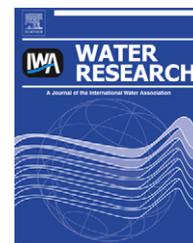


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Synthesis, characterization and application of a novel starch-based flocculant with high flocculation and dewatering properties

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ABSTRACT

Flocculation process is one of the most widely used techniques for water and wastewater treatment, and also for sludge dewatering. Synthesis of natural biopolymers or modification of natural biopolymers as environmentally friendly flocculants is highly desired in the field of environmental protection. In this work, a water soluble copolymer flocculant, STC-*g*-PDMC (starch-graft-poly (2-methacryloyloxyethyl) trimethyl ammonium chloride) was synthesized through grafting a monomer, (2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC), onto starch initiated by potassium persulphate. Acetone and ethanol were used for copolymer precipitation and purification in the synthesis, which diminished the toxicity during the synthesis process. The graft copolymer was characterized using Fourier-transform infrared spectroscopy, ¹H nuclear magnetic resonance, X-ray powder diffraction, thermogravimetric analysis and elemental analysis. The prepared STC-*g*-PDMC exhibited a highly effective flocculation capability for kaolin suspensions compared with starch and polyacrylamide as control. The charge neutralization effect played an important role in the flocculation process at low flocculant dosages. When it was used as dewatering agent for anaerobic sludge, the conditioned sludge could be easily filtered after the dosage reached 0.696% of the dry weight of sludge. Such a graft copolymer is a promising green agent for wastewater treatment and sludge dewatering applications.

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1. Introduction

Flocculants play an important role in flocculation process, one of the most widely used cost-effective techniques for water and wastewater treatment, and also for sludge dewatering (Bolto and Gregory, 2007; Harif et al., 2012; Jarvis et al., 2012; Pourrezaei et al., 2011; Rebhun et al., 1998; Yang et al., 2012; Zhang et al., 2010). Although inorganic and synthetic organic polymer flocculants exhibit high efficiency and popularity in flocculation process in the past several decades,

some of them often lead to secondary pollution and new environmental problems (Song et al., 2010; Xing et al., 2010). Therefore, synthesis of natural biopolymers or modification of natural biopolymers as environmentally friendly flocculants is still highly desired. Compared with the traditional inorganic flocculants and synthetic organic flocculants, the modified natural biopolymers are generally nontoxic and biodegradable (Kaith et al., 2010; Lanthong et al., 2006; Moreno-Chulim et al., 2003), which is essential from a sustainability point of view.

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Starch, one of the most abundant natural organic resources in the world, has been modified to yield highly efficient and environmentally friendly flocculants. (Chen et al., 2007; Hebeish et al., 2010; Jiang et al., 2010; Xing et al., 2010; You et al., 2009). Various modification methods have been employed, such as etherification (Jiang et al., 2010; Moghadam et al., 2007), esterification (Chen et al., 2007), oxidation (Mathew and Adlercreutz, 2009; Tolvanen et al., 2009), cross-linking (Kaith et al., 2010; Ozmen et al., 2008) and graft copolymerization (Li et al., 2007; Zhang and Zhuo, 2000) with the hydroxyl group on the starch backbone.

Among these modification methods, grafting has been proven to be a convenient and effective approach, facilitating the improvement of flocculation ability (Li et al., 2007; Zhang and Zhuo, 2000). Grafting can combine some of the properties of both initial components and meanwhile generate some new features for specific application purposes. The flexible long chain grafted onto the rigid or semi-rigid backbone can increase the conformational freedom of flocculant in solution and surface, which enhances adsorption and bridging effects. In order to improve flocculation ability, the grafting reaction can introduce specific functional groups into the original polymer through the selection of suitable monomers. In addition, the graft copolymer based on natural organic polymer is usually renewable and biodegradable to a large extent thanks to the polysaccharide backbone (Song et al., 2010).

Colloids in water and sludge are usually negatively charged, and thus the cationic flocculant is suitable for charge neutralization, and favorable for flocculation. However, synthetic cationic polymers, such as PDMC [poly (2-methacryloyloxyethyl) trimethyl ammonium chloride] and PDMDAAC [poly(dimethyldiallylammonium chloride)], are on one hand expensive, and on the other hand hydrophilic, which makes them difficult for transportation and storage, and thus holdbacks their extensive application. Moreover, their molecular weights are usually not sufficiently high, which is another evident drawback for its utilization as a flocculant. Thus, synthesis of a cationic biopolymer flocculant to overcome these disadvantages of the traditional synthetic cationic polymers is greatly desirable.

Therefore, in this study, in order to synthesize a highly efficient and environmentally friendly flocculant with a broad utilization range, a cationic vinyl monomer, (2-methacryloyloxyethyl) trimethyl ammonium chloride (DMC), was selected for being grafted onto the natural organic polymer, starch, initiated by potassium persulphate (KPS). The grafting of DMC onto starch backbone was expected to introduce cationic properties and increase molecular weight, and thus improve the flocculation ability. During the synthesis process, acetone and ethanol were used to precipitate the copolymer in the solution and to remove the homopolymer, respectively. These two solvents could avoid the toxicity coming from the solvents in the purification process. After the preparation of the newly graft copolymer, STC-*g*-PDMC (starch-graft-poly(DMC)), its flocculation and dewatering abilities were evaluated with kaolin suspensions and anaerobic sludge respectively. This work is expected to present a new green water-soluble flocculant with a high flocculation efficiency and dewatering capability.

2. Material and methods

2.1. Materials

Starch was purchased from Sinopharm Chemical Reagent Co., China. DMC, polyacrylamide (PAM), acetone, ethanol and KPS, all of analytical reagent grade, were purchased from Shanghai Chemical Reagent Co., China. All the reagents were used directly without further purification. Kaolin (6250 mesh, 2 μ m) was obtained from Sanhe Kaolin Ltd., China. Anaerobic sludge was obtained from Wangxiaoying Wastewater Treatment Plant, Hefei, China.

2.2. Graft copolymerization of DMC onto starch

A given amount of starch was added into boiled water to achieve a concentration of 5%. The solution was heated and stirred by a magnetic stir bar until it became clear. After the solution was cooled down to room temperature, DMC solution was added with a constant stirring and bubbling of a slow stream of nitrogen. Then, the reaction container was placed in a preset water bath and a given amount of KPS was added into the solution as an initiator. After that, the mixture was continuously stirred under nitrogen atmosphere. At the end of the reaction, the grafted polymer was precipitated in acetone and separated through filtration. Thereafter, the homopolymer formed in the reaction was removed using ethanol in Soxhlet apparatus. The extracted products were dried in a vacuum oven at 50 °C until a constant weight was obtained. The grafting percentage was calculated according to the following equation:

$$\% \text{ grafting} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where W_1 and W_2 are the weights of original and grafted samples, respectively.

2.3. Characterization of the graft copolymer

Infrared spectra of starch and the graft copolymer were recorded with a Fourier-transform infrared spectroscopy (FTIR) spectrometer (Magna-IR 750, Nicolet Instrument Co., USA) using a potassium bromide disc technique. The ^1H nuclear magnetic resonance (^1H NMR) spectra were measured with a 300-MHz spectrometer (AVANCE) with standard pulse programs in D_2O . X-ray powder diffraction (XRD) patterns of the polymers were obtained with an X-ray diffractometer (D/Max-rA, Japan) with graphite monochromatized Cu K α radiation ($\lambda = 1.54056\text{\AA}$). Thermogravimetric analysis (TGA) of starch and the graft copolymer was performed using a thermal analyzer (TGA-50, Shimadzu Co., Japan) under nitrogen atmosphere with a heating rate of 10 °C/min to 800 °C. Elemental analysis was performed on an automatic elemental analyzer (Vario EL III, Hanau, Germany).

2.4. Jar tests

As the most extensively used flocculant for wastewater treatment, PAM (with a MW 3×10^6) was selected as a control

to evaluate the flocculation ability of STC-g-PDMC in this study. Flocculation abilities of starch, PAM and STC-g-PDMC were evaluated using 0.25 wt% of kaolin suspension as described previously (Wang et al., 2007). The flocculants in solution form were added into 500-mL kaolin suspension. The suspension was then immediately started to stir at a constant speed of 200 rpm for 2 min, followed by a slow stirring at 40 rpm for 10 min. Thereafter, the sample was left to settle down for 5 min. At the end, the transmittance of the solution was measured at a wavelength of 420 nm.

2.5. Sludge conditioning tests

The dewatering ability of the graft copolymer for sludge was measured using Buchner funnel test, the most common method for dewatering ability measurement (Lo et al., 2001). A certain dosage of flocculant was added into 80 mL sludge at a stirring of 200 rpm for 0.5 min. Then, the conditioned sludge was poured into a Buchner funnel to filter under a vacuum pressure of 0.06 MPa for 30 min or until the vacuum could not be maintained (in <30 min). The filterability of the sludge is measured by the specific resistance of the sludge (R):

$$R = \frac{2PA^2b}{\mu\omega} \quad (2)$$

where R is the specific resistance of the sludge (m/kg); P is the filtration pressure (N/m²); A is the filter area (m²); μ is the viscosity of the filtrate (N s/m²); ω is the weight of cake solids per unit volume of filtrate (kg/m³), which can be calculated using the following equation:

$$\omega = 1/C_i / (100 - C_i) - C_f / (100 - C_f) \quad (3)$$

where C_i is the initial moisture content, %; C_f is the final moisture constant, %; b is the slope of filtrate discharge curve (t/V versus V) (s/m⁶), where t is the filtration time (s) and V is the volume of the filtrate. Afterwards, the sludge cake was dried at 105 °C until a constant weight was obtained.

3. Results and discussion

3.1. Physicochemical characteristics of STC-g-PDMC

Fig. 1 shows the infrared spectroscopy of starch and the STC-g-PDMC. Three new adsorption peaks, at 1729, 1480 and 953 cm⁻¹, were observed in the spectrum of the STC-g-PDMC compared with starch. The new peak at 1729 cm⁻¹, came from the vibrating adsorption of carbonyl groups in the grafting PDMC. The other two peaks at 1480 cm⁻¹ and 953 cm⁻¹ could be assigned to the methyl groups of ammonium and quaternary ammonium in PDMC, respectively. The appearance of the new peaks in the spectrum of the STC-g-PDMC indicated that DMC was successfully grafted onto starch. The grafting reaction is illustrated in Fig. 2.

The ¹H NMR spectroscopy of the STC-g-PDMC and the corresponding assignment of the signals are shown in Fig. 3. The most significant signal at 3.2 ppm was attributed to the spectrum of protons of the methyl groups on the quaternary ammonium salt. The protons of hydroxyl groups in starch

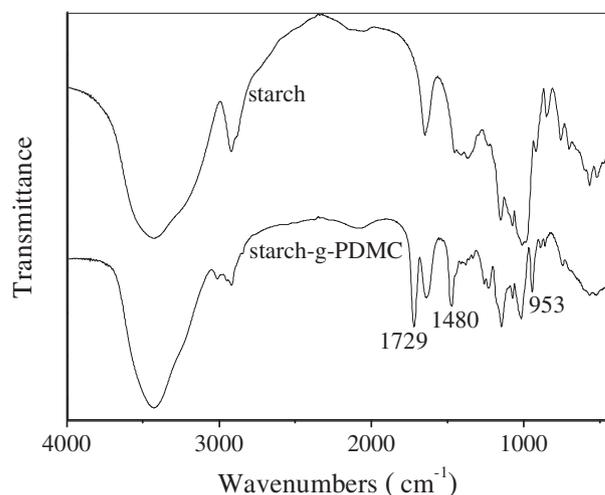


Fig. 1 – FT-IR spectra of starch and the STC-g-PDMC.

backbone appeared at 4.7 ppm. The two splitting peaks at 3.88 and 3.91 ppm were attributed to the proton signals of H-1' in the grafting chain. The proton signals of H-2', H-3' and H-4' were observed at 1.1, 4.4 and 3.6 ppm, respectively. The proton signal of starch backbone were observed at 5.3 ppm for H-1, at 3.5 ppm (overlapped by H-4') for H-2, at 1.9 ppm for H-4 and at 3.8 ppm for H-3, H-5 and H-6. The ¹H NMR spectroscopy confirmed the grafting of DMC onto starch backbone.

The XRD profiles of the STC-g-PDMC exhibited distinct crystalline peaks, compared with those of starch (Fig. 4). The profiles of starch showing four peaks around $2\theta = 15^\circ, 17^\circ, 18^\circ$ and 23° exhibited a characteristic A-type X-ray diffraction pattern. The graft copolymer, STC-g-PDMC, had a dispersive broad peak and showed no crystal starch peak, suggesting a decrease in crystallinity. The loss in crystallinity indicated that the introduction of DMC onto starch backbone destroyed the original ordered structure of starch.

The TGA results also confirm the occurrence of graft copolymerization. As shown in Fig. 5, the thermal behavior of starch-g-PDMC was distinct from that of starch. Starch had weight losses in two stages as shown in its TGA profiles. The first weight loss occurred between 30 and 150 °C, which might correspond to the loss of absorbed and bound water. The second stage of weight loss started at 280 °C and continued up to 480 °C, which was likely because of the decomposition of starch. The differential TGA (DTG) curve of starch shows that the temperatures for the quickest weight loss in two stages

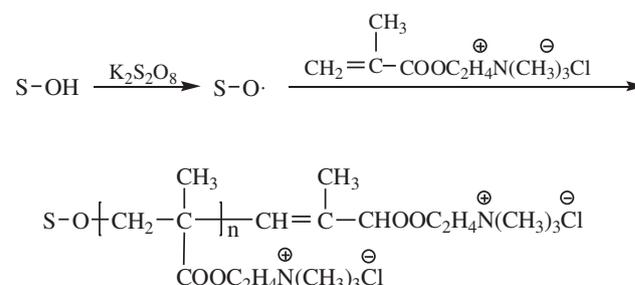


Fig. 2 – Schematic representation of graft-copolymerization of starch.

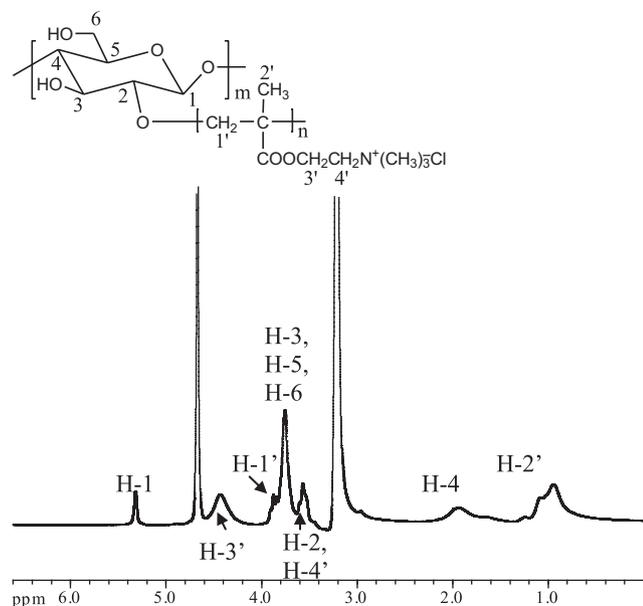


Fig. 3 – ^1H NMR spectroscopy of the STC-g-PDMC.

were 100 °C and 320 °C, respectively. In comparison, the TGA curve of STC-g-PDMC showed three stages of weight losses. Correspondingly, the three quickest weight losses occurred at 102 °C, 269 °C and 420 °C, respectively. Compared with starch, the STC-g-PDMC exhibited two different quickest weight loss temperatures, one was lower and the other was higher than the quickest weight loss temperature for starch, indicating that the grafting of PDMC onto starch backbone significantly changed the thermal stability of starch.

The occurrence of the grafting could also be deduced from the increase of N-content in the graft copolymer. There is no element N in the starch, and thus the N-content should be 0% in the original polymer starch. Table 1 lists the comparison of elemental analysis experimental values and theoretical values (calculated according to the grafting percentage). The experimental value for each element agrees well with the theoretical value. The cationic degree of the STC-g-PDMC could be therefore calculated according to the grafting percentage and the elemental analysis values.

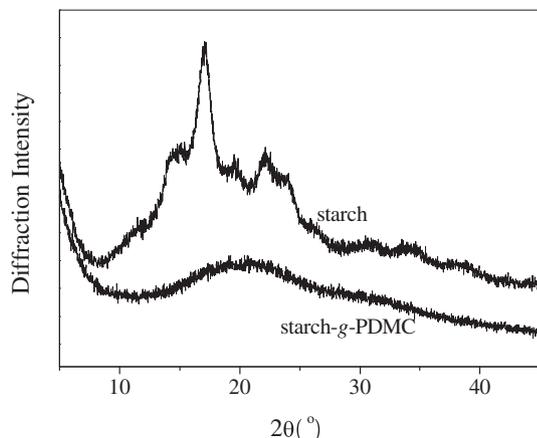


Fig. 4 – XRD of starch and the STC-g-PDMC.

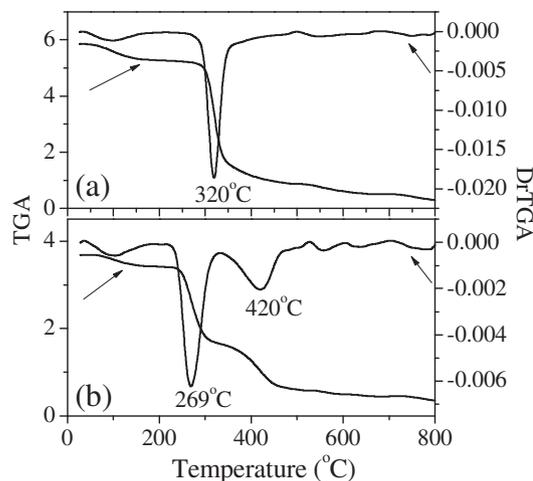


Fig. 5 – TGA and DTG of (a) starch and (b) the STC-g-PDMC.

Table 2 summarizes the solubilities of starch and the STC-g-PDMC in 1.0% acetic acid, water and 0.1 M NaOH solutions, respectively. Starch is insoluble in acetic acid, water or NaOH solution at ambient temperature. The STC-g-PDMC could be dissolved in water to form a turbid solution, and can be easily dissolved in acetic acid and NaOH solutions to form solutions.

After DMC was grafted onto starch backbone, the hydrophilicity of starch increased, because DMC is a quaternary ammonium salt and the monomer and homopolymer could be dissolved in water readily. On the other hand, the original inter-molecular and intra-molecular hydrogen bonding were destroyed in the grafting process. As a result, the graft copolymer became dissolved in acidic, neutral and alkaline solutions. Obviously, the increase in solubility is one of the most remarkable advantages for the graft copolymer when it is used as a flocculant.

3.2. Flocculation ability of STC-g-PDMC

The flocculation experiments of kaolin suspensions with starch, PAM and the STC-g-PDMC (grafting percentage of 209%) were conducted at pH 4.0, 7.0 and 10.0, respectively (Fig. 6). Starch can't be used as flocculant directly because it did not show any flocculation ability under all tested conditions. The graft copolymer STC-g-PDMC showed high flocculation effects under acidic, neutral and alkaline conditions. For example, at pH 4.0, the turbidity of the kaolin suspension decreased to 25 NTU even at a flocculant dosage as low as

Table 1 – Comparison of element contents determined by experimental analysis and theoretical calculation.

Element	Content	
	Experimental value (%)	Theoretical value (%)
C	49.93	49.98
H	8.44	8.18
N	4.86	4.92
O	24.45	24.66

Table 2 – Solubility of starch and STC-g-PDMC in acidic, neutral and basic solutions.

	Acidic (HAC, 1%)	Neutral (H ₂ O)	Basic (NaOH, 0.1M)
Starch	Not soluble	Not soluble	Not soluble
STC-g-PDMC	Soluble	Soluble, but milky	Soluble

0.1 mg/L. In addition, the graft copolymer exhibited high flocculation effects in a flocculant dosage range from 0.1 to 6 mg/L, implying that it has a broad flocculation window. This is one of the advantages of the graft copolymer. The linear grafting chain of PDMC on the semi-rigid starch backbone increased the adsorption bridging ability and the flexibility of the flocculant. Thus, the dispersion re-stabilization for the colloids caused by charge reversion would be attenuated. On the other hand, the graft copolymer exhibited a higher flocculation ability under acidic conditions than that under alkaline conditions at flocculant dosage of 0.1 mg/L. This is likely because of the difference of zeta potential for kaolin suspension under acidic conditions ($\delta = -10$ mV at pH of 4.0) and alkaline conditions ($\delta = -28$ mV at pH of 10.0). One notable phenomenon was that the graft copolymer showed a decent flocculation capability even under very alkaline conditions (e.g., at pH 10.0), while PAM showed very poor flocculation capability under the same condition. PAM flocculated the kaolin suspension through adsorption bridging and sweep-floc mechanisms. When the STC-g-PDMC was used as flocculant, in addition to those two mechanisms, the charge neutralization also played a big role. Under alkaline conditions, the zeta potential of the kaolin suspension was very low (-28 mV at pH 10.0), which made the colloids very stable in the suspension, and the adsorption bridging and sweep-floc mechanism hardly took effect under this condition. However, the cationic characteristic of the STC-g-PDMC on the other

Table 3 – Dewatering capabilities for sludge of STC-g-PDMC and PAM.

Flocculant dosage (%)	Specific resistance ($\times 10^{13}$ m/kg)	
	PAM	STC-g-PDMC
0.174	8.248	1.784
0.348	3.489	0.803
0.522	3.110	0.488
0.696	2.856	0.204
0.870	2.022	0.082
1.304	1.506	0.040

hand, was only slightly influenced by the alkaline pH condition, as it originated from the grafted quaternary ammonium salts.

3.3. Dewatering capacity of STC-g-PDMC

Table 3 lists the specific resistance of the sludge after being conditioned with PAM and the STC-g-PDMC at various dosages. When the STC-g-PDMC was used as sludge conditioner, the specific resistance of the conditioned sludge decreased with an increase in dosage. The conditioned sludge could be easily filtered when the dosage reached 0.696% and up of the dry weight of sludge (specific resistance $< 0.4 \times 10^{13}$ m/kg). When PAM was used as sludge conditioner, the specific resistance of the conditioned sludge also decreased with an increase in dosage. However, the specific resistance of the sludge conditioned by PAM was much higher than that by the STC-g-PDMC at the same dosage. The conditioned sludge was still difficult to filter, even the PAM dosage reached as high as 1.304% of dry weight of the sludge (specific resistance = 1.506×10^{13} m/kg). The specific resistance of the conditioned sludge treated with the STC-g-PDMC was only around 2.67% of that with PAM at the same dosage of 1.3%. STC-g-PDMC can facilitate charge neutralization, adsorption and bridging effects. The charge neutralization effect can reduce the thickness of hydrated shell on the surface of particles through diminishing the surface tension of water and compressing the thickness of the electric double layer. In addition, the flexible grafting chain of the graft copolymer in water can absorb a large amount of tiny particles and then flocculate them to big and dense flocs. As a result, the amount of capillaries will be decreased and the diameter of the residual capillaries will be augmented. Finally, the amount of big voids will be increased, which makes the flow of free water more fluently, reduces the pressure of capillary water and decreases the quantity of capillary water (Chang et al., 1993). Compared with PAM, the STC-g-PDMC exhibited a great application potential as a sludge conditioner with a high efficiency at low dosages.

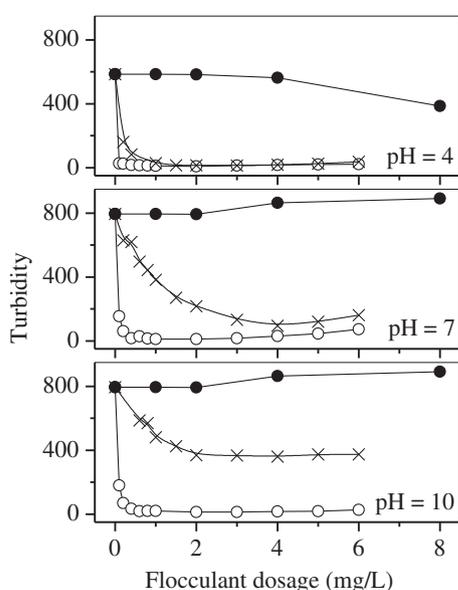


Fig. 6 – Flocculation performance of starch, PAM and the STC-g-PDMC in kaolin suspension of 0.25% (w/v) at pH 4.0, 7.0 and 10.0. —●—: starch; —×—: PAM; —○—: STC-g-PDMC.

4. Conclusions

A novel highly-efficient flocculant, STC-g-PDMC was synthesized by grafting a cationic monomer, DMC onto starch initiated by KPS. The success of the grafting was confirmed by FTIR, ¹H NMR, XRD, TGA and elemental analysis characterization. The graft copolymer exhibited a high efficient

flocculation ability for 0.25 wt% kaolin suspensions under acidic, neutral and basic conditions. The charge neutralization effect played an important role in the flocculation process at low flocculant dosages. As a sludge conditioner for sludge dewatering, the graft copolymer was also been proven to be superior to PAM. The novel flocculant, which was obtained through a simple synthesis process, is nontoxic, easily biodegradable and ultimately environmentally friendly. The grafting of cationic DMC onto starch backbone enhanced the cationic properties and increased molecular weight of the copolymer, and thus improved its flocculation ability and fields of application. Meanwhile, the grafting of cationic monomer to the starch backbone improved the solubility of the copolymer, and thus made it easier and more convenient to be used in various water treatment processes.

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