



Optimized conditions in preparation of giant reed quaternary amino anion exchanger for phosphate removal

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ABSTRACT

Giant reed (GR) was modified into giant reed quaternary amino anion exchanger (GR-QE) for the removal of phosphate by reacting with epichlorohydrin, ethylenediamine (EDA) and triethylamine in the presence of N,N-dimethylformamide (DMF). Factors like GR dosage, temperatures and volumes of organic liquid chemicals were used in single-factor experiments and orthogonal experiments for determining optimal conditions, with phosphate removal efficiency and zeta potentials as indicators. The results indicated that the optimal conditions obtained in the orthogonal experiments were consistent with those in the single-factor experiments. The GR utilization on a large-scale was realized, and the dosage of EDA was considered as the key influential factor in the preparation of GR-QE. Under these conditions, the nitrogen content in GR-QE was about 7.78%, while it was 0.9% in GR. The phosphate removal was about 82.1%, zeta potential was 23.2 mV.

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1. Introduction

Lake eutrophication has become a serious environmental problem [1], and phosphorus is generally considered to be a limiting factor in water eutrophication [2]. So sewage treatment plants are always required to make corresponding restrictions on the emissions of total phosphorus. It is difficult for conventional bio-chemical treatment to guarantee the discharge standard and tertiary treatment is often used for this purpose. Several methods have been used to remove phosphorus from water, including reverse osmosis [3], biological de-nitrification [4], electro-dialysis [5] and adsorption [6].

At present, there have been adsorbents prepared by agricultural residues (AR) such as bagasse [7], peanut shells [8], pomace [9], sawdust [10], coconut shells [11], banana peel [12], etc. However, a large amount of liquid chemicals need to be added during the preparation reactions, and as a result, those adsorbents cannot be promoted for a large-scale utilization.

Giant reed (GR) is one of the best-known fibre crops, whose industrial potential is now being intensively reconsidered [13]. An appropriate chemical composition in GR with 21.1% lignin, 31.1% cellulose (as α -cellulose), 30.3% hemicelluloses and 12.1% extractives [14], suggests a broad potential application to adsorbent production; this is due to the large amount of easily available

hydroxyl groups existing in the cellulose, hemicelluloses and lignin, which can easily actuate a series of chemical reactions, such as esterification, etherification and copolymerization [15].

There have been reports about research on tertiary amino anion exchanger prepared from AR [16–18], but there is no information concerning quaternary amino anion exchanger prepared from GR intended for phosphate removal. In this paper, giant reed quaternary amino anion exchanger (GR-QE) is prepared from GR after reacting with epichlorohydrin, ethylenediamine (EDA) and triethylamine in the presence of N,N-dimethylformamide (DMF). The main objective of this study is to discuss the preparation of GR-QE from GR. Single influential factor and orthogonal tests are designed for determining optimal reaction conditions. Characteristics of GR-QE prepared under the optimized synthesis conditions are discussed, using instruments such as scanning electron micrographs (SEM) analyzer, surface area analyzer, nitrogen content analyzer and Fourier transform infrared spectroscopy (FT-IR) analyzer. The results of this research will provide a new synthetic method to produce efficient and low-cost anion exchanger for phosphate removal.

2. Materials and methods

2.1. Materials

GR was obtained from Jinan, Shandong, China. The raw GR was washed with distilled water and dried at 100 °C for 72 h. Then it was sieved into particles with diameter from 100 to 250 μ m.

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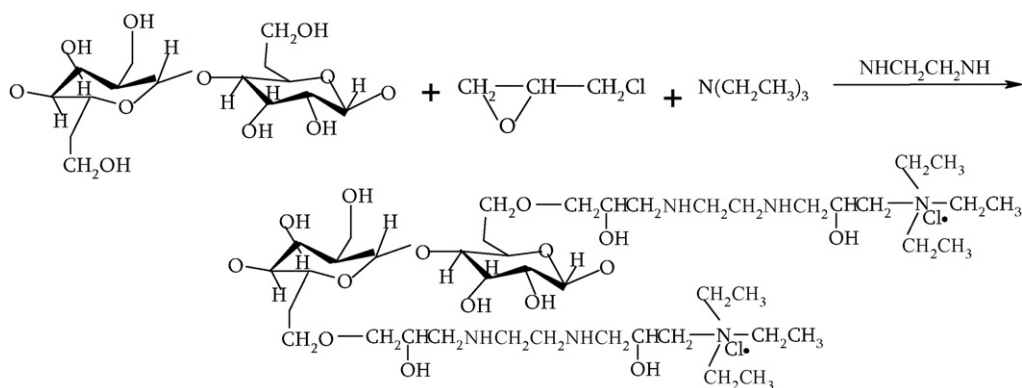


Fig. 1. Synthetic reactions of GR-QE.

2.2. Reaction process and the product

Batch experiments were conducted using GR (1–5 g) with 10 ml of epichlorohydrin and DMF (2–12 ml) in a 250 ml three-neck round bottom flask at 40–100 °C for 45 min. Batch volumes (0–3 ml) of EDA were added in the flask; the reactants were stirred for 5 min and heated for 45 min at 40–100 °C. Then, 2–20 ml of 99% triethylamine (w/w) was added and the mixture was stirred for 5 min, followed by heating for 120 min at 40–100 °C.

The primary product was washed by 200 ml of distilled water to remove the excessive chemical substances, then dried at 100 °C for 12 h and sieved to get particles smaller than 250 μm. The final product was obtained after a second cycle of washing, drying and sieving, and was used in the adsorption experiments [7,17,18].

The synthesis of GR-QE is shown in Fig. 1 [17,19,20]. The inter-reactivity of triethylamine with cellulose were poor, thus epichlorohydrin, as a cross-linking agent to react with cellulose, could improve the reactivity, and produce cellulose ether [21,22]. Cellulose ether could efficiently react with EDA after the ring opening of epoxide group in cellulose ether, and the other amido group in EDA was induced to react with triethylamine in an excess of epichlorohydrin.

2.3. Characteristics of GR-QE

2.3.1. Nitrogen content and total exchange capacity (TEC mEq g⁻¹)

The nitrogen content of GR-QE was measured by element analyzer (Elementar Vario EL III, German). TEC could be calculated from the nitrogen content according to the following equation [17].

$$\text{TEC}(\text{mEq g}^{-1}) = \text{N}\% / 1.4$$

TEC is the total exchange capacity (mEq g⁻¹); N% is the total nitrogen content; and 1.4 is the correction coefficient.

2.3.2. Zeta potential (mV)

In order to evaluate the potential of GR-QE for anionic pollutant removal, it was necessary to measure the change of surface charge of GR-QE in contrast with GR. The zeta potential of GR-QE and GR was determined by electro-kinetic analyzer (JS94H Shanghai Zhongchen Digital Technical Apparatus Co., Ltd, China).

2.3.3. SEM analysis and FT-IR analysis

SEM studies of the samples were carried out using Hitachi Model S-520 (Japan) scanning electron microscope at an applied voltage of 26 kV. The samples were mounted on aluminum stubs and coated with gold in Hitachi HUS-5 GB vacuum evaporator. IR spectra were recorded on a PerkinElmer "Spectrum BX" spectrometer in

the 4000–400 cm⁻¹ region. The FT-IR spectrometer was linked to a personal computer loaded with the IRDM (IR Data Manager) program to process the recorded spectra. The specimens were pressed into small discs using a spectroscopically pure KBr matrix.

2.3.4. Specific surface area

Specific surface area measurements were performed with an automatic BET surface area analyzer (Model F-Sorb 2400, Beijing Jinaipu Technical Apparatus Co., Ltd., China). The detection limit of this instrument, using N₂, is 0.01 m² g⁻¹.

2.4. Single-factor experiments

In the single-factor experiments, the presumed optimal conditions for the synthesis in this work were 1 g of GR, 10 ml of epichlorohydrin, 2 ml of EDA, 12 ml of DMF, 15 ml of triethylamine, and experimental temperature was 100 °C [17,18,23]. So a single selected factor was varied, while all other factors were fixed simultaneously in the optimal conditions obtained in every step.

2.5. Orthogonal experiments

Based on the results obtained in single influential factor experiments, the orthogonal experiments with seven factors and three levels were designed, and 18 synthesis conditions were carried out at GR of 3, 4, and 5 g; DMF of 2, 5, and 12 ml; temperature 1 of 50, 60 and 70 °C; EDA dosage of 1.5, 2.0 and 2.5 ml; temperature 2 of 50, 60 and 70 °C; triethylamine dosage of 5, 10 and 15 ml and temperature 3 of 60, 70 and 85 °C. All selected factors were examined using an orthogonal L₁₈ (3)⁷ experiment, with phosphate removal and zeta potential as indicators.

2.6. Phosphate removal experiment

An aliquot of 0.1 g of GR-QE was mixed with 50 ml of 50 mg/L KH₂PO₄ solution in the 100-ml flask at room temperature (20 ± 2 °C) and then shaken at 120 rpm for 60 min. The phosphate concentration was determined spectrophotometrically by Ammonium-molybdate colorimetric method, using a UV-vis spectrophotometer (model UV754GD, Shanghai) at an absorbance wavelength of 700 nm [24].

3. Results and discussion

3.1. Single-factor experiments

3.1.1. Maximization of GR on the preparation of GR-QE

A major objective of this work was to explore the possibility of large-scale utilization of GR for the preparation of GR-QE. To realize

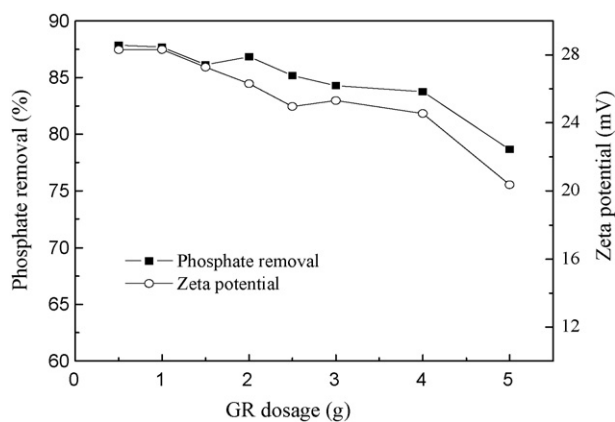


Fig. 2. Effect of GR dosage on the phosphate removal and zeta potential of GR-QE.

the GR utilization on a large-scale, we should use GR as much as possible, and the dosages of liquid chemicals should be limited due to their high costs and harm to the environment.

The effect of GR dosage on the preparation of GR-QE is shown in Fig. 2. As shown in Fig. 2, the phosphate removal gradually decreased from 87.8% to 83.8% as the GR dosage increased from 0.5 to 4 g. A sharp drop of phosphate removal was observed when the GR dosage was more than 4 g; this could be explained by the insufficiency of other chemical substances when the GR was excessive in the synthesis system, which would reduce the functional groups of GR-QE [16]. The trend of zeta potential was similar to that of phosphate removal. Fig. 3 shows the change of weight of GR-QE with the increase of GR dosage. The weight of GR-QE increased from 6.91 to 9.70 g when the GR dosage increased from 0.5 to 4 g. With the further increase of GR dosage, the weight of GR-QE decreased from 9.70 to 9.01 g. It indicated that 4 g of GR produced the highest weight. As the GR dosage increased from 0.5 to 4 g, a slight decrease was observed in phosphate removal and the weight of GR-QE increased significantly; it indicated that 4 g of GR dosage was more economical than other GR dosages, and therefore the dosage was maintained for subsequent experiments.

In this work, GR-QE was obtained by reaction of plenty of GR with a small amount of chemicals and it was a promising adsorbent for removal of phosphate. As a result, GR could be utilized on a large-scale for the preparation of adsorbents in this study.

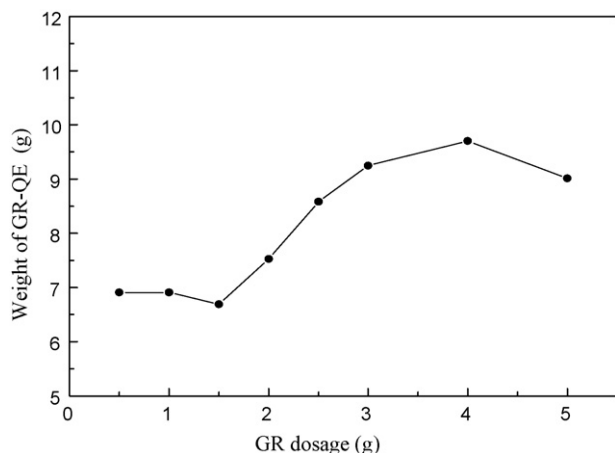


Fig. 3. Effect of GR dosage on the weight of GR-QE.

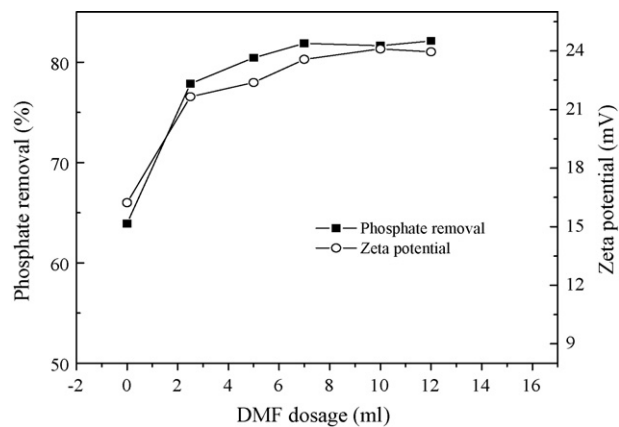


Fig. 4. Effect of DMF dosage on the phosphate removal and zeta potential of GR-QE.

3.1.2. Effect of DMF dosage on the preparation of GR-QE

Owing to its stable chemical property, DMF was used as an organic solvent in this work [21], and the effect of DMF dosage on the phosphate removal of GR-QE is shown in Fig. 4. With the addition of 2 ml of DMF, the phosphate removal increased rapidly from 63.9% to 77.9%. With the increase of DMF dosage from 5 to 12 ml, phosphate removal changed insignificantly (80.4–82.1%). The effect of DMF on zeta potential produced a similar trend to that of phosphate removal. So an optimal DMF dosage was determined in the range of 5–12 ml (7 ml was selected for the following experiments).

3.1.3. Effect of EDA dosage on the preparation of GR-QE

In this work, EDA was used as a modifying agent to facilitate the reaction between the cellulose ether and triethylamine [25]. Fig. 5 shows the effect of EDA dosage on the preparation of GR-QE. As shown in Fig. 5, less GR-QE was carried out when the EDA dosage was less than 1 ml, with phosphate removal lower than 30%. The phosphate removal increased significantly from 29.9% to 82.8% as the EDA dosage increased from 1 to 2 ml, and then remained in equilibrium when the EDA dosage was higher than 2 ml. So 2 ml of EDA was selected as an optimal dosage for the synthesis of GR-QE, and therefore, the optimal dosage was maintained for following experiments.

3.1.4. Effect of triethylamine dosage on the preparation of GR-QE

Fig. 6 shows the effect of the dosage of triethylamine on the performance of preparation. A sharp increase of phosphate removal was observed with the triethylamine dosage increasing from 2 to

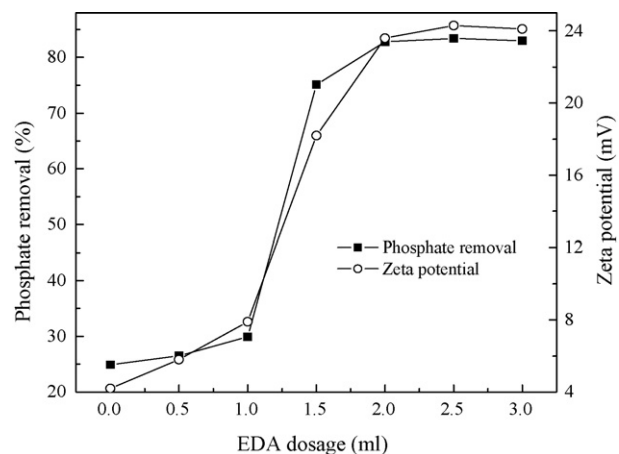


Fig. 5. Effect of EDA dosage on the phosphate removal and zeta potential of GR-QE.

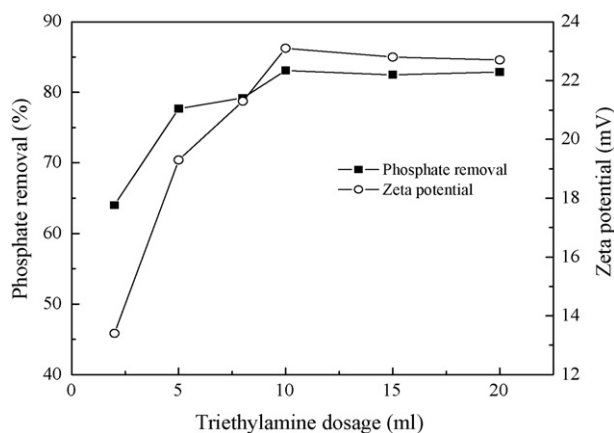


Fig. 6. Effect of triethylamine dosage on the phosphate removal and zeta potential of GR-QE.

5 ml. The highest phosphate removal (83.2%) was obtained at 10 ml of triethylamine, however, little modification effect was observed with the further increase of triethylamine dosage from 10 to 20 ml; this could be due to the insufficiency of epichlorohydrin under the reaction conditions [16,26]. An excess of epichlorohydrin was required for the graft reaction to react with triethylamine and EDA, because epichlorohydrin induced the cross-linking reaction by some functional groups [26–28]. When the triethylamine dosage was higher than 10 ml, the graft reaction would cease due to the insufficiency of the functional groups of epichlorohydrin.

Zeta potential of GR-QE as illustrated in Fig. 6 suggests that the effect of the dosage of triethylamine on the zeta potential was similar to that of phosphate removal. As a result, the dosage range of triethylamine was about 8–20 ml (10 ml was selected for the following experiments).

3.1.5. Effect of experimental temperature on the preparation of GR-QE

The liquid chemicals, epichlorohydrin, EDA and triethylamine were successively added into the synthesis system for the preparation of GR-QE, which involved three synthesis stages. Stage 1: the cellulose of GR was activated to react with epichlorohydrin to produce the cellulose ether. Stage 2: cellulose ether efficiently reacted with EDA after the ring opening of epoxide group in cellulose ether. Stage 3: the other amido group in EDA was induced to react with triethylamine [26]. As a result, the effects of experimental temperatures on the preparation of GR-QE might be different in the three synthesis stages, and it was necessary to discuss their respective experimental temperatures designed for the three synthesis stages. The experimental temperatures in the three synthesis stages were defined as temperature 1, temperature 2 and temperature 3, respectively. The presumed optimal temperature for the synthetic reaction was 100 °C in the three stages [17,18,23]. This experiment was performed by varying temperature in one stage, while simultaneously keeping temperatures in the other stages constant.

Fig. 7 illustrates the effect of experimental temperatures on the performance of prepared GR-QE. As indicated in Fig. 7, the effect of temperature 1 on the phosphate removal was insignificant, with a higher phosphate removal obtained at 60 °C, and therefore, the optimal temperature (60 °C) was maintained for following experiments. A more significant effect of temperature 2 on the phosphate removal was observed when the temperature 2 is lower than 60 °C. The phosphate removal was less than 32.6% at temperature 2 lower than 40 °C, however, it sharply increased from 32.6% to 82.8% with the temperature 2 increasing from 40 to 60 °C, which indicated that a higher temperature was required at this stage. 60 °C was

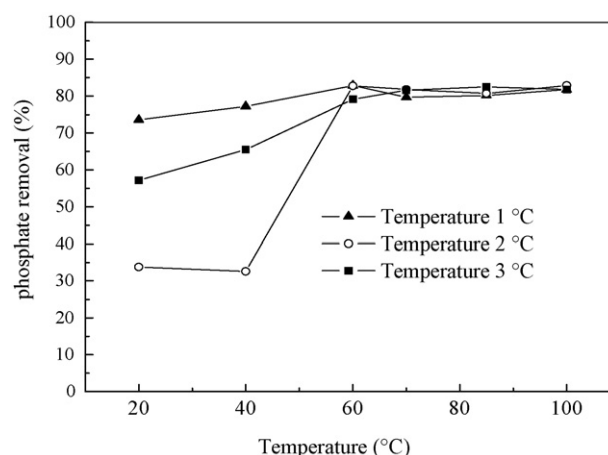


Fig. 7. Effect of experimental temperatures on the phosphate removal of GR-QE.

selected for the following experiments. The effect of temperature 3 on the performance of prepared GR-QE is also shown in Fig. 7. A slow increase was observed in phosphate removal from 57.2% to 81.6% as the temperature 3 increased from 40 to 70 °C, and the phosphate removal was steady with the further increase in temperature from 70 to 100 °C. The results indicated that temperature 2 played a more important role in the three experimental temperatures, and a better phosphate removal was realized when the experimental temperature was higher than 60 °C.

The effect of experimental temperatures on the zeta potential was similar to that of phosphate removal (Fig. 8). The results as shown above indicated that the optimal experiment temperature was in the range of 60–70 °C.

Based on the results obtained in the single-factor experiments, the optimized dosages of the reactants used in the preparation of GR-QE could be concluded as: GR:epichlorohydrin:DMF:EDA:triethylamine = 4 g:10 ml:5 ml:2 ml:10 ml and the experimental temperature was selected at 60–70 °C.

3.2. Orthogonal experiment

Orthogonal experiment is a highly efficient and economic method, which is orthogonally designed to examine the multiple factors [29,30]. In addition to reflecting the effects of all selected factors on the performance of prepared GR-QE, orthogonal experiment can also provide more detailed information on the key influential factor of GR-QE preparation.

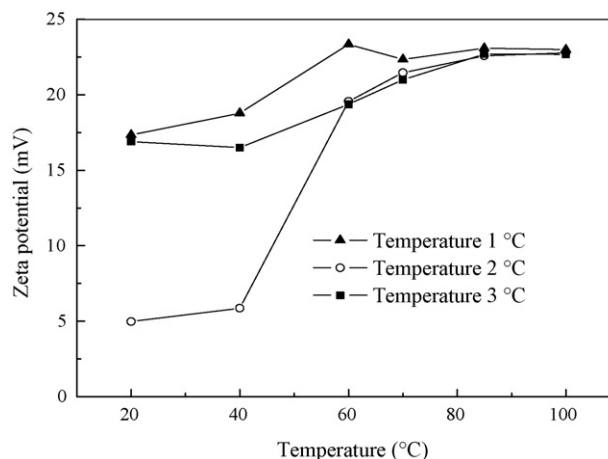


Fig. 8. Effect of experimental temperatures on the zeta potential of GR-QE.

Table 1
Reaction conditions determined by orthogonal experiments.

No.	GR dosage (g)	DMF dosage (ml)	Temperature (1 °C)	EDA dosage (ml)	Temperature (2 °C)	Triethylamine dosage (ml)	Temperature (3 °C)	Phosphate removal (%)	Zeta potential (mV)
1	3	2	50	1.5	50	5	60	65.5	12.2
2	3	5	60	2.0	60	10	70	71.6	16.8
3	3	12	70	2.5	70	15	85	74.4	17.1
4	4	2	50	2.0	60	15	85	71.9	14.8
5	4	5	60	2.5	70	10	60	82.1	23.2
6	4	12	70	1.5	50	5	70	73.4	18.2
7	5	5	50	1.5	70	10	85	69.3	13.2
8	5	12	60	2.0	50	15	60	72.5	15.8
9	5	2	70	2.5	60	5	70	71.7	14.9
10	3	12	50	2.5	60	10	60	75.2	15.9
11	3	2	60	1.5	70	15	70	70.9	13.0
12	3	5	70	2.0	50	5	85	75.0	17.6
13	4	5	50	2.5	50	15	70	72.0	17.8
14	4	12	60	1.5	60	5	85	58.8	11.3
15	4	2	70	2.0	70	10	60	68.9	12.6
16	5	12	50	2.0	70	5	70	68.9	13.8
17	5	2	60	2.5	50	10	85	76.0	17.9
18	5	5	70	1.5	60	15	60	63.7	14.6

Table 2
Analysis of orthogonal L₁₈ (3)⁷ experiment.

	GR dosage (g)	DMF dosage (ml)	Temperature (1 °C)	EDA dosage (ml)	Temperature (2 °C)	Triethylamine dosage (ml)	Temperature (3 °C)	Phosphate removal (%)	Zeta potential (mV)
k_1^a	72.6	72.2	72.6	67.8	73.2	70.3	72.1	71.5	–
k_2	73.4	72.8	72.5	73.3	71.5	72.9	72.7	72.7	–
k_3	71.2	70.5	72.0	76.1	72.4	73.9	72.2	72.6	–
R^b	2.2	2.3	0.6	8.3	1.7	3.6	0.6	2.76	–
$k_1'^c$	15.4	14.2	14.6	13.7	16.6	14.7	15.7	–	15.0
k_2'	16.3	17.2	16.3	15.2	14.7	16.6	15.8	–	15.6
k_3'	15.0	15.4	16.4	17.8	15.5	15.5	15.3	–	15.8
R'^d	1.3	3.0	1.8	4.1	1.9	1.9	0.5	–	2.1

^a $k_i = (\sum \text{the phosphate removal of single-factor})/6$.

^b $R_i = \max k_i - \min k_i$.

^c $k_i' = (\sum \text{the zeta potential of single-factor})/6$.

^d $R_i' = \max k_i' - \min k_i'$.

Results and the conditions of orthogonal experiments with seven factors and three levels are demonstrated in Table 1. As shown in Table 1, the parameters of the highest phosphate removal (82.1%) and zeta potential (23.2 mV) were obtained in experiment no. 5, and it was observed that the synthesis conditions of experiment no. 5 accorded with the optimal results obtained in the single-factor experiments. As a result, synthesis conditions selected from the optimized results would be acceptable in the preparation of GR-QE.

The key influential factor is determined by the discussion of k and R values which are used in the range analysis of orthogo-

nal tests, where k is the average of the data at one level of the single-factor and R is the difference between the maximal value and minimal value of k [26]. The k values reflected the effects of various levels on the preparation of GR-QE and the R values represented the effects of various factors [30]. As a result, the highest R value demonstrated the major effect of the factor on the preparation of GR-QE. The calculated k and R values are shown in Table 2.

With phosphate removal and zeta potential used as the indicators, R values of the seven factors (GR dosage, DMF dosage, temperature 1, EDA dosage, temperature 2, triethylamine dosage, temperature 3) were 2.2, 2.3, 0.6, 8.3, 1.7, 3.6, 0.6 and 1.3, 3.0,

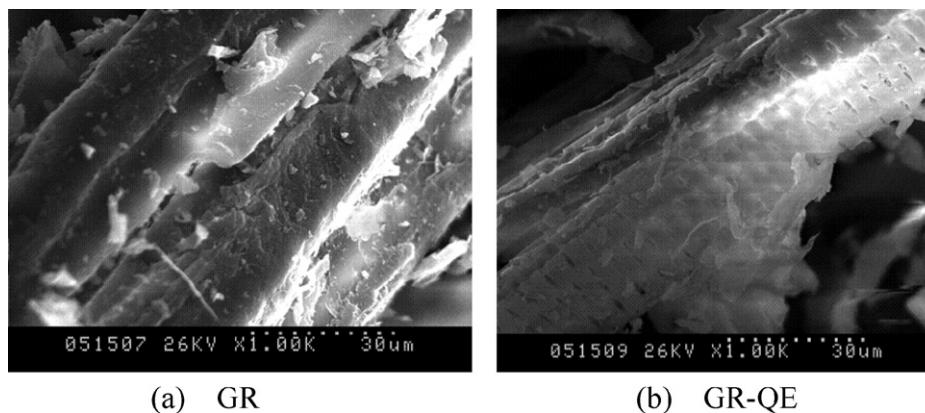
**Fig. 9.** SEM of the GR and GR-QE.

Table 3
Change of element content of GR.

	N (%)	C (%)	H (%)	TEC (mEq g ⁻¹)
GR	0.93	43.77	5.75	0.66
GR-QE	7.78	43.71	7.85	5.56

1.8, 4.1, 1.9, 1.9, 0.5, respectively. The results indicated that EDA dosage obtained the highest *R* value, and therefore, EDA dosage was considered as the key influential factor in the preparation of GR-QE.

3.3. Characteristics of GR-QE prepared by the optimized synthesis conditions

To study the characteristics of GR-QE prepared by the optimized synthesis conditions, the structure of the GR-QE obtained from the orthogonal experiment no. 5 was analyzed, using SEM analyzer, nitrogen content analyzer and FT-IR analyzer.

3.3.1. SEM analysis

The results of SEM measurements in the structures of GR-QE and GR are shown in Fig. 9. Smoother surfaces were observed in the structure of the GR-QE in comparison with the raw surface of GR, indicating that the order of cellulose was improved during the process of modification. Based on the work reported by Wang et al. [31], it was known that a large number of adsorption sites existed in the smoother surface of GR-QE, which would be beneficial to the phosphate removal.

3.3.2. Nitrogen content analysis

The elemental changes of carbon, hydrogen and nitrogen between GR-QE and GR are shown in Table 3. The changes of carbon and hydrogen contents could be negligible, however, nitrogen content in GR-QE increased significantly from 0.93% to 7.78%; this demonstrated an increase in amino groups after the triethylamine was grafted into the structure of GR-QE [26]. TEC values estimated from the nitrogen content of GR-QE and GR are also given in Table 3. There was a correlation between nitrogen content and exchange capacity of adsorbents [32]. A significant increase in TEC value indicated an excellent phosphate removal of GR-QE.

3.3.3. FT-IR analysis of GR-QE

Fig. 10 shows the IR spectral change of GR and GR-QE. In contrast to the IR spectral of GR, the increase of various groups was observed in the IR spectral of GR-QE. More ketone groups were observed in GR-QE at the band intensity of 2920 cm⁻¹ [33]. The band intensity

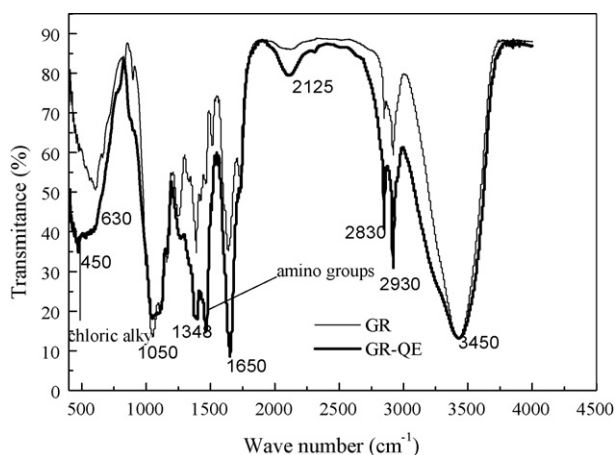


Fig. 10. FT-IR analysis of GR-QE.

of 1650 cm⁻¹ indicated the increase of aromatic cyclic groups in GR-QE [34]. The band intensity of 630 cm⁻¹ was associated with the special vibration of chloric alky groups, which demonstrated the function of epichlorohydrin in the preparation of GR-QE [26]. A large number of amino groups were observed at the band intensity of 1348 cm⁻¹; this further validated the excellent phosphate removal capacity of GR-QE [34,35].

3.3.4. Specific surface areas

Specific surface areas of GR-QE and GR were 7.6 and 5.3 m² g⁻¹, respectively. Although a slight increase in specific surface area of GR-QE was observed after the chemical modification, the small specific surface area still suggested the insignificance of surface adsorption in the sorption process [36].

4. Conclusions

The optimal results obtained in the orthogonal experiments were in accordance with those in the single-factor experiments, and the optimal dosages of the reactants used in the preparation of GR-QE could be concluded as: GR:epichlorohydrin:DMF:EDA:triethylamine = 4 g:10 ml:5 ml:2 ml:10 ml and the experimental temperature was selected at 60–70 °C. GR was realized for a large-scale utilization, and EDA dosage was the key influential factor that affected the synthesis reaction.

Characteristics of GR-QE prepared by the optimized results demonstrated that a large number of amino groups existed in the structure of GR-QE. The excellent phosphate removal of GR-QE was validated by the significantly high TEC value of GR-QE.

Acknowledgements

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