Novel cationic polyamidine: Synthesis, characterization, and sludge dewatering performance

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ABSTRACT

In this study, a new and facile route was employed for synthesis of polyamidine with abundant cations and attractive five-membered ringlike structural unit. N-vinylformamide and acrylonitrile copolymerized firstly to form intermediates, and the intermediates were processed with hydrochloric acid to produce polyamidine. A series of polymerization conditions (e.g. polymerization time, temperature and dosage of initiator) were optimized through productivity, viscosity and cationic degree as evaluation. SEM analysis illustrated that the amidinization process could reduce the size of spaces between molecular and created compact structure, which would contribute to good flocculation performance and high viscosity. FT-IR, XPS and NMR spectra presented a rather clear structure of polyamidine. 34.3% of sludge was sedimentated through the flocculation of polyamidine in the early stages. In contrast, only 6.8% of sludge was sedimentated by polyacrylamide. The moisture content in dehydrated floc could be reduced to 77.7% when 60 mg/L polyamidine was added. These results demonstrated that the polyamidine showed a great potential in the practical application of sludge dewatering.

Introduction

With the development of urbanization and industrialization, municipal sewage and industrial effluent treatments produced abundant sewage sludges. These sewage sludges can be used to prepare fertilizer, fodder, cement additive, fuel admixture after sludge dewatering and other further processes (Wu et al., 2010; Liang et al., 2014). However, the vast pathogenic bacteria, parasite, and heavy metals, especially the high water content (WC) in the sewage sludge (WC, 95%-98%) resulted in it being more difficult to stack, transport, further treat and re-use (Liu et al., 2015; Wang et al., 2016). Therefore, sludge dehydration should be the primary and emergent task for sludge treatment. In various types of sludge dewatering equipment, dewatering agents are always indispensable additives. Normally, the common dewatering agents are cationic polyacrylamide (PAM), nonionic PAM, anionic PAM and other novel chemical conditioners, like Fe(II)-activated persulfate oxidation (Addai-Mensah, 2007; Lin et al., 2012; Tanaka et al., 2014; Zhen et al., 2012a, 2012b, 2012c, 2013). As far as we know, there are still few reports related to the dewatering of sewage sludge that using polyamidine as flocculant.

As a kind of important intermediate in organic synthesis, amidine is widely used in pesticide and medicine, such as parasiticide, diuretic, antibiotic and anti-inflammatory (Khan et al., 2008). Amidine is an organic compound that the carbonyl oxygen in acylamino is replaced with imidogen. While, polyamidine is an organic compound containing...
amidine groups in polymer molecular chain. Generally, polyamidines possess two typical structures: linear-chain structure with amidine group as polymer backbone and cyclic structure with amidine group as pendant group. It is worth mentioning that this cyclic polyamidine containing five-membered rings is a cationic polymer, which shows exceptional performance such as high charge density, good stability and hypotoxicity. Consequently, polyamidine has recently gained growing interest in different fields—applications including papermaking, dyestuff and water treatment due to its good performance as flocculant.

The research and development of polyamidine have been nearly sixty years. The term polyamidine was first mentioned in 1959 by Grundman et al. (1959). Their work developed the field of polyamidine and resulted in several practical applications. Kurita et al. (1977) used the polyaddition of bisketenimines with various diamines to afford linear polyamidines. And then their structures were confirmed via elemental analysis and infrared characterization. Mathias and Overberger (1979) prepared an aromatic polymer containing formamide groups in the polymer backbone using aromatic diamines, a,a-dichloromethyl ether and triethylformate as monomers. Then these polymers were characterized by viscosity, microanalysis, and nuclear magnetic resonance and infrared spectroscopy (IR). Rillich et al. (1993) synthesized aliphatic polyformamidines by reaction of aliphatic diamines with triethylformate in the presence of catalytic amounts of acetic acid. The polymer structure has been confirmed by IR and nuclear magnetic resonance (NMR) spectroscopy. Sato et al. (1994) synthesized polyamidine with five-membered rings which feeds on N-vinylformamide and acrylonitrile. The products possessed high positive charge density and exhibited improved performance in dehydration, filtration and stability. Sawayama et al. (1995) improved the reaction conditions of polyamidine and studied its application in paper additive.

In addition, many scholars have devoted their efforts to the application of polyamidines (Lin et al., 2002; Sharavanan et al., 2004; Aleksandrova et al., 2004; Guo et al., 2015; Wang and Zhang, 2008; Jin et al., 2009). Lin et al. (2002) prepared a new chelating fiber from a hydrolyzate of poly(N-vinylformamide/acrylonitrile) by a wet-spinning method. The fiber has high binding capacities and good adsorption properties for heavy metal ions, such as Cu$^{2+}$, Cr$^{3+}$, Co$^{2+}$, Ni$^{2+}$, and Mn$^{2+}$. Sharavanan et al. (2004) studied hydrolytic degradation of an aliphatic polyacetalidinamide at different pH values. The degradation of polyamidine occurred at neutral and basic conditions whereas under acidic conditions the polyamidamine was stable. The results showed that aliphatic polyamidamines were potential carriers for active compounds which can be released by the hydrolytic degradation of the polymer (Sharavan et al., 2004). Aleksandrova et al. (2004) studied the photophysical properties and mechanism of charge-carrier photogeneration in supramolecular polyamidine structures. Wang and Zhang (2008) synthesized a ring-like polyamidine, characterized it by Fourier transform infrared spectra (FT-IR) and ultraviolet (UV), and got a good turbidity removal effect in sludge dewatering. Jin et al. (2009) prepared this cationic polymer by acidic hydrolysis of poly(N-vinylformamide-co-acrylonitrile) and used FT-IR and $^1$H NMR to prove that it contained cationic amine groups, cationic 5-member ring amidine groups and 6-member ring amidine groups. The application of polyamidine is still relatively new and is under development.

Herein, we reported on a novel cationic polyamidine which had five-membered ring-like unit in its structure. N-vinylformamide and acrylonitrile copolymerized firstly to form intermediates, and the intermediates were processed with hydrochloric acid to produce polyamidine. The polyamidine possessed high molecular weight and the amido in five-membered ring-like structural unit contributed to the high charge density. Moreover, this distinctive structure was conducive to extend in aqueous solution to contact more contaminants. All of the above advantages and the hydrophobicity of polymer would be beneficial to the dewatering of sludge. And some characterization methods were used to investigate the properties of cationic polyamidine, e.g. scanning electron microscope (SEM), ultraviolet-visible spectrum (UV–vis), FT-IR, thermogravimetric analysis–differential thermal gravimetric analysis (TG-DTG), X-ray photoelectron spectroscopy (XPS) and NMR spectra. Moreover, the prepared product has been successfully applied to sludge dewatering and shows good results, demonstrating its potential use in environmental protection.

1. Materials and methods

1.1. Materials

The chemical used in the polymerization experiment included N-vinylformamide (NVF), acrylonitrile (AN), 2,2’-Azobis(2-methylpropionamide) dihydrochloride (AIBA, high purity grade, purchased from BioDuly Co., Ltd., Nanjing, China). HCl and NaOH were supplied by Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Acetone, poly(vinylsulfate) potassium salt (PVSK), toluidine blue (T.B.) and other chemicals were of analytical reagent grade. Deionized water was used in the experiment. Sludge was drawn from secondary sedimentation tank of Guangda sewage treatment plant (Jinan, China). The collected sample was stored at 4°C. Within 48 hr of collection, the sludge was prepared for experimentation. The main characteristics of sludge are as follows: temperature 20.5°C, pH 6.7, turbidity 57.3 NTU, water content 99.4%, sludge settling ratio 86%, and mixed liquor suspended solids 5.85 g/L.

1.2. Methods of characterization

The surface morphology was examined using JEOL JSM-6480LV SEM with the magnification of 7000. A GBC Cintra 20 UV–vis spectrophotometer with 1.0 cm quartz cell was used for recording UV–vis spectra of intermediates and polyamidine. The FT-IR of polymer was recorded with Perkin–Elmer "Spectrum BX" spectrometer in the range of 4000–400 cm$^{-1}$. TG-DTG was carried out with thermo gravimetric analyzer (SHI-MADZU, TGA-50). The samples were heated from 10 to 800°C in N$_2$ flow at a rate of 10°C/min. XPS was used to analyze the surface binding state and elemental speciation of polyamidine. The measurements were performed by a spectrometer (ESCALAB 250) with MgK$_\alpha$ radiation (1486.71 eV of photons) as the X-ray source. And the sample was
characterized with NMR spectra (Varaininova600) to ensure the structure of polyamidine. The synthetic and following experiments were carried out in duplicate \( (n=2) \) and the mean values were presented here. The experimental error of results was within \( \pm 5\% \).

1.3. General method for copolymerization

The polymer was synthesized in water solution based on a mixture of NVF and AN with a molar ratio of 1:1. The compound was heated to 40–60°C under flow of nitrogen gas. Then copolymerization was started by adding 0.05–0.2 mL AIBA (1 g/L) as initiator and nitrogen gas stream continued for another 5 min. After 3–7 hr of copolymerization, 10 mL of concentrated hydrochloric acid and 20 mL of deionized water were added to the suspension. Then the mixture was heated to 110°C and held for 4 hr under stirring to amidinize the polymer. Extraction of the polymer was conducted in acetone and the precipitated polymer was dried under vacuum. Finally, it was purified with supercritical carbon dioxide (SCCO2) to remove the residual monomers and initiators, and then the solid cationic polyamidine was obtained. The process can be described as follows (Fig. 1).

1.4. Optimization tests for polyamidine polymerization conditions

1.4.1. Determination of the productivity

The reaction was a copolymerization of two monomers and the functional groups do not increase or decrease during the reaction. The productivity (\( \% \)) was calculated roughly by the ratio of the weight of solid polyamidine \( (m) \) and the weight of raw materials \( (M) \), which was shown in Eq. (1).

\[
\text{Productivity} = \frac{m}{M} \times 100\% \\
\tag{1}
\]

1.4.2. Determination of the viscosity

The viscosity of polyamidine solution was measured by Ubbelohde viscometer. To prepare the polyamidine solution, 0.1 g of polyamidine was dissolved in 100 mL deionized water. Then the solution was measured by Ubbelohde viscometer after being balanced for 20 min in the water bath under 20°C.

1.4.3. Determination of cationic degree

A certain amount of polyamidine \( (0.1 \text{ g}) \) was dissolved in 100 mL deionized water to prepare polyamidine solution with the concentration of 1 g/L. The solution \( (10 \text{ mL}) \) was diluted with the deionized water to 100 mL. Then 2–3 drops of T.B. indicator were added. PVSK standard solution was used to titrate until the color of the solution turned from blue to purple. Blank test was performed at the same time. The amount of PVSK was used to calculate the cationic degree \( (\text{mmol/g}) \) using Eq. (2).

\[
\text{Cationic degree} = \frac{(V-V_0) \times C}{m} \times 100\% \\
\tag{2}
\]

In Eq. (2), \( V \) (mL) is the volume of PVSK standard solution consumed by the sample, \( V_0 \) (mL) is the volume of PVSK standard solution consumed by the blank sample, \( C \) (mol/L) is the concentration of PVSK standard solution, and \( m \) (g) is the weight of the sample.

1.5. Tests of flocculation dewatering

A series of 100 mL of sludges were packed in 100 mL of measuring cylinder. Thereafter, the polyamidine \( (0, 1.5, 2, 3, 4, \text{ and 5 mL}) \) with concentration of 1 g/L was mixed with the sludges and stirred for 10 sec (concentrations of polyamidine in sludge: 0, 15, 20, 30, 40, 50 mg/L). The volumes of sedimentated sludges were then detected at different time.

A series of polyamidine \( (0, 1, 2, 3, 4, \text{ and 5 mL}) \) with a concentration of 1 g/L were added into 100 mL sludge suspensions and stirred for 10 sec (dosage of polyamidine was given as 0, 10, 20, 30, 40, 50 and 60 mg/L). The turbidity of supernatant was then measured after sedimentation for 30 min. This sedimentated sludge was first pretreated by vacuum filtration for 5 min and weighted. The filtered sludge was put in constant temperature drying oven until constant weight (105°C). The moisture content of sludge was then evaluated.

![Fig. 1 – Synthesis procedure of polyamidine.](image-url)
2. Result and discussion

2.1 Optimization of polymerization conditions for polyamidine

Before the tests of characterization and dewatering performance of polyamidine, optimization of polymerization conditions should be determined. The optimization conditions were based on the polymerization temperature, polymerization time and initiator dosage.

2.1.1. Temperature and time optimization

Optimization of polymerization conditions that were based on the temperature (40, 45, 50 and 60°C) is shown in Fig. 2a. The productivity and relative viscosity of polyamidine were first increased and then decreased as the temperature increased from 40 to 60°C. The productivity reached a maximum at temperature of 45°C and the optimal relative viscosity achieved at temperature of 50°C. It was obvious that the relative viscosity increased significantly (from 1.42 to 1.64) with a narrow increase in temperature from 45 to 50°C, while productivity showed little change from 45 to 50°C. As a result, 50°C was considered as the optimal temperature.

At the beginning of temperature-rise period, the rising temperature would accelerate the decomposition of initiator. In this process, the solution was polymerized slowly which resulted in the increase in viscosity. This phenomenon was assigned to the high growth rate of free radicals that overcame the negative effect of cage effect. When the reaction temperature exceeded 50°C, the reaction speed increased rapidly, partially due to the increase in solution flowability and decrease in cage effect. The monomer polymerized rapidly in a short term, and the solution viscosity increased rapidly to form semisolid, even presented vitrification. The increase of viscosity reduced the free space of monomer and free radical remarkably. Consequently, the speed of polymerization was suppressed by the reduction of diffusion rate of monomer and free radical, which resulted in the decrease in the productivity.

The productivity of polymer that was affected by polymerization time (3–7 hr) was evaluated and the results are shown in Fig. 2b. Results indicated that time of polymerization would also dominate the productivity of polymer to some extent. The productivity was increased with the rise in polymerization time and the productivity was almost constant at time of 5–7 hr. This indicated that polymerization time of 5 hr would be optimal for polymerization of polyamidine.

2.1.2. Amount of the initiator optimization

Productivity, cationic degree and relative viscosity of polyamidine that was determined by the amount of initiator (0.05, 0.10, 0.15 mL) effects of initiator dosage on the productivity and the cationic degree of polyamidine at time: 5 hr, temperature: 50°C, effects of initiator dosage on the viscosity of polyamidine solution at time: 5 hr, temperature: 50°C. In this process, the solution was polymerized slowly which resulted in the increase in viscosity. This phenomenon was assigned to the high growth rate of free radicals that overcame the negative effect of cage effect. When the reaction temperature exceeded 50°C, the reaction speed increased rapidly, partially due to the increase in solution flowability and decrease in cage effect. The monomer polymerized rapidly in a short term, and the solution viscosity increased rapidly to form semisolid, even presented vitrification. The increase of viscosity reduced the free space of monomer and free radical remarkably. Consequently, the speed of polymerization was suppressed by the reduction of diffusion rate of monomer and free radical, which resulted in the decrease in the productivity.

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Fig. 2 – Effects of temperature (a) on the productivity and relative viscosity of polyamidine at time: 5 hr, dosage of initiator: 0.15 mL, effects of polymerization time (b) on productivity at temperature: 50°C, dosage of initiator: 0.15 mL, effects of initiator dosage on the productivity and the cationic degree of polyamidine (c) at time: 5 hr, temperature: 50°C, effects of initiator dosage on the viscosity of polyamidine solution (d) at time: 5 hr, temperature: 50°C. *,**: 0.05 mL initiator polymerization did not happen.
and 0.20 mL) are shown in Fig. 2c and d. Results indicated that a low initiator dosage (0.05 mL) was not enough to initiate the polymerization of the monomers. The productivity of polyamidine increased with the increased in initiator dosage from 0.1 to 0.15 mL (Fig. 2c). When the initiator dosage was more than 0.15 mL, the productivity of polyamidine decreased. Cationic degree of polyamidine as a function of initiator dosage was also determined and the degree was first increased and then decreased with the amount of initiator increased (Fig. 2c). It reached the maximum when the initiator dosage was 0.15 mL. The relative viscosity of the polyamidine also achieved the maximum when the initiator dosage was 0.15 mL (Fig. 2d). These results indicated that the monomers could not polymerize completely at low initiator dosage. But both the molecular weight of polymer and viscosity of solution were decreased when dosage of initiator was higher (0.2 mL). Considering the effects of initiator dosage on the productivity, cationic degree and viscosity of polyamidine, 0.15 mL of initiator was selected as the optimum dosage. The detailed illustration was discussed as follows.

The low dosage of initiator (0.05 mL) could not overcome the negative effect of cage effect, so the polymerization reaction did not happen. When it further increased to 0.1 mL, more free radicals that existed in the reaction system would make the reactions occur easily and the productivity reached a maximum with the dosage of initiator increased to 0.15 mL. While the dosage of initiator was high enough to 0.2 mL, the produced free radicals would speed up the reaction velocity. The monomer polymerized rapidly in a short term, and the solution viscosity increased rapidly to form semisolid, even forming vitrification, which would inhibit the productivity.

For intrinsic viscosity, the low viscosity would be observed with less initiator (0.10 mL), partially due to the low concentration of free radicals, low degree of polymerization and slow polymerization rate. When the dosage was increased to 0.15 mL, a series of advantageous polymerization conditions have been reached, such as increased free radicals concentration, the increasingly rapid polymerization rates. The productivity increased and viscosity attained its maximum 1.67 at this dosage. When the dosage exceeded 0.2 mL, excessive free radicals that were originated from higher initiator dosage would lead to more polymerization point or copolymerization point. The competition for monomers by excessive active centers resulted in the decrease in the degree of polymerization, which led to the decrease of viscosity.

Basically, polymerization temperature of 50°C, polymerization time of 5 hr and 0.15 mL of initiator were employed for optimizing the polymerization conditions of polyamidine. The optimized polyamidine was then used in subsequent characterization and dewatering performance tests.

### 2.2. Characterization of the polyamidine

#### 2.2.1. SEM of intermediate product and polyamidine

The morphology of intermediate product and polyamidine was observed by SEM. As shown in Fig. 3a, the intermediate product was randomly compact and stacked together, showing platy morphology. There were a lot of empty spaces in the polymers. After processing, the polyamidine was apparently dense with relatively homogenous structure morphology (Fig. 3b, ×5000; Fig. 3c, ×10,000). The treatment could reduce the size of spaces between molecular and create compact structure. This would provide high viscosity and therefore contribute to the satisfied flocculation capacity.

#### 2.2.2. UV–visible spectrum and FT-IR spectrum

The intermediate product and polyamidine were analyzed using UV–vis after being dissolved in dimethylsulfoxide to study its functional groups. The results were shown in Fig. 3d. An obvious peak appeared at about 270 nm indicated carbonyl groups in intermediate product. Contrastively, the peak of polyamidine was shifted to 220 nm and the peak at 270 nm was almost disappeared. This change indicated that carbonyl groups were transformed to amidine groups with conjugated double bond due to the amidinization process.

FT–IR was used to characterize the functional groups on polyamidine (Fig. 3e). A stretching vibration of the NH bond was located at 3445.53 cm⁻¹. The weak C=N bond at 2241.86 cm⁻¹ corresponded to the CN groups and it was reduced during amidinization process. A peak at 1574.40 cm⁻¹ was assigned to the NH bending vibration. Compared with the range of wave number of normal secondary amine, the NH bending vibration was shifted to a higher wave number indicating that there was a strong electron withdrawing group on it. This phenomenon might be attributed to the Cl⁻ group. The stretching vibrations of C=N and C≡N were observed at 1415.91 cm⁻¹ and 1126.33 cm⁻¹, respectively, which demonstrated that amidinization reaction had already proceeded.

#### 2.2.3. TG-DSC curves

Fig. 3f shows TG-DTA curves of polyamidine powder. Loss of humidity, phase transition and degradation processes can be seen from the curve (Juntapram et al., 2012; Azarifar et al., 2013). Attributed to the evaporation of absorbed water, the initial endothermic first stage occurred in the range of 17–140°C with a mass loss of 2.8%. An endothermic small peak at 196.7°C was assigned to the glass transition temperature (Tg) of polyamidine. As the temperature rises, a sudden large loss occurred above 185°C. The large weight loss above 185°C was caused by the thermal decomposition of the polymer and an endothermic DTA peak corresponded to this decomposition. A large weight loss of 77.3% was attributed to the thermal degradation of polymer backbone, with an enthalpy of 1091 J/g. All these results showed that the prepared polyamidine was stable at room temperature, which provided support for the next test.

#### 2.2.4. XPS analysis

Surface measurements by XPS were carried out for intermediate product and polyamidine. Fig. 4 shows the wide spectra and detailed regions acquired for the intermediate product and polyamidine. There were only three elements (C, N and O) in Fig. 4a1. Because polyamidine was obtained by heating intermediate product in solution of HCl, Cl functionalities was analyzed in the wide spectra of polyamidine (Fig. 4b1).

The C 1s spectrum of the intermediate product and polyamidine (Fig. 4a2 and b2) surface comprised a major peak component at a binding energy (BE) of 284.6 eV, associated with the C-C and C-H species (Deng et al., 2003; Dąbrowska et al., 2013; Balaji et al., 2016). And two minor peak components with
Fig. 3 – Scanning electron microscope (SEM) analysis of intermediate product (a, ×5000) and polyamidine (b, ×5000; c, ×10,000), UV–visible spectrum (d) of intermediate product and polyamidine, Fourier transform infrared (FT-IR) spectrum (e), thermogravimetric analysis-differential thermal gravimetric analysis (TG-DSC) curves (f) of polyamidine.

Fig. 4 – X-ray photoelectron spectroscopy (XPS) of intermediate product (a1), C1s (a2), N1 s (a3), O1s (a4); XPS of polyamidine (b1), C1s (b2), N1 s (b3), O1s (b4), Cl2p (b5).
BEs at 286.1 and 287.9 eV were attributable to the carbon atom bonded to nitrogen in C–N, C=N in ring, and carbon double bonded to oxygen (C=O), respectively (Ren et al., 2016; Xu et al., 2016). The N 1s spectrum consisted of two peak components for the intermediate product: a major peak component attributable to the C–N species at the BE of 399.5 eV, and a minor one at 400.2 eV attributable to the C–N species (Zhang et al., 2014) (Fig. 4a3 and b3). Curve fitting of the O1s photopeaks of the XPS spectra (Fig. 4a4 and b4) showed the existence of C=O (BE: 531.6 eV). The XPS data of Cl2p (Fig. 4b5) photo-peaks yielded components at 199.1 and 197.5 eV. They could be assigned to the chlorine of chemical adsorption and chloramine groups (Debiemme-Chouvy et al., 2007; Xu et al., 2013).

2.2.5. 13C NMR and 1H NMR spectra
The 13C NMR and 1H NMR spectra of polyamidine are shown in Fig. 5. Series peaks round δ 40 in the 13C NMR spectrum (Fig. 5a) could be assigned to carbon skeleton –CH–CH2–. The highest chemical shift (δ 56.8) could be assigned to –N=CH– group. The observed peak at δ 121.0 was assigned to C═N and the peak at δ 171.3 corresponded to C═N, which further validated the five-membered ring-like structural unit. The four peaks from δ 112.8 to 118.6 were C–F group and the peak at δ 161.9 was C═O group. Both of them originated from the trifluoroacetic acid as solvent. For the 1H NMR spectrum (Fig. 5b), the peak at δ 3.2 ascribed to –CH–C═N, δ 1.9 ascribed to –CH2–, δ 4.0 ascribed to –CH–N and δ 2.6 ascribed to –CH–CN in the polymerization unit. Combined with those aforementioned characterizations, a rather clear structure of polyamidine was presented in Fig. 5c.

2.3. Flocculation dewatering effect of polyamidine

2.3.1. Sludge sedimentation through the flocculation of polyamidine
The relation between the volume of sludge (reflecting the flocculation dewatering effect on sludge), additive dosage of polyamidine and flocculation time was shown in Fig. 6a. The sedimentation effect was enhanced when the additive dosage of polyamidine was increased from 0 to 5 mL (30 min). When the additive dosage of polyamidine reached 40 mg/L, flocculation effect achieved optimal performance (volume of sludge could be reduced to 45.0%). Similarly, the sedimentation effect was increased as the increase in flocculation time in the same dosage of polyamidine, and began to flatten after 10 min. All these results demonstrated good flocculation dewatering effect of polyamidine on sludge.

A dosage (40 mg/L) of PAM was also employed to show its flocculation dewatering effect on sludge and result indicated that volume of sludge could be reduced to 55.6%. Compared with the PAM, polyamidine (40 mg/L) showed remarkable results of sludge settling (Fig. 6b). Favorable flocculation effect can be observed in the beginning of polyamidine injection. There is obvious difference starting within the first 1 min. Through the flocculation of polyamidine 34.3% of sludge was sedimentated. In contrast, only 6.8% of sludge was sedimentated by the PAM. After 30 min, more than half of sludge was sedimentated through the flocculation of polyamidine.

A possible sludge dewatering mechanism of polyamidine was proposed as shown in Fig. 7. The dewatering mechanism mainly depends on hydrophobic regions and cationic groups (Lv et al., 2014). The mechanism may be considered to consist of adsorption, flocculation, and dehydration processes. The colloid of sludge carried negative charge, while polyamidine was rich in positive charge. Polyamidine could neutralize some electric charge of sludge colloidal particles and made colloidal particles to sedimentate. With the charge neutralization, the surface tension of colloidal particles would be weakened. The bridge connection action of polymer could link other colloidal particles to form flocs. The capillary water and absorbed water in the flocs could be removed by the tighten role in molecular chain and the extrusion of sludge coagulum.

Fig. 5 – 13C nuclear magnetic resonance (NMR) spectrum (a), 1H NMR spectrum of polyamidine (b) and scheme evaluated based on 1H NMR spectrum of polyamidine (c).
2.3.2. Turbidity of supernatant

A series of polyamidine (0, 1, 2, 3, 4, 5 and 6 mL) with a concentration of 1 g/L were added into 100 mL of sludge suspensions and stirred for 10 sec (dosage of polyamidine was given as 0, 10, 20, 30, 40, 50 and 60 mg/L). The turbidity of supernatant was measured after sedimentation for 30 min. As shown in Fig. 8a, the turbidity of supernatant was decreased gradually from 58.5 to 10.3 NTU with the increase of polyamidine dosage from 0 to 60 mg/L. A better effect can be obtained at 30–60 mg/L polyamidine for the removal of turbidity (80.0%–84.6%); this also validated the availability of polyamidine as a novel flocculant.

Moisture content of sedimentated sludge that was dehydrated via vacuum filter was also determined (Fig. 8b), and finally, the moisture content in dehydrated sludge could be reduced to 77.67% when 60 mg/L polyamidine was added. This indicated that the capillary water and absorbed water in the flocs could be removed by the using of polyamidine through the tighten role in

Fig. 6 – Effects of polyamidine dosage on the flocculation effect (a), comparison of flocculation effect between PAM and polyamidine (b).

Fig. 7 – Possible sludge dewatering mechanism for the polyamidine.

Fig. 8 – Turbidity of supernatant (a) and moisture content (b) as a function of dosage of polyamidine.
molecular chain and the extrusion of sludge coagulum. As a consequence, polyamidine is expected to have wide applications in sludge dewatering.

As might be expected, a good performance of polyamidine in enhancing sludge dewatering was observed. A further research on the mechanism of enhancing sludge dewatering would be carried out in our future work.

3. Conclusion

In this investigation, polyamidine was synthesized by copolymerization of N-vinylformamide and acrylonitrile with a molar ratio of 1:1 using AIBA (0.15 mL) initiation at 50°C for 5 hr. SEM, UV–vis and TG-DTG were measured to characterize the prepared polyamidine. The results of FT-IR, XPS and NMR indicated that the molecules of the polyamidine consisted of a five-membered ring-like structural unit. The stronger hydrophobic regions and cationic degree in the polyamidine molecule were beneficial for improving sludge dewaterability. Experimental data showed that polyamidine possessed good flocculation dewatering effect. As a consequence, polyamidine is expected to have wide applications in sludge dewatering.

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