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Synthesis of Cationic Modified Poly (γ - Glutamic Acid) and Evaluation of its Flocculation Performance in Seawater

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A new environmentally friendly flocculant was synthesized by cationic modified poly(γ-glutamic acid) (γ-PGA). The flocculant was prepared via chemical reaction between γ-PGA and 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTMA). γ-PGA, as a new type of microbial flocculant with water-soluble, biodegradable, non-toxic and edible characteristics in water treatment has broad application prospects. The cationic degree of cationic modified γ-PGA was characterized by conductivity meter. Infrared spectrometry (FTIR) and ^{1}H NMR were explored to determine chemical structure of the composite flocculant. The influence of etherification agent, reaction temperature, reaction time, as well as the molar ratio of etherifying agent and NaOH on flocculation performance were investigated. The results showed that the turbidity of the seawater distinctly decreased from 95 NTU to 10 NTU with 2 mg/L modified γ- PGA.

1. Introduction

In recent years, with the rapid modern industrial development (Xu et al., 2012), more and more water resources are being polluted, we humans have less available fresh water (Antony et al., 2012). Development of seawater desalination technology is an effective method to solve deficiency of fresh water resources (Liu et al., 2012). Desalination of seawater by reverse osmosis (RO) (Dore et al., 2005), compared to other seawater desalination technologies such as electrodialysis and distillation, was chosen as an appropriate technique for production of drinking water (Choi et al., 2009). However, seawater composition is more complex (Cho et al., 2006), including vast suspended particle bacteria (Chinu et al., 2010), organic matter and so on (Fritzmann et al., 2007). Membrane fouling is a major challenge for RO system (Sheikholeslami et al., 2002). In order to reduce particles deposit on the membrane (Prihasto et al., 2009), the pretreatment of the seawater is widely used (Shon et al., 2005). Flocculation has been proven to be an economical and efficient method for pretreatment in seawater desalination (Shon et al., 2009).

Polyelectrolytes have become the best choice for removing suspended solids in sewage treatment and water purification (Bolto B et al., 2007). γ-PGA as an emblematic "green" flocculant has attracted great interest for the characteristics of effectiveness (Sinha et al., 2001), nontoxic and good biodegradability (Coviello et al., 2007). Furthermore, the carboxylic group endows it excellent chelating ability (Fan et al., 2000). Nevertheless, the carboxylic group itself makes the flocculation performance of γ-PGA so scanty that limits its potential applications (Ravishankar et al., 1995). In order to improve the flocculation performance, we synthesized a novel cationic modified γ-PGA (Pal et al., 2005). Cationic modified natural macromolecules are a conventional method for modifying flocculants (Wilke et al., 1995). Researches on modified chitosan and starch have been implemented (Ahmad et al., 2008). For instance, Wei et al. (2011) got cationic modified chitosan using chitosan and 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTMA) as raw materials. Sheng (Sheng et al., 2007) has synthesized cationic modified starch by acrylamide and starch. Cationic modification γ-PGA has an obvious effect of flocculating sedimentation due to the mainly negatively charged for the suspended solids in the seawater.

In this study, cationic modified γ-PGA applied as an effective flocculant to remove suspended solids from the seawater. The cationic modified γ-PGA was synthesized by using γ-PGA and CHPTMA as the starting

materials. The cationic degree of cation-modified γ-polyglutamic acid was characterized by the conductivity from the side, the higher the conductivity of the solution, the more the ions of solution, which indicates that the modification of the polymer cationic degree is higher.

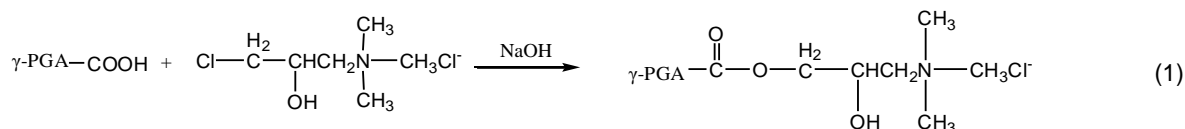## 2. Experimental

2.1 Reagents and instruments

Absolute ethyl alcohol and sodium hydrate were purchased from Tianjin NO.6 Chemical Reagent Factory (Tianjin, P.R. China). γ-PGA was obtained from Tianjin Peiyang Biotrans biotech Co., Ltd (Tianjin, P.R. China). CHPTMA was purchased from Tokyo Kasei Kogyo Co., Ltd.(Tokyo, Japan). All reagents were reagent grade and were used without further purification. All the water used in the experiment is distilled water. Seawater from Tang Gu, Tianjin, China was used in this study. The turbidity of the seawater used in this study was 95 NTU.

The experimental instruments used in this research include Advance III plus 400 MHz Nuclear Magnetic Resonance, BRUKER TENSOR 27 Fourier transform infrared spectroscopy (FTIR), Electric vacuum drying oven, DF-101S thermo-static magnetic stirrer, CJB-DS magnetic stirrer and WGZ-800 turbidity instrument.

2.2 Synthesis of cationic modified γ-PGA

2.2.1. Study on molar amount of etherification agent

1.0 g of γ-PGA was dissolved in a round-bottom flask containing 10 mL water and heated at 50 °C for 1 h under stirring. 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08 mol of CHPTMA was slowly added into the round-bottom flask. After 5 min, 10 mL of NaOH (etherifying agent: NaOH = 1:1.3, molar ratio) was slowly added into the round-bottom flask, and reacted at 50 °C for 5 h with magnetic stirring. After reaction finished, reaction solution was added to the absolute alcohol to precipitate the product. White solid was obtained after washed the precipitate with absolute alcohol and dried. Relevant synthetic reaction is expressed in equation (1).

$$\gamma\text{-PGA}\!-\!COOH \ + \ Cl\!-\!\underset{OH}{\overset{H_2}{C}}\!-\!CHCH_2\underset{CH_3}{\overset{CH_3}{N}}\!-\!CH_3Cl^- \ \xrightarrow{\ NaOH\ } \ \gamma\text{-PGA}\!-\!\overset{O}{\overset{\|}{C}}\!-\!O\!-\!\underset{OH}{\overset{H_2}{C}}\!-\!CHCH_2\underset{CH_3}{\overset{CH_3}{N}}\!-\!CH_3Cl^- \tag{1}$$

2.2.2 Study on reaction temperature

1.0 g of γ-PGA was dissolved in a round-bottom flask containing 10 mL water and heated at 50 °C for 1 h under stirring. 0.07 mol of CHPTMA was slowly added into the round-bottom flask. After 5 min, 10 mL of NaOH (9.1 mol) was slowly added into the round-bottom flask, and reacted at 30, 40, 50, 60, 70 °C for 5 h with magnetic stirring.

2.2.3. Study on reaction time

1.0 g of γ-PGA was dissolved in a round-bottom flask containing 10 mL water and heated at 50 °C for 1 h under stirring.0.07 mol of CHPTMA was slowly added into the round-bottom flask. After 5 min, 10 mL of NaOH (9.1 mol) was slowly added into the round-bottom flask, and reacted at 50 °C for 3, 4, 5, 6, 7 h with magnetic stirring, respectively.

2.2.4. Study on the added amount of NaOH

1.0 g of γ-PGA was dissolved in a round-bottom flask containing 10 mL water and heated at 50 °C for 1 h under stirring. 0.07 mol of CHPTMA was slowly added into the round-bottom flask. After 5 min, 10 mL of NaOH (etherifying agent: NaOH = 1:1~1:1.5, molar ratio, respectively) was slowly added into the round-bottom flask, and reacted at 50 °C for 5 h with magnetic stirring.

For the study from 2.2.2 to 2.2.4, when the reaction is finished, all the post-processing method of the reaction solution is the same with the study on the molar amount of etherification agent.

2.3 Measurement of the conductivity of cationic modified γ-PGA

0.1 g of cationic modified γ-PGA was dissolved in a beaker and diluted with 100 mL water. The conductivity of the solution was measured by conductivity meter (DDSJ-308A).

2.4 Measurement of the flocculation efficiency of cationic modified γ-PGA

0.01 g of cationic modified γ-PGA was dissolved in beaker containing 100 mL water. Predetermined doses of flocculants were added into 100 mL seawater samples. Then, the samples were stirred rapidly (600 rpm) for 2 min followed by a slow mixing (200 rpm) for 10 min, and finally allowed to settle for 30 min. After settling, the turbidity of the supernatants was determined by turbidity instrument.

3. Results and discussion

3.1 FTIR analysis of synthetic products

Figure 1. shows the FTIR spectrum of γ-PGA and cationic modified γ-PGA. It can be seen from curve (a) that the characteristic absorption peak of N-H bond stretching vibration appears at the wavenumber of 3,452.73 cm^{-1}, the absorption peaks at 1,643.2 cm^{-1} is asymmetric stretching vibration band of –CONHR in amide group, indicating that it is amide group. The absorption peak at 1,453.76 cm^{-1} and 1,412.99 cm^{-1} are attributed to the bending vibration of –CH_2 or –CH_3. The peak at 2,800-3,000 cm^{-1} is symmetric and asymmetric stretching vibration peaks of saturated C-H bond. The absorption peak at 1,000-500 cm^{-1} are plane swing vibration and bending vibration of $(CH_2)_n$. The curve (b) has the above characteristic peaks, and in addition, it has the absorption peak of 2,358.86 cm^{-1} which is the absorption peak of quaternary ammonium. It can be inferred that cationic modified γ-PGA has been successfully synthesized.
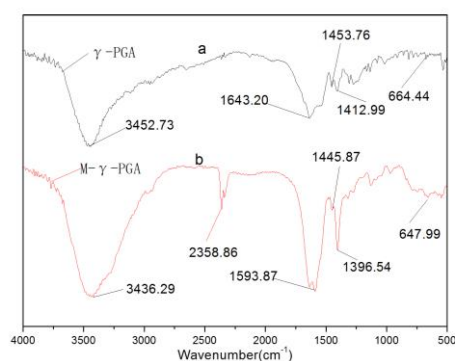

Figure 1: FTIR spectrum of γ-PGA (curve a) and cationic modified γ-PGA (curve b)

3.2 ^1H NMR spectrum of synthetic products

Figure 3. shows the spectra of ^1H NMR of γ-PGA and cationic modified γ-PGA in D_2O. It can be seen from the ^1H NMR spectrum that 4.79 ppm is the solvent residual peak of D_2O. The peak of 4.07 ppm is attributed to the characteristic peak of A–CH, 2.29 ppm is attributed to C-CH_2, 2.01 and 1.87 ppm are ascribed to B-CH_2. 3.09 ppm is characteristic of –CH_3. Therefore, we think the cationic modified γ-PGA we synthesized has basically met our needs.
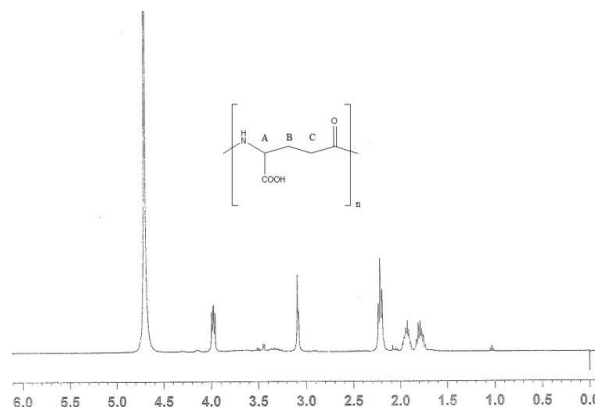

Figure 2: ^1H NMR spectrum of cationic modified γ-PGA

3.3 Influence of etherification agent dosage on conductivity

The cationic degrees of cationic modified γ-PGA are one of the important factors that affect the flocculation performance, which etherification agent dosage can affect the cationic degrees of cationic modified γ-PGA. The effect of the etherification agent dosage on the conductivity of cationic modified γ-PGA was studied consequently. The result is shown in Figure 4. It is observed that the electrical conductivity reaches the highest value when the etherification agent is 0.07 mol, because the electrical conductivity is positively correlated with the flocculation performance, when the etherification agent is 0.07 mol, the result is what we desire; flocculation performance is poor when the etherification agent is smaller and bigger than 0.07 mol. Its reason is that the number of reactive groups is constant when the amount of γ-PGA is constant. This result

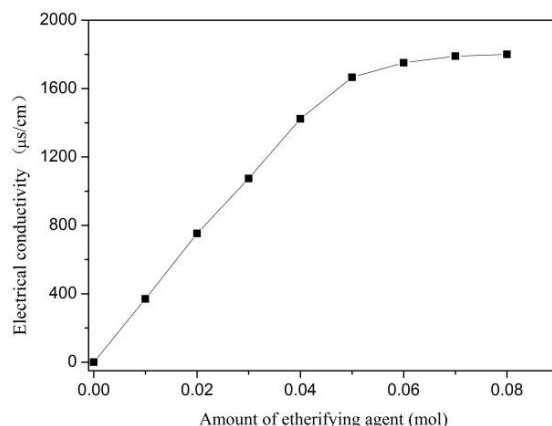demonstrates that the optimum condition for cationic modified γ-PGA synthesis is the molar quantity of 0.07 mol.

Figure 3: Influence of etherification agent on conductivity (m(γ-PGA)=1.0 g)

3.4 Influence of reaction temperature on conductivity

It is observed from Figure 4 that the electrical conductivity is above 1800 when the reaction temperature is 50 °C, the flocculation performance is relatively ideal compared with the reaction temperature is lower or higher than 50 °C. Its reason is that with the increase of temperature, the γ-PGA particles are expanding, and the reaction is more likely to occur. In addition, high temperature can gelatinize γ-PGA and cause the decomposition of cationic modified γ-PGA and etherifying agent. This result demonstrates that the optimum condition for cationic modified γ-PGA synthesis is the reaction temperature of 50 °C.

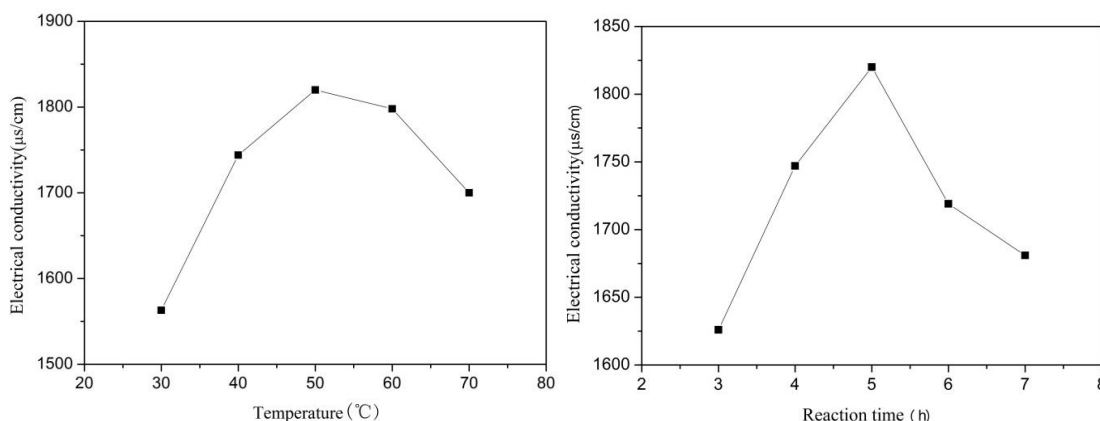*Figure 4: Influence of reaction temperature and reaction time on conductivity (m(γ-PGA) = 1.0 g)*

3.5 Influence of reaction time on conductivity

Figure 4 shows that the flocculation performance achieves the expected effect when the reaction time is 5h, at which, the conductivity value is more than 1800. While as to other reaction time, the performance is relatively poor, when at the reaction time of 3h, the conductivity is just almost 1625. This is because the reaction time is too long, resulting in the decomposition of cationic modified γ-PGA. This result demonstrates that the optimum condition for cationic modified γ-PGA synthesis is the reaction time of 5 h.

3.6 Influence of NaOH dosage on conductivity

The cationic degrees of cationic modified γ-PGA are one of the important factors that affect the flocculation performance, which NaOH dosage can affect the cationic degrees of cationic modified γ-PGA. It is seen (Figure 5) that when molar ratio of etherification agent and NaOH is 1:1.3, the flocculation performance is the most ideal. However, the flocculation effect is poor when the molar ratio of etherification agent and NaOH is smaller or bigger than 1:1.3. Its reason is that the NaOH dosage is so high that causing the side effects. This result demonstrates that the optimum condition for cationic modified γ-PGA synthesis is the molar ratio of etherification agent and NaOH of 1:1.3.
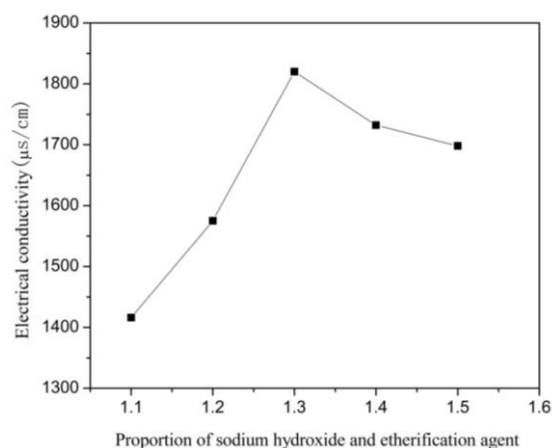
Figure 5: Influence of NaOH on conductivity (m(γ-PGA)=1.0 g)

3.7 Turbidity removal of γ-PGA and cationic modified γ-PGA

Turbidity is one of the important indexes that characterize flocculation efficiency. Generally, the turbidity removal increases with increasing dosage of flocculants. Based on Figure 6, the turbidity removal increased with increasing dosage of cationic modified γ-PGA up to 2 mg.L^{-1}. However, beyond 2 mg.L^{-1}, the turbidity removal started to decrease. At flocculant concentration of 1.5 mg.L^{-1}, the flocculation efficiency was as much as 80 %. The maximum flocculation efficiency, 84.2 %, was reached at an flocculant concentration of 2 mg.L^{-1}. However, the flocculation efficiency of γ-PGA was only about 40 % to treat same seawater. Cationic modified γ-PGA has better flocculation performance than γ-PGA.

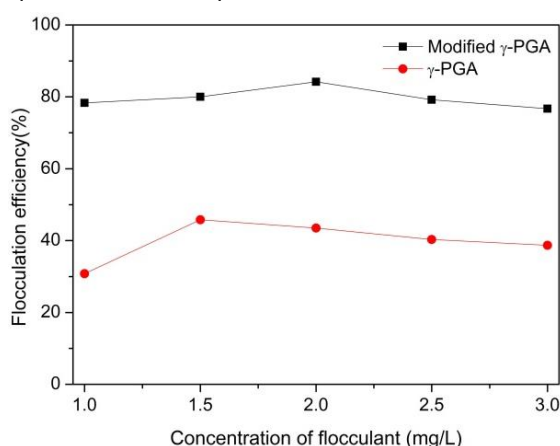*Figure 6: Turbidity removal of γ-PGA and cationic modified γ-PGA*

4. Conclusion

Cationic modified γ-PGA was synthesized by the reaction of γ-PGA and 3-chloro-2-hydroxypropyl trimethyl ammonium chloride. The optimum synthetic conditions for cationic modified γ-PGA are the molar ratio of etherifying agent and NaOH which is 1.0:1.3, etherification agent of 0.07 mol, reaction temperature of 50 °C, and reaction time of 5 h. The flocculation efficiency of cationic modified γ-PGA is close to 85 % with flocculant concentration of 2 mg/L. However, the flocculation efficiency of γ-PGA was only about 40 % to treat same seawater. Cationic modified γ-PGA has better flocculation performance than γ-PGA. The cationic modified γ-PGA, attributing to the high performance and biodegradable, are expected to be a promising candidate for future water treatment.

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