesize a cationic flocculant to remove the negatively charged EEs. Based on the previous studies, it is suggested to use ultrasonic-initiated copolymerization method to prepare the flocculant due to the advantages of this method [15]. For example, the ultrasonic-initiated copolymerization method is easy to control and environment-friendly [16]. In this study, the acrylamide (AM) and hydrophobicacryloyloxyethyl dimethylbenzyl ammonium chloride (AODBAC) were used as the monomers to prepare the copolymer P(AM-AODBAC) (PAA) through ultrasonic-initiated copolymerization. Meanwhile, 17β-estradiol (E2), a common and representative member of EEs, was chosen as the target to evaluate the flocculation performance of PAA.

The objectives of this study are to (1) synthesize the PAA thorough ultrasonic-initiated polymerization technique; (2) characterize the structural characters of the polymers by FT-IR spectroscopy, ^{1}H NMR spectroscopy,SEM and TG/DSC; (3) assess the E2 removal efficiency of PAA and stabilize the optimal flocculation conditions; and (4) investigate and summarize the possible mechanism involved in the flocculation process.

2. Materials and methods

2.1. Materials

Reagents used in this experiment were as follows: The monomer acrylamide (AM) was obtained from Shanghai Meryer Chemical Technology Co., LTD (Shanghai, China). Acryloyloxyethyl dimethylbenzyl ammonium chloride (AODBAC) (80 wt % in water) was purchased from Shanghai Orgchem Chemical Co., LTD (Shanghai, China). The urea $[CO(NH_2)_2]$ was provided by Aladdin. The initiator 2,2′-azobis [2-(2-imidazolin-2-yl) propane] dihydrochloride (VA-044) was supported by Shanghai Nuohey Chemical Technology Co., Ltd. (Shanghai, China). The water used in the experiment was deionized water. E2 (97.0%) was purchased from Tokyo Chemical Industry (Tokyo, Japan). Polyacrylamide (PAM) was home-made in laboratory. In the above reagents, AM and AODBAC are of technical grade and the remains are of technical grade.

2.2. Preparation of copolymers

The polymer PAA (PAA-1, PAA-2 and PAA-3) were synthesized by ultrasonic-initiated copolymerization and its synthetic procedure was shown as follows. Firstly, a given amount of AM, AODBAC, urea and deionized water was added into a 100 mL quartz jar and shaken 5 min to get a homogeneous solution. Secondly, the pH of the above solution was adjusted to 5 by 0.5 mol L^{-1} HCl or NaOH. Thirdly, the aqueous solution was nitrogenized for 30 min at room temperature, followed by the addition of a certain dose of initiator VA0-44. Finally, the quartz jar was covered the cap and exposed under the ultrasonic radiation (frequency, 45 KHz, KQ 2200E, Kunshan ultrasonic instrument Co., LTD, China) at 35°C for 20–30 min [15]. The preparation of PAM was similar to that of PAA. The alcohol and acetone were used to purify the product. Later, the product after purification was dried in a vacuum oven at 95°C for 12 h. The possible reaction mechanism for PAA is displayed in Fig. 1.

2.3. Characterization of copolymers

The intrinsic viscosities of polymers were determined by an Ubbelohde viscosity meter (Shanghai Shenyi Glass Instrumental Co. Ltd., China) at 30°C in a 2 mol L^{-1} NaCl aqueous solution [17]. The cationic degree (CD) was measured using colloid titration method [18]. Besides, the FT-IR spectra and ^{1}H NMR of polymers were recorded on a 550 Series II infrared spectrometer (Mettler Toledo Instruments Co., Ltd., Switzerland) using KBr pellets and an Avance 500 nuclear magnetic resonance spectrometer (Bruker Company, Ettlingen, Germany) using D_2O as solvent, respectively. The SEM analysis was performed on MIRA 3 LMU SEM system (TES-CAN Company, Czech Republic). Thermogravimetric (TGA) and differential scanning calorimetry (DSC) were conducted on a DTG-60H synchronal thermal analyzer (Shimadzu, Kyoto, Japan) at a heating rate of 10°C·min^{-1} under a nitrogen flow of 20 mL·min^{-1} from 20 to 600°C. The details of the polymers are illustrated in Table 1.

2.4. Analytical methods

The details of the analytical method for the E2 was described as follows. The content of the E2 was investigated by a HPLC (Shimadzu, Japan), equipped with a COSMOSIL 3C18-MS-II column (5 μm, 4.6 × 150 mm, Nacalai Tesque, Inc., Japan). During the E2 treatment progress, a solution sample with 2 mL after being filtered through 1 μm glass fiber filter was collected for detection in different time intervals. Meanwhile, the aliquots of 10 mL solution sample were injected to the HPLC coupling with a mobile phase of a mixture of water/acetonitrile (v/v = 55:45) ata flow rate of 1.0

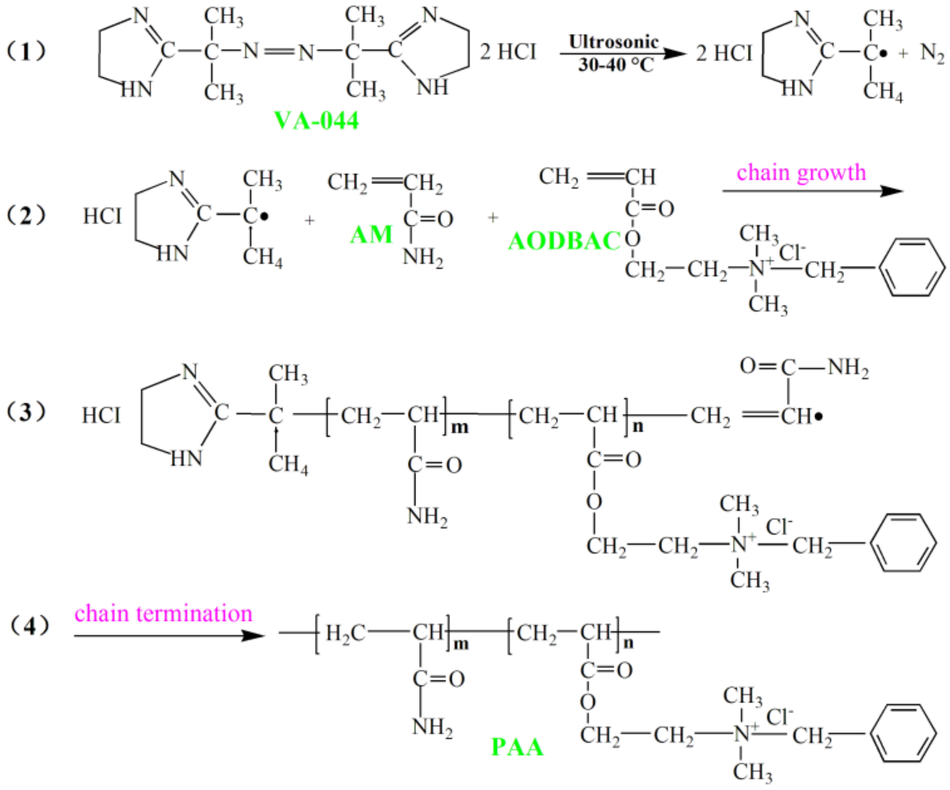

Fig. 1. The possible reaction mechanism for synthesis PAA (PAA-1, PAA-2 and PAA-3).

Table 1
The details of flocculants used in the characterization and flocculation tests

Flocculants[a]	Cationic degree (%)	Intrinsic viscosity (dL·g^{-1})	Conversion rate (%)
PAA-1	20.0	6.17	99.7
PAA-2	30.0	6.13	99.6
PAA-3	40.0	6.11	99.8
PAM	/	6.15	99.9

[a] PAA-X(X = 1, 2 and 3): copolymer of AODBAC and AM by ultrasonic-initiated copolymerization with a cationic degree of (20%, 30% and 40%); PAM: homopolymer of AM by ultrasonic-initiated copolymerization method.

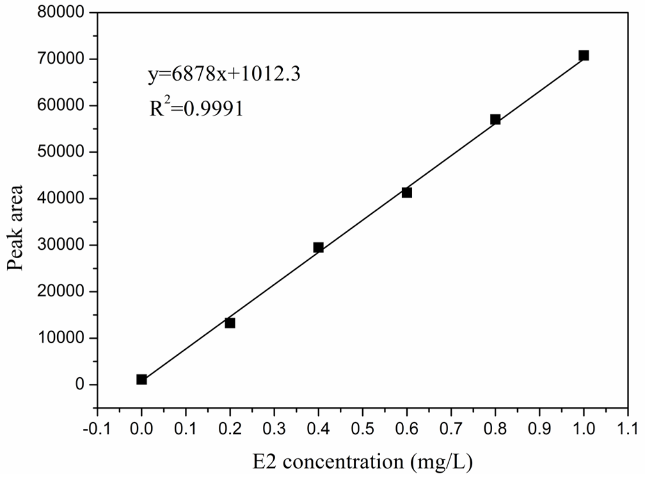

Fig. 2. The calibration curve for E2.

mL min^{-1}, and the detected wavelength was set at $\lambda = 205$ nm. The calibration curve for E2 measurement was added and named Fig. 2.

2.5. Jar testing

A program-controlled Jar-test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) were used to perform the flocculation experiments at ambient temperature. Before flocculation, the pH of the 500 mL simulative E2 wastewater (0.6 mg/L) in a 1000 mL glass beaker was adjusted to the set value by 0.5 mol L^{-1} HCl or NaOH. The flocculation test contained three stages of mixing (rapid mixing, slow mixing and settling). Rapid mixing at 250 rpm continued 2 min and a certain amount of flocculant was added in this stage. Subsequently, a slow stirring was performed at 120 rpm for 10 min, followed by a setting time of 30 min. During the flocculation progress, the floc size was recorded by a laser diffraction instrument (Mastersizer 2000, Malvern, U.K.), and the zeta potential of the supernatant was investigated by a Zetasizer Nano ZS90 (Malvern Instruments Ltd., Malvern, UK). Meanwhile, the E2 content after flocculation was measured and the removal rate of E2 was calculated by Eq. (1) expressed as follows.

$$\text{Removal rate}(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

In Eq. (1), C_0 represented the initial E2 concentration and C_t represented the E2 concentration after flocculation. All the experiments were conducted in triplicates and their average was the final results.

3. Results and discussion

3.1 Characterization of flocculants

3.1.1. FTIR spectral analysis

The FT-IR spectra ofPAM, PAA-1, PAA-2 and PAA-3 were investigated and the results are illustrated in Fig.3. The characteristic adsorption peaks for PAM were observed at 3441 and 1664 cm^{-1} and which were attributed to the stretching vibration of $-NH_2$ and C=O groups, respectively [15]. It was found that the adsorption peaks of the PAA-1, PAA-2 and PAA-3 were similar except for the difference in the peak area. Except for the peaks observed at 3441 and 1664 cm^{-1}, the asymmetric stretching vibrations of $-CH_3$ and $-CH_2-$ groups were observed at 2940 and 2841 cm^{-1}, respectively [12,19]. The adsorption peak at 1452 cm^{-1} was derived from combined action of the bending vibration of $-CH_2-$ in $-CH_2-N^+$ group and benzene skeleton vibration in AODBAC [20]. Besides, the benzene skeleton vibration peaks were also observed at 770 and 703 cm^{-1} in AODBAC [21].The peaks at 1120 and 1357 cm^{-1} were ascribed the stretching vibration of C–O– in ester groups and $-CH_3$ bending vibrations in $-N^+(CH_3)_2-$ of AODBAC. Thus, a conclusion could be draw from the above FT-IR spectra data that copolymers (PAA-1, PAA-2 and PAA-3) were successfully synthesized through the copolymerization of AM and AODBAC.

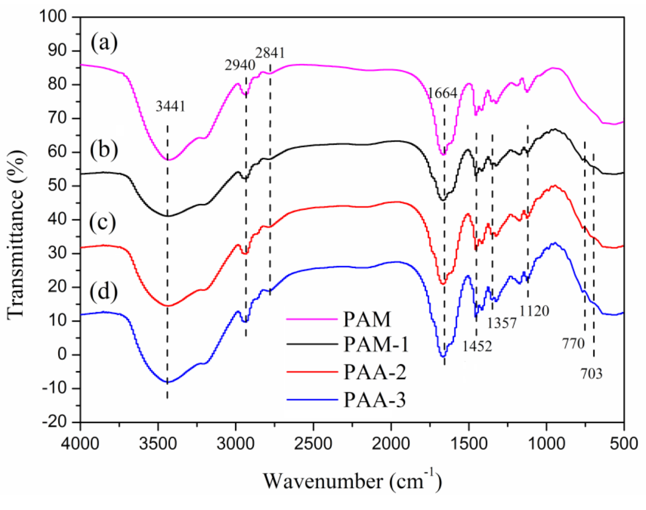

Fig. 3. FT-IR spectra of (a) PAM, (b) PAA-1, (c) PAA-2 and (d) PAA-3.

3.1.2. DSC/TGA analysis

The thermal stability of the copolymer PAA-3 was investigated through the DSC/TGA analysis. As shown in Fig. 4, three steps of the weight loss was expressed in the thermal gravimetric curve of PAA-3. The first stage occurred in the range of 30–200°C with a weight loss of 17.8 wt%, owing to the moisture evaporation [22]. Because PAA-3 had plenty of hydrophilic groups in its molecular chain, it would induce PAA-3 to combine with water molecules. When the heating temperature increased, these water molecules evaporated, and thus resulting in a weight loss. The second stage occurred in the range of 200–350°C with a weight loss of 23.4 wt%, owing to the imine reaction of the amide group and the thermal decomposition of methyl in the quaternary ammonium groups [23]. The third stage occurred beyond 350°C with a weight loss of 45.7 wt%, which was due to the thermal decomposition of the copolymer. A mild change of the thermal gravimetric curve was observed in the range of 460–600°C, which indicated that the PAA-3 was completely carbonized and decomposed [24]. Based on the above DSC/TGA analytical results, it manifested that PAA-3 had a favorable thermal stability and it could be applied and stored in normal temperature.

3.1.3. ^1H NMR spectral analysis

The ^1H NMR spectrum of PAM and PAA-3 is displayed in Fig. 5 to further analyze its structure property. The resonance peaks at 1.63 ppm and 2.19 ppm were assigned to the protons of $-CH_2-$ (a) and –CH– (b) at backbone of the polymer PAM and PAA-3, respectively [15]. Meanwhile, the resonance peaks at 4.61 ppm represented the protons of–$O-CH_2-$(c) in AODBAC. The resonance peaks of $-CH_2-N^+$ (d) group was illustrated at $\delta = 3.77$ ppm in AODBAC [25]. The resonance peaks at 3.20 ppm was associated with the protons of the $-CH_3$ (e) boned with the quaternary ammonium N^+ [26]. Protons in the $-CH_2-$ group connected to the phenyl group were found at $\delta = 4.55$ ppm (f). The resonance

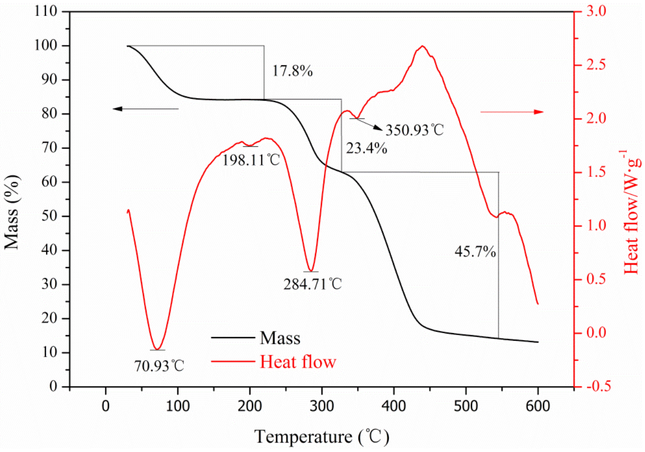

Fig. 4. Thermal gravimetric curve of PAA-3.

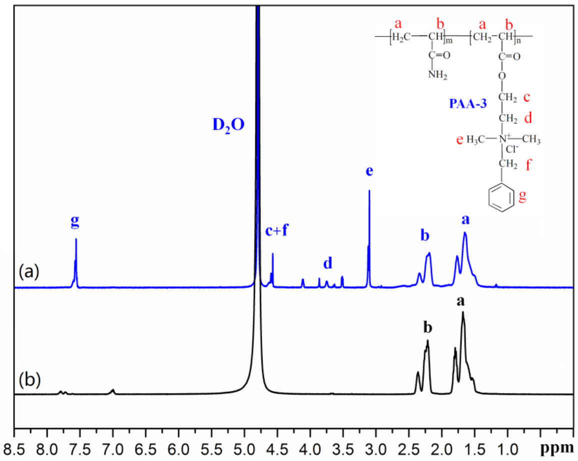

Fig. 5. ^{1}H NMR spectrum of (a) PAA-3 and (b) PAM.

peaks of the phenyl group was shown at δ = 7.54 ppm (g) [21]. Besides, the sharp resonance peak at δ = 4.80 ppm came from the protons of solvent D_2O. Based on the above analyses, the characteristic peaks of AM and AODBAC monomers were all observed, which manifested that the PAA-3 was successfully copolymerized by AM and AODBAC.

3.1.4. SEM of polymers

The SEM results of the polymers are demonstrated in Fig. 6. The two type polymers (PAM and PAA-3) displayed obviously visual difference in the surface morphology. It was found that PAM was characterized with a smooth and regular surface morphology. Due to the homopolymer character, PAM had a long polymer chain and a amide side chain with low space resistance, and thus the PAM chain folded together to form a dense structure with relatively few holes [20]. Evidently, the profound and visual

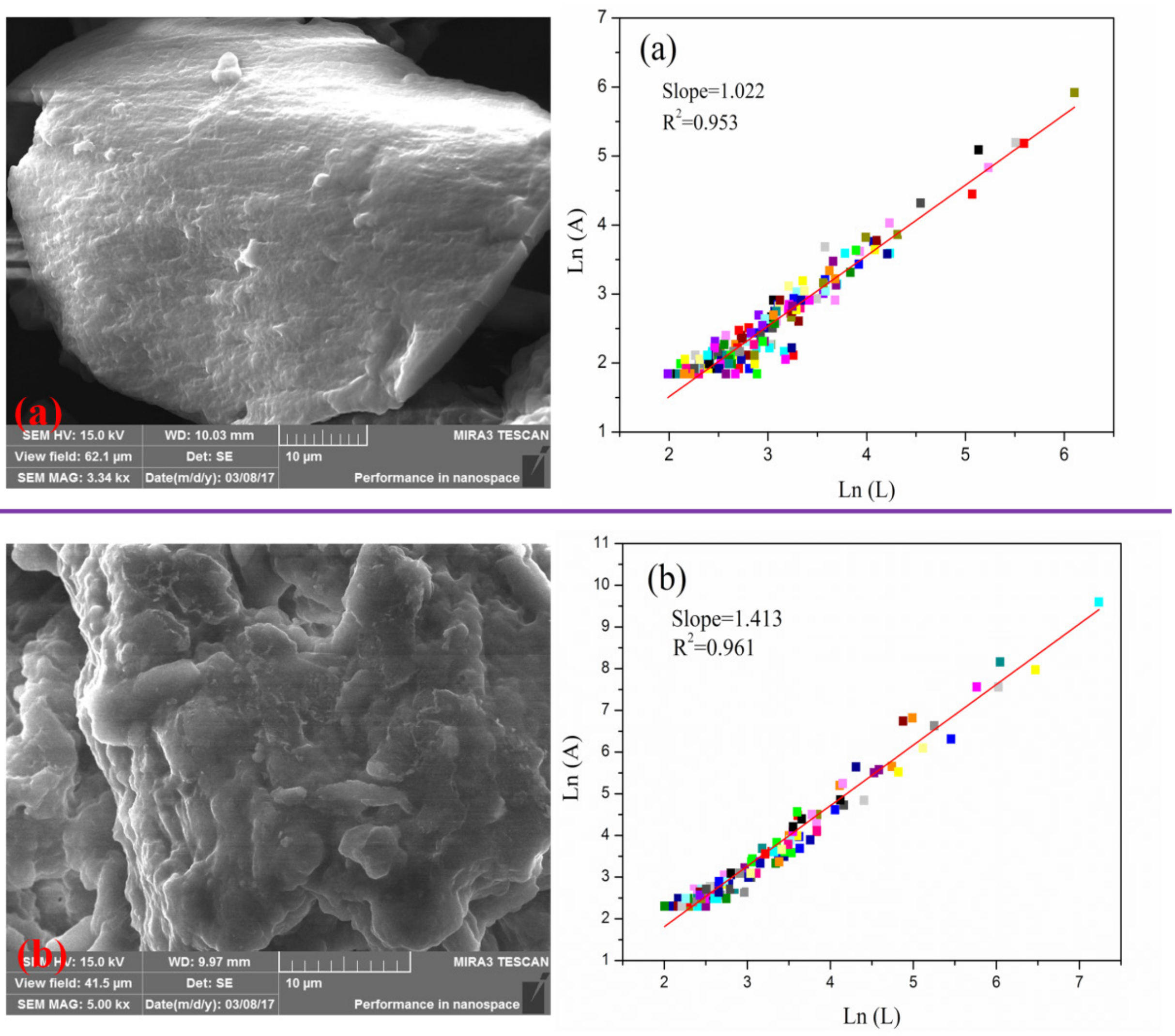

Fig. 6. SEM images of (a) PAM and (b) PAA-3.

morphological change was observed after grafting with AODBAC. When the AODBAC was grafted on the polymer chain of PAM, the original chemical structure and property was destroyed and changed, and hence a rough structure with more holes was observed for PAA-3. In order to further compare the polymer surface morphology difference between PAM and PAA-3, the average fractal dimensions of the PAM and PAA-3 were investigated by using Image-Pro Plus 6.0 software [27]. The analysis result manifested that PAA-3(1.413) had a higher fractal dimension value than PAM (1.022), which indicated that the surface of PAA-3 was more rough and amorphous than PAM. Similar finding has been reported by the previous study [28].

4. Flocculation performance

4.1. The effect of pH and dosage

In Fig. 7 the effects of pH and dosage on the E2 removal by the polymers were studied to gain further insight into the flocculation process. Under various pH (pH = 4, 7 and 10) and dosage (dosage = 1–7 mg/L) conditions, the E2 removal rate showed different variation tendencies, which indicated that the pH and flocculation dosage played a vital role during the flocculation process.

Under the acidic condition (pH = 4) in Fig. 7a, the flocculants showed a similar variation trend on the E2 removal, and the trend firstly increased to a maximum and then decreased gradually with the increase of flocculants dosage from 1 mg/L to 7 mg/L. Because the lower flocculant dosage could not generate enough number of active groups and linear polymer chain to capture and anchor the E2 colloids, and thus a low E2 removal was observed. Meanwhile, the relatively strong acid environment resulted in a protonation of amino group ($-NH_3^+$) and cross-linking of polymer chain, and thereby worsening the streach and extension of the polymer [29,30]. As a result, the bridging effect decreased and the flocculation efficiency of E2 removal was not improved. On the contrary, a cake effect and electrostatic repulsion caused by the excessive dosage prevented the floc growth and reduced the flocculation efficiency. Thus, the excessive dosage was unfavorable for improvement of the flocculation efficiency. Among the four flocculants, PAA-3 displayed the most excellent flocculation performance with the lowest dosage than the other three in the following order: PAA-3 (E2 removal rate: 75.3%, dosage: 2.0 mg/L) > PAA-2 (E2 removal rate: 58.9%, dosage: 3.0 mg/L) > PAA-1 (E2 removal rate: 49.7%, dosage: 4.0 mg/L) > PAM (E2 removal rate: 27.2%, dosage: 4.0 mg/L). In addition to the bridging effect, the PAA-3 with the 40% cationic degree had a great number of $-N^+-(CH_3)_3$ active groups would combine with the E2 colloids to obtain a prominent flocculation performance [31].

Under the neutral condition (pH = 7) in Fig. 7b, the flocculation performance was improved greatly. Compared with the acidic condition (pH = 4), the suited dosage of the flocculants declined, whereas the corresponding E2 removal rate increased. For example, the suited dosage was 1.0 mg/L for PAA-3, 2.0 mg/L for PAA-2, 2.5 mg/L for PAA-1 and 4.0 mg/L for PAM with a high E2 removal rate of 92.3%, 76.6%, 64.2% and 35.1%, respectively. The the neutral condition contributed to a linear distribution of the polymers and low charge repulsion, thus it was facile for the flocculant to show a prominent flocculation performance. On one hand, the flocculants with the positive charge would neutralized the negatively charged E2 colloidal particles completely. On the other hand, the destabilized E2 colloidal particles were captured and aggregated together to form large flocs

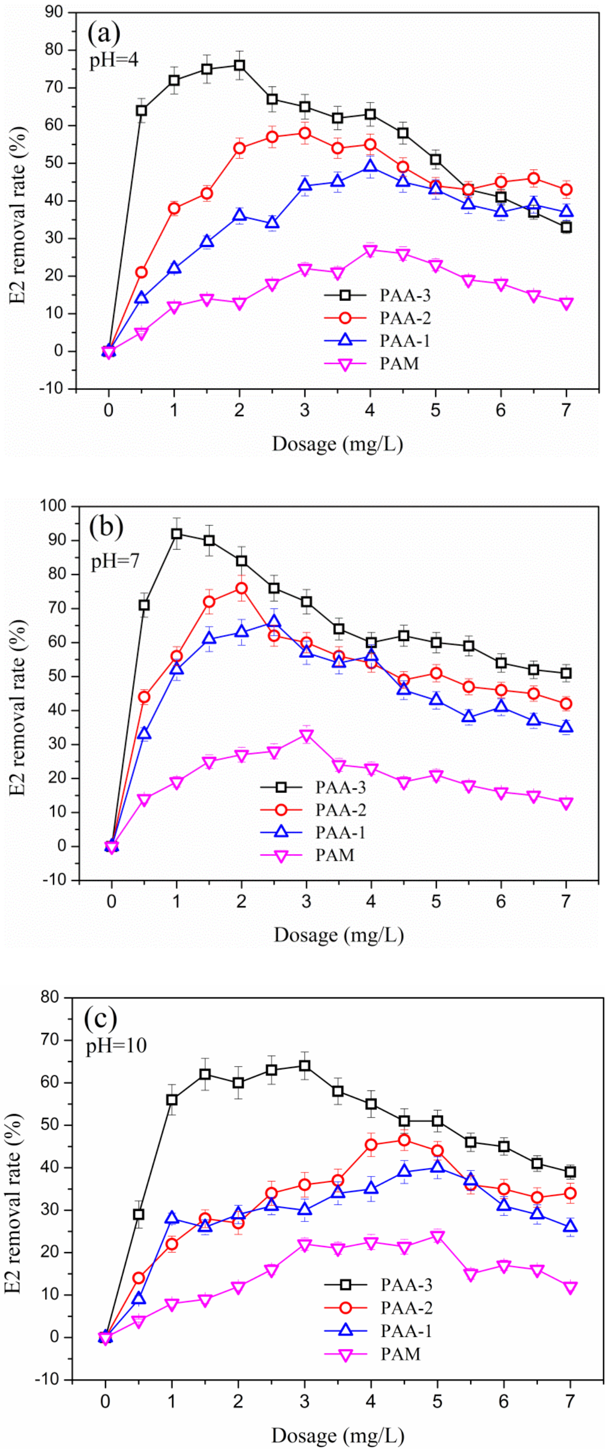

Fig. 7. The E2 removal rate after flocculation at (a) pH = 4, (b) pH = 7 and (c) pH = 10.

through bridging effect [32]. Meanwhile, the PAA-3 was demonstrated to perform the best in the E2 removal among the flocculants, which indicated that the flocculat with high cationic degree was favorable for the E2 removal.

Under the alkaline condition (pH = 10) in Fig. 7c, a worsening flocculation performance was observed. It not only increased the dosage but also reached a relatively low E2 removal rate compared with those at acidic or neutral condition. For instance, the optimal dosage was 3.0 mg/L for PAA-3, 4.5 mg/L for PAA-2, 5.0 mg/L for PAA-1 and 5.0 mg/L for PAM with a low E2 removal rate of 64.8%, 46.1%, 40.3% and 24.7%, respectively. It was obvious that the pH affected the flocculation performance greatly, and the flocculants performed undesirablely at alkaline condition (pH = 10). At pH = 10, a large numbers of negatively charged OH^- groups caused the $-NH_2$ group of the flocculants to hydrolyze. Meanwhile, more OH^- groups would wrap the E2 colloids and form a negative group, and hence it increased the electrostatic repulsion and decreased the flocculants charge neutralization abilty [33]. Consequently, it deteriorated the flocculation performance. Besides, the hydrophobic E2 with the hydroxy chemical groups became more stable in the alkaline condition, which increased the E2 removal difficulty.

4.2. Floc size

The floc size was an important factor which influenced the flocculation performance of E2 removal. Large floc size was more conductive to E2 separation, while the small floc was hard for settlement, thus resulting a low removal efficiency. Fig. 8 displays the flocs size expressed as the median equivalent diameter (d_{50}) for the flocculants at various pH conditions. For each flocculant (PAA-3, PAA-2, PAA-1, and PAM), the floc size was in the following order: flocs at the neutral condition (pH = 7) > flocs at the acidic condition (pH = 4) > flocs at the alkaline condition (pH = 10). The polymer chain of the flocculant spread and extended well at neutral condition (pH = 7), and thereby it was suitable for the improvement of the bridging ability. Besides, the neutral condition coupled with a low charge repulsive force between the polymer and E2 colloid particles was also benefited for the flocculation occurrence. Moreover, it was found that the flocculant with a higher cationic degree showed a more larger floc size and the floc size was in the following order: PAA-3 > PAA-2 > PAA-1 > PAM, which indicated that the effect of charge neutralization played an key role in the E2 removal process. The more lager floc size always indicted an excellent flocculation behavior of the flocculants and a high E2

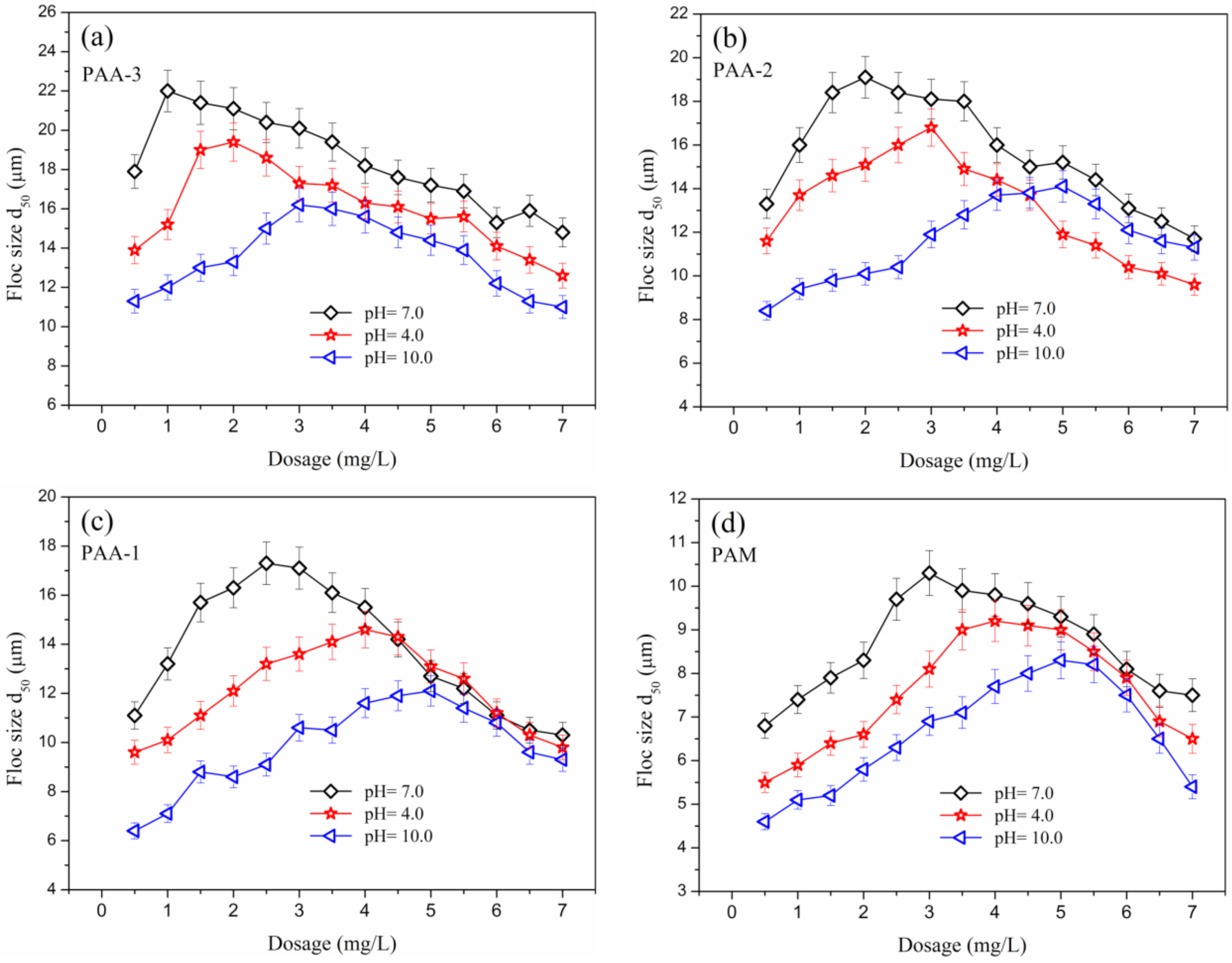

Fig. 8. The floc size for (a) PAA-3, (b) PAA-2, (c) PAA-1 and (d) PAM at various pH conditions.

removal and separation efficiency [25,27]. Besides, the PAM with a floc size ranged from 4.6 µm–10.4 µm also manifested that the effect of bridging and adsorption other than charge neutralization also made a contribution to a large floc size that was facile for the E2 separation and removal.

4.3. Effect of stirring speed, stirring time and sedimentation time

During the important stage of moderate stirring, the slow stirring stage was always used to promote the collision and contact between the relatively small flocs generated in the rapid mixing stage [34]. The polymer chains partially adsorbed on the surface of the small flocs would capture and intercept the approaching flocs to further grow to large flocs in the slow stirring stage. Meanwhile, the slow stirring resulted in a moderated shear force that would rebuild and reestablish the structure of the already formed flocs to obtain more compact flocs. Therefore, the effect of stirring speed and stirring time on the E2 removal was investigated and the results are shown in Figs. 9a and 9b.

In Fig. 9a, the E2 removal rate initially increased and then decreased with the increasing stirring speed at various pH conditions (pH = 4.0, 7.0 and 10.0). When the stirring speed at 120 rpm, the E2 removal rate reached the maximum. Because of the relatively low stirring speed, the collision and contact of the small flocs was not enough to achieve large and compact flocs. By contrast, when the stirring speed was too high, the hydrodynamic shear force would destroy the formed flocs, and hence these integrated flocs were broken down and their residues were left in the supernatant. As a result, the E2 removal rate was declined. Therefore, the stirring speed was set at 120 rpm in this experiments. As presented in Fig. 9b, the E2 removal rate sequentially increased within 2–10 min and a slight decline of E2 removal rate was observed with the further increasing of stirring time (>10 min). The insufficient stirring time brought a low efficient collision contact of the small flocs, and thus the bridging effect did not work completely in the agglomeration and growth of flocs [35]. As a result, the flocculation performance was undesirable. However, the formed flocs were fragile at excess stirring time, and which resulted in a decrease of settling property. Therefore, 10 min was selected as the suited stirring time in this experiments.

In Fig.9c, the effect of sedimentation time on the E2 removal rate was investigated to estimate the sedimentation property of flocs at various pH conditions (pH = 4.0, 7.0 and 10.0). It was evident that the flocculant PAA-3 showed a high efficiency on E2 removal rate within the first 5 min. Besides, the E2 removal rate increased slightly with the increase of sedimentation time from 5 to 30 min, and no further increase was observed when the sedimentation time exceeded 30 min. Meanwhile, a slight fluctuation of E2 removal rate was displayed in the range of sedimentation time from 30 to 60 min, and this phenomenon was due to the slow growth and settlement of small flocs. Thus, the sedimentation time was determined as 30 min in this experiment.

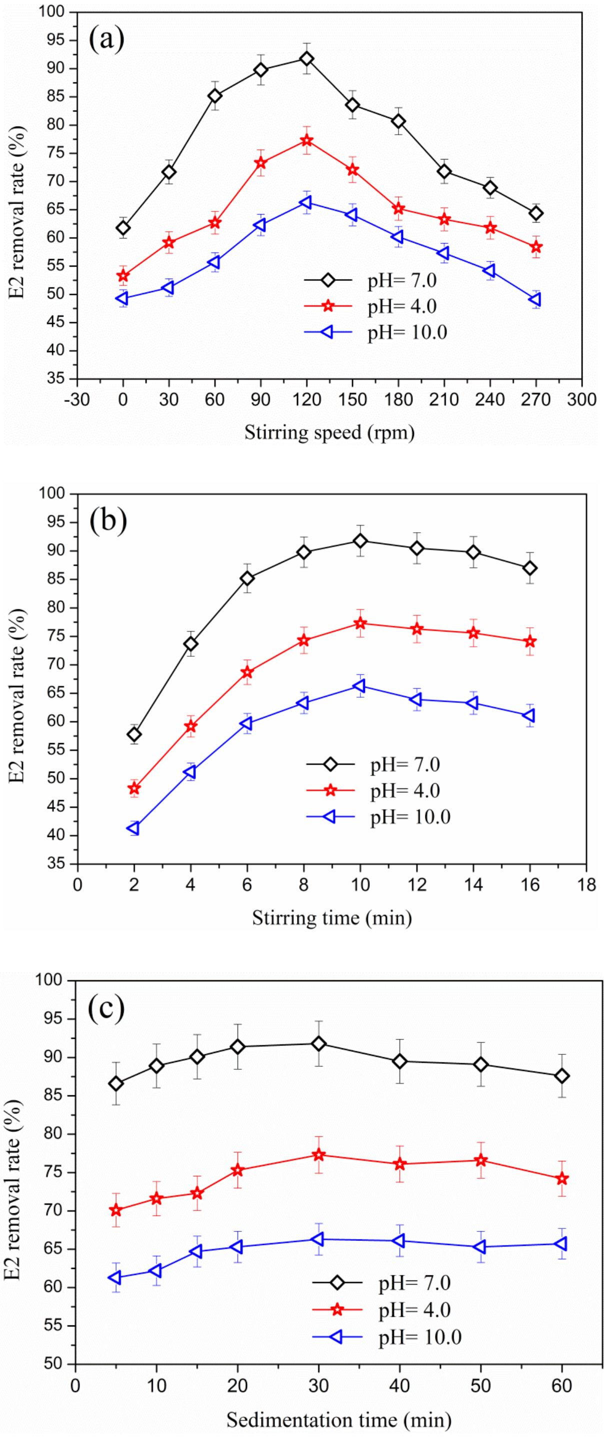

Fig. 9. The effect of (a) stirring speed, (b) stirring time and (c) sedimentation time on E2 removal rate at various pH conditions (PAA-3 was used).

4.3. Effect of the E2 concentration

The effect of the E2 concentration (0.2, 0.4, 0.6, 0.8 and 1.0 mg/L) on the PAA-3 flocculation performance was examined at pH = 7 and the result is displayed in Fig. 10. Obviously, the suited E2 concentration was 0.6 mg/L, and an excellent performance on the E2 removal was observed in this condition. The variation tendency of the E2 removal rate was similar at different E2 initial concentrations. It ini-

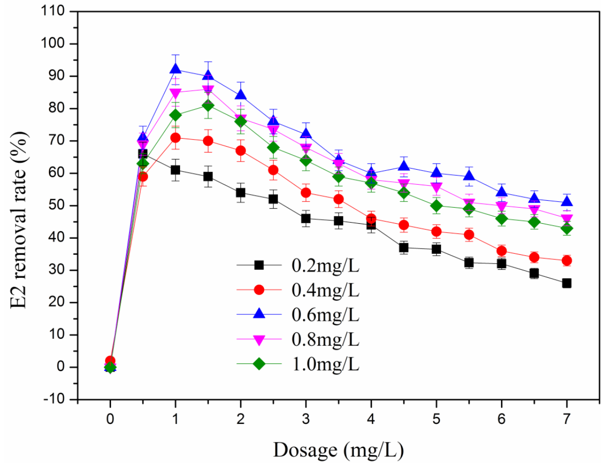

Fig. 10. The effect of the E2 concentration on the flocculation performance (PAA-3 was used).

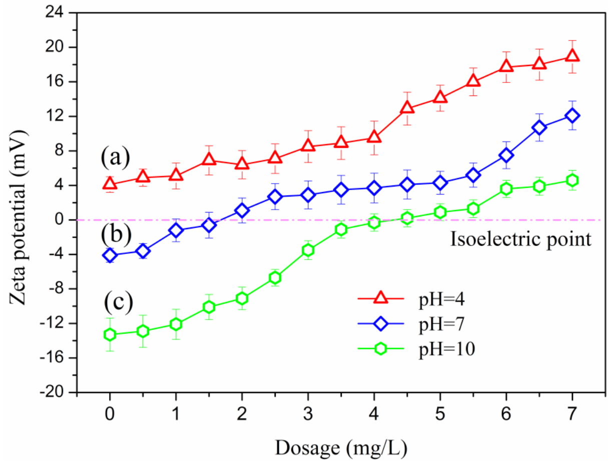

Fig. 11. The zeta potential after flocculation at (a) pH = 4, (b) pH = 7 and (c) pH = 10 (PAA-3 was used).

tially increased fast to a top value around at 1.0 mg/L and then gradually decreased with the increasing flocculant dosage. The rapid formation of large and compact flocs occurred in the condition of a relatively higher E2 initial concentration and an enough flocculant dosage through the effect of bridging and charge neutralization. When the E2 concentration exceeded a certain value, the excess flocculant dosage would cause the polymer chain of the flocculant to wrap around E2, and thus the flocculant exhibited protection rather than flocculation [27]. Therefore, the suited E2 initial concentration was determined as 0.6 mg/L for the flocculation performance in this experiment.

4.4. Flocculation mechanism

The analysis zeta potential was a vital and essential method to analyze the surface charge characteristics of the colloids, and thus further understanding the mechanism involved in the flocculation process [36,37]. As shown in Fig. 11, the zeta potential of the supernatant after flocculation at various pH conditions (pH = 4.0, 7.0 and 10.0) was investigated. The E2 illustrated a negative charge of –4.2 mV at pH = 7, and it changed with the variation of pH, which indicated that the pH condition had a huge compact on the E2 removal. Because the positive charge property of the cationic PAA-3, the zeta potential value at different pH conditions all presented an alike tendency of gradually increasing with the increase of dosage. The zeta potential was positive at the acidic condition (pH = 4), it indicated that the negative charged E2 colloids was completely neutralized through charge neutralization and aggregated together by bridging and cross linking effects. Meanwhile, the further increasing of flocculant dosage would result in a higher electrostatic repulsion, which reduced the flocculation efficiency. At the neutral condition (pH = 7), the desirable flocculation performance occurred around at the isoelectric point through the combination of charge neutralization and patching, adsorption and bridging. At the same time, it was suggested that the neutral condition was favorable for the E2 flocculation. At the alkaline condition (pH = 10), the zeta potential was negative when the flocculation dosage was less than 4.0 mg/L, and it would generate a strong charge repulsion between the E2 colloids. However, the suited PAA-3 dosage was 3.0 mg/L (<4.0 mg/L) and the E2 colloids charge repulsion appeared at the alkaline condition (pH = 10), it meant that the dominated effect was adsorption and bridging rather than charge neutralization [38].

Based on the above analyses, the possible flocculation mechanism was summarized and is shown in Fig. 12. Generally, there possible flocculation models were appropriately proposed for the acidic (pH = 4), neutral (pH = 7)and alkaline (pH = 10) conditions, respectively. Under the acidic condition (pH = 4), the E2 colloids and the flocculants were all positive charged, the generated electrostatic repulsion weakened the charge neutralization ability, and the adsorption and cross linking effects contributed much to large and loose E2 flocs. Under the neutral condition (pH = 7), the suited dosage was near with that of is electric point. The negatively charged E2 colloids was neutralized thoroughly by charge neutralization and the destabilized E2 colloids was captured and aggregated to form larger and denser E2 flocs under the effects of the bridging and patching. Under the alkaline (pH = 10) conditions, the flocculation system was negatively charged when the dosage less than 4 mg/L, which indicated that the main flocculation effect was adsorption rather than charge neutralization. In this case, the E2 flocs was gathered together to form small and loosen flocs just under the effect of bridging [39].

5. Conclusion

A flocculant PAA with different cationic degree was successfully prepared through ultrasonic-initiated copolymerization technique. The structure properties of the PAA was characterized by FT-IR, ^{1}H NMR, SEM and TG/DSC to confirm its successful formation. The PAA with different cationic degree was used in the E2 flocculation. The flocculation results manifested that the flocculant PAA-3 with 40% cationic degree had the most excellent E2 removal performance among PAA-2 (30% cationic degree), PAA-1 (20% cationic degree) and PAM. The flocculant with a higher

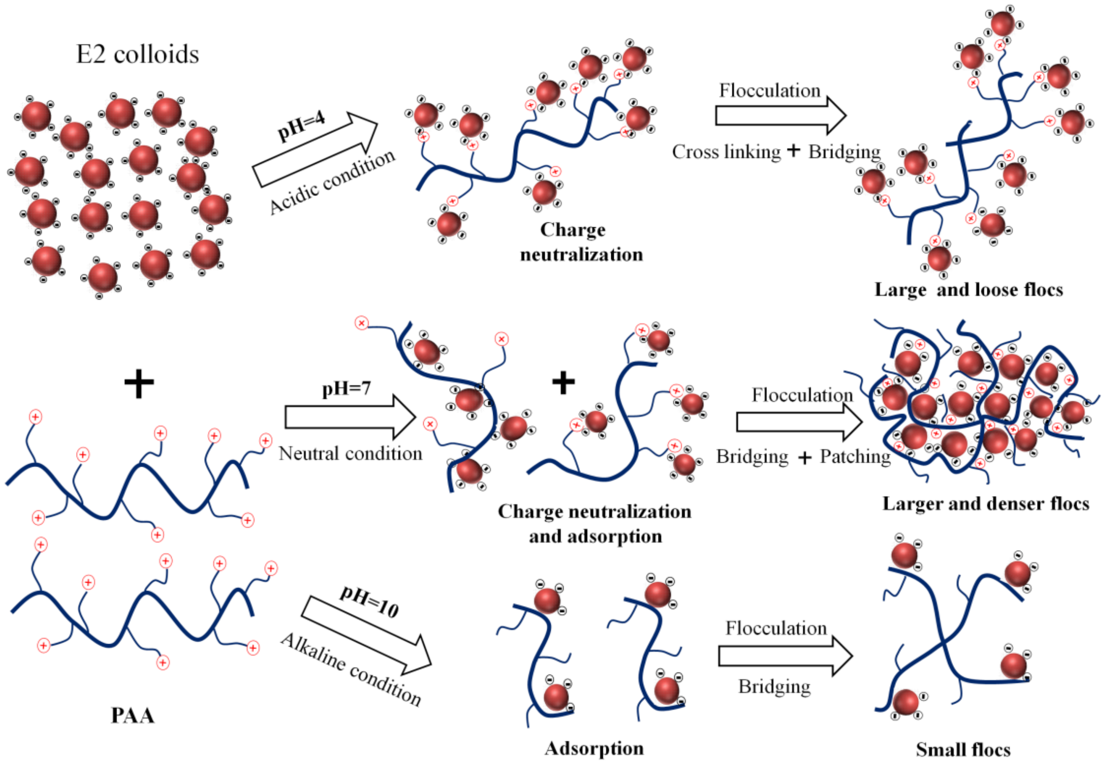

Fig. 12. The possible flocculation mechanism of the flocculant.

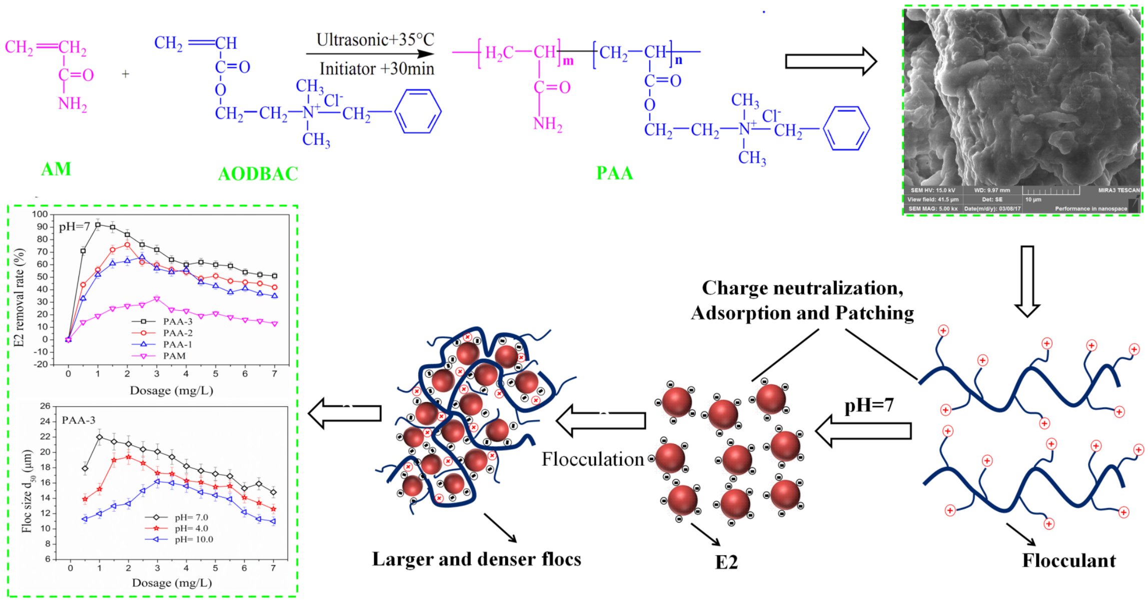

Fig. 13. Graphic abstract.

cationic degree had a stronger charge neutralization ability and a large number of active groups, and thus it was benefit for the improvement of flocculation performance. Meanwhile, the the neutral condition (pH = 7) was more favorable for the E2 flocculation no matter which kind of the flocculant was used. Moreover, the optimal flocculation conditions was concluded as a stirring speed of 120 rpm, stirring time of 10 min, sedimentation time of 30 min and E2 initial concentration of 0.6 mg/L. Finally, the involved flocculation mechanism was discussed for different pH condition. The analytical results suggested that the charge neutralization and adsorption effects happened together in the the neutral condition (pH = 7) rather than acidic (pH = 4) and alkaline (pH = 10), thus resulting a prominent flocculation performance.

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References

[1] A. Begum, S.K. Gautam, Dechlorination of endocrine disrupting chemicals using $Mg^0/ZnCl_2$ bimetallic system, Water Res., 45 (2011) 2383–2391.

[2] C. Jung, A. Son, N. Her, K.D. Zoh, J. Cho, Y. Yoon, Removal of endocrine disrupting compounds, pharmaceuticals, andpersonal care products in water using carbon nanotubes: A review, J. Ind. Eng. Chem., 27 (2015) 1–11.

[3] J. Jiang, S.Y. Pang, J. Ma, H.L. Liu, Oxidation of phenolic endocrine disrupting chemicals by potassium permanganate in synthetic and real waters, Environ. Sci. Technol., 46 (2012) 1774–1781.

[4] B. Yang, G.G. Ying, J.L. Zhao, S. Liu, L.J. Zhou, F. Chen, Removal of selected endocrine disrupting chemicals (EDCs)and pharmaceuticals and personal care products (PPCPs) during ferrate (VI) treatment of secondary wastewater effluents, Water Res., 46 (2012) 2194–2204.

[5] A.R. Reis, K. Tabei, Y. Sakakibara, Oxidation mechanism and overall removal rates of endocrine disrupting chemicals by aquatic plants, J. Hazard. Mater., 265 (2014) 79–88.

[6] N. Cai, P.L. Casanova, Sorption of carbamazepine by commercial graphene oxides: A comparative study with granular activated carbon and multiwalled carbon nanotubes, J. Colloid. Interf. Sci., 426 (2014) 152–161.

[7] H. Zhao, D. Zhang, P.H. Du, H.T. Li, C.M. Liu, Y.P. Li, H.B. Cao, J.C. Crittenden, Q.G. Huang, A combination of electro-enzymatic catalysis and electrocoagulation for the removal of endocrine disrupting chemicals from water, J. Hazard. Mater., 297 (2015) 269–277.

[8] A.J.C. Semião, A.I. Schäfer, Removal of adsorbing estrogenic micropollutants by nanofiltration membranes. Part A-Experimental evidence, J. Membr. Sci., 431 (2013) 244–256.

[9] V.M. Rwehumbiza, R. Harrison, L. Thomsen, Alum-induced flocculation of preconcentrated Nannochloropsis salina: Residual aluminium in the biomass, FAMEs and its effects on microalgae growth upon media recycling, Chem. Eng. J., 200 (2012) 168–175.

[10] K.E. Lee, T.T. Teng, N. Morad, B.T. Poh, Y.F. Hong, Flocculation of kaolin in water using novel calcium chloride-polyacrylamide ($CaCl_2$-PAM) hybrid polymer, Sep. Purif. Technol., 75 (2010) 346–351.

[11] L. Joseph, J.R.V. Flora, Y.G. Park, M. Badawy, H. Saleh, Y. Yoon, Removal of natural organic matter from potential drinking water sources by combined coagulation and adsorption using carbon nanomaterials, Sep. Purif. Technol., 95 (2012) 64–72.

[12] H.L. Zheng, L. Feng, B.Y. Gao, Y.H. Zhou, S.X. Zhan, B.C. Xu, Effect of the Cationic block structure on the characteristics of sludge flocs formed by charge neutralization and patching, Materials, 10 (2017) 478.

[13] B. Bolto, J. Gregory, Organic polyelectrolytes in water treatment, Water Res., 41 (2007) 2301–2324.

[14] Z. Yang, H. Yang, Z.W. Jiang, T. Cai, H.J. Li, H.B. Li, A.M. Li, R.S. Cheng, Flocculation of both anionic and cationic dyes in aqueous solutions by the amphoteric grafting flocculant carboxymethyl chitosan-graft-polyacrylamide, J. Hazard. Mater., 254 (2013) 36–45.

[15] L. Feng, H.L. Zheng, B.Y. Gao, C.L. Zhao, S.X. Zhang, N. Chen, Enhancement of textile-dyeing sludge dewaterability using a novel cationic polyacrylamide: role of cationic block structures, RSC Adv., 7 (2017) 11626–11635.

[16] K. Sankar, V. Rajendran, Ultrasound assisted free radical polymerization of glycidyl methacrylate by a new disite phase-transfer catalyst system: A kinetic study, Ultrason. Sonochem., 19 (2012) 1205–1212.

[17] K.H. Han, G.S. Jeon, I.K. Hong, S.B. Lee, Prediction of solubility parameter from intrinsic viscosity, J. Ind. Eng. Chem., 19 (2013) 1130–1136.

[18] J.P Wang, Y.Z. Chen, Y. Wang, S.J. Yuan, G.P. Sheng, H.Q. Yu, A novel efficient cationic flocculant prepared through grafting two monomerson to chitosan induced by gamma radiation, RSC Adv., 17 (2012) 494–500.

[19] X. Li, H.L. Zheng, B.Y. Gao, Y.J. Sun, X.M. Tang, B.C. Xu, Optimized preparation of micro-block CPAM by response surface methodology and evaluation of dewatering performance, RSC Adv., 7 (2017) 208–217.

[20] L. Feng, H.L. Zheng, Y.L. Wang, S.X. Zhang, B.C. Xu, Ultrasonic-template technology inducing and regulating cationic microblocks in CPAM: characterization, mechanism and sludge flocculation performance, RSC Adv., 7 (2017) 23444–23456.

[21] Y. Liao, H.L. Zheng, L. Qian, Y.j. Sun, L. Dai, W.W. Xue, 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., 53 (2014) 11193–11203.

[22] I. Gómez, E.M. Otazo, H. Hernández, E. Rubio, J. Varela, M. Ramírez, I. Barajas, A.J. Gordillo, Thermal degradation study of PVA derivative with pendant phenylthionecarbamate groups by DSC/TGA and GC/MS, Polym. Degrad. Stabil., 112 (2015) 132–136.

[23] J.T. Ma , P. Cui, L. Zhao, R.H. Huang, Synthesis and solution behavior of hydrophobic association water-soluble polymers containing arylalkyl group, Eur. Polym. J., 38 (2002) 1627–1633.

[24] S.Q. Shen, Z.F. Zhu, F.D. Liu, Introduction of poly[(2-acryloyloxyethyl trimethyl ammonium chloride)-co-(acrylic acid) branches onto starch for cotton warp sizing, Carbohyd. Polym., 138 (2016) 280–289.

[25] Z.A. Zhang, H.L. Zheng, F. Huang, X. Li, S.Y. He, C. Zhao, Template polymerization of a novel cationic polyacrylamide: sequence distribution, characterization, and flocculation performance, Ind. Eng. Chem. Res., 55 (2016) 9819–9828.

[26] Z.L. Yang, B.Y. Gao, C.X. Li, Q.Y. Yue, B. Liu, Synthesis and characterization of hydrophobically associating cationic polyacrylamide, Chem. Eng. J., 161 (2010) 27–33.

[27] L. Feng, H.L. Zheng, B.Y. Gao, S.X. Zhang, C.L. Zhao, Y.H. Zhou, B.C. Xu, Fabricating an anionic polyacrylamide (APAM) with an anionic block structure for high turbidity water separation and purification, RSC Adv., 7 (2017) 28918–28930.

[28] C. Margaritescu, M. Raica, D. Pirici, C. Simionescu, L. Mogoanta, A.C. Stinga, A.S. Stinga, D. Ribatti, Podoplanin expression in tumor-free resection margins of oral squamous cell carcinomas: an immuno histochemical and fractal analysis study, Histol. Histopathol., 25 (2010) 701–711.

[29] L.S. Zheng, Y.Q. Yang, X.D. Guo, Y. Sun, Y. Qian, L.J. Zhang, Mesoscopic simulations on the aggregation behavior of p H-responsivepolymeric micelles for drug delivery, J. Colloid. Interf. Sci., 363 (2011) 114–121.

[30] F. Kurayama, S. Suzuki, T. Oyamada, T. Furusawa, M. Sato, N. Suzuki, Facile method for preparing organic/inorganic hybrid capsules using amino-functional silane coupling agent in aqueous media, J. Colloid. Interf. Sci., 349 (2010) 70–76.

[31] F. Roselet, D. Vandamme, M. Roselet, K. Muylaert, P.C. Abreu, Effects of pH, salinity, biomass concentration, and algal organic matter on flocculant efficiency of synthetic versus natural polymers for harvesting microalgae biomass, Bioenerg. Res., 10 (2017) 427–437.

[32] E. Antunes, F.A.P. Garcia, P. Ferreira, A. Blanco, C. Negro, M.G. Rasteiro, Modelling PCC flocculation by bridging mechanism using population balances: Effect of polymer characteristics on flocculation, Chem. Eng. Sci., 65 (2010) 3798–3807.

[33] B.J. Liu, W.T. Meng, M.Y. Zhang, H.X. Zhang, In situ charge neutralization on governing particle coagulation nucleation and size distribution inmacroemulsion polymerization, RSC Adv., 6 (2016) 88701–88706.

[34] D.S. Wang, R.B Wu, Y.Z. Jiang, C.W.K. Chow, Characterization of floc structure and strength: Role of changing shear rates under various coagulation mechanisms, Colloid. Surf. A-Physicochem. Eng. Asp., 379 (2011) 36–42.

[35] K.E. Lee, N. Morad, T.T. Teng, B.T. Poh, Development, characterization and the application of hybrid materials in coagulation/flocculation of wastewater: A review, Chem. Eng. J., 203 (2012) 370–386.

[36] E.A.L. Maldonado, M.T.O. Guzman, J.L.J. Baizaval, A.O. Terán, Coagulation-flocculation mechanisms in wastewater treatment plants through zeta potential measurements, J. Hazard. Mater., 279 (2014) 1–10.

[37] P. Raj, W. Batchelor, A. Blanco, E. Fuente, C. Negro, G. Garnier, Effect of polyelectrolyte morphology and adsorption on the mechanism of nanocellulose flocculation, J. Colloid. Interf. Sci., 481 (2016) 158–167.

[38] H.L. Zheng, J.Y. Ma, C.J. Zhu, Z. Zhang, L.W. Liu, Y.J. Sun, X.M. Tang, Synthesis of anion polyacrylamide under UV initiation and its application in removing dioctylphthalate from water through flocculation process, Sep. Purif. Technol., 100 (2016) 201–210.

[39] J.Y. Ma, J. Shi, H.C. Ding, G.C. Zhu, K. Fu, X. Fu, Synthesis of cationic polyacrylamide by low-pressure UV initiation for turbidity water flocculation, Chem. Eng. J., 312 (2017) 20–29.