



Preparation and characteristics of quaternary amino anion exchanger from wheat residue

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ABSTRACT

Quaternary amino anion exchanger (QE) was prepared from wheat residue (WR) after reaction with epichlorohydrin and triethylamine in the presence of *N,N*-dimethylformamide and catalyst. The single influential factor experiments and orthogonal tests were carried out in order to obtain the optimal conditions for the preparation of wheat residue quaternary amino anion exchanger (WR-QE). The parameters of the influential factors, which included the types of catalysts, the amounts of WR and triethylamine, and experimental temperatures (activating temperature, catalytic temperature and reacting temperature) were also defined. The results indicated that pyridine was a suitable catalyst, and the catalytic temperature was a key factor of experimental temperatures. The optimal synthesis reaction parameters of dosages were WR:epichlorohydrin:pyridine:triethylamine = 2 g:20 ml:15 ml:30 ml. Optimal experimental temperature was 100 °C. Under these conditions, the nitrogen content of WR-QE was 6.0%, compared with WR of 0.4%. The yield was 556.3%. Nitrate removal was 89.1%; this was higher than the nitrate removal of wheat residue tertiary amino anion exchangers (WR-TE) of 6%–10%.

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1. Introduction

Agricultural residues (AR) are regarded as abundant and available biological resources. While only 2–5% of AR in China is utilized in the industry, the remaining is burned without proper utilization, causing significant waste and pollution. Today, there is an increasing interest in AR for their low-cost and availability. AR have been utilized in the production of a diversity of chemicals, including activated carbon [1], ethanol [2] and ion exchangers [3].

Generally, ion exchangers are produced by polycondensation or polymerization [4] reactions which have several disadvantages such as long synthesis cycles, high costs, and reaction byproducts poisonous to the environment and humans. Further development of ion exchangers has been investigated, and some studies have exhibited the preparation of ion exchangers from AR, including sugarcane bagasse [5], peanut hull [6], apple pomace [7], sawdust [8], coconut husk [9], orange peel [10], banana pith [11] and pine bark [5].

Wheat residue (WR) is one of the major AR in China, which accounts for 15.2% of the AR. Therefore, large-scale use of WR for ion exchangers may reduce AR waste. The predominant constituents of WR are cellulose (32.1%), hemicellulose (29.2%), lignin (16.4%), and other components (22.3%), making it a suitable chem-

ical composition in comparison with other AR [12]. Cellulose, hemicelluloses and lignin structures have a large amount of easily available hydroxyl groups; these hydroxyl groups can be used for the preparation of various functional polymers [13].

Research about tertiary amino anion exchanger prepared from AR (AR-TE) has been reported in previous work [5,12,14], but there is no information concerning quaternary amino anion exchanger (QE) prepared from WR used for nitrate removal in the present literature. The main objective of this paper is to discuss the preparation of wheat residue quaternary amino anion exchanger (WR-QE) from WR after reaction with epichlorohydrin and triethylamine in the presence of *N,N*-dimethylformamide and catalyst. The optimal synthesis conditions were determined by batch experiments of single influential factor and orthogonal tests. The characteristics of WR-QE and its property for nitrate removal were studied, compared with those of the AR tertiary amino anion exchangers (AR-TE) studied by Orlando [12,14].

2. Materials and methods

2.1. Materials

WR was obtained from Liao Cheng, Shandong, China. The raw WR was washed with distilled water, dried at 60 °C for 6 h and sieved into particles ranging from 100 to 250 μm with bulk density of 250 kg m⁻³.

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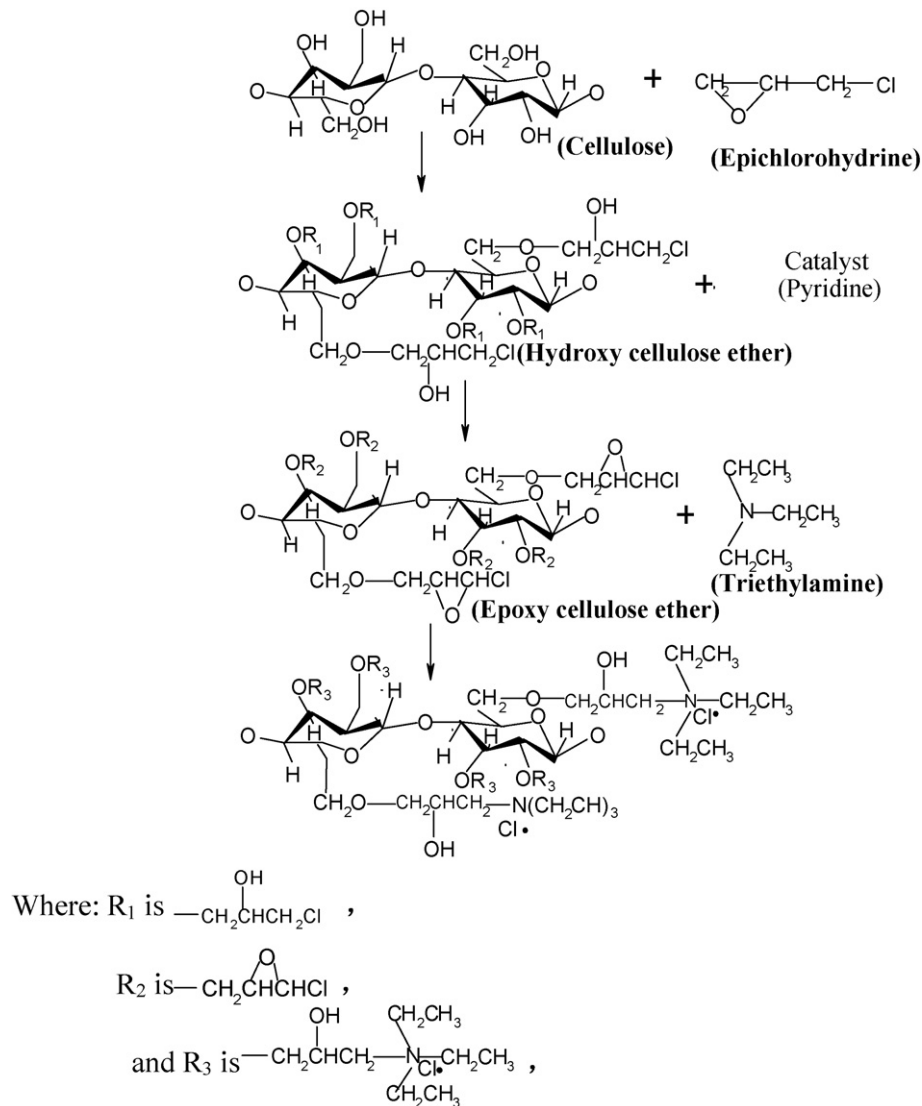


Fig. 1. Synthetic reactions of WR-QE.

2.2. Preparation of WR-QE

Batch experiments were conducted using WR with 20 ml of epichlorohydrin and 25 ml of *N,N*-dimethylformamide in a 250 ml three-neck round bottom flask at 50–100 °C for 1 h. Batch volumes (5–25 ml) of catalyst were added and the solutions were stirred for 1 h at 50–100 °C, followed by adding 15–40 ml of 99% triethylamine (w/w) for graft reaction, stirring the mixtures for 3 h at 50–100 °C.

The primary product was washed with 500 ml of distilled water to remove the residual chemicals, then dried at 60 °C for 12 h and sieved to obtain particles of less than 250 μm . The final product was obtained after a second cycle of washing, drying and sieving. It was used in all adsorption experiments [12,15].

The synthetic reactions of WR-QE using WR as a starting material are shown in Fig. 1 (cellulose as example). The reaction between epichlorohydrin and cellulose was induced after the hydroxyl groups in the cellulose molecule activated, producing hydroxy cellulose ether [16]. The hydroxy cellulose ether was then cyclized by the catalyst existing in the alkaline condition to produce the epoxy cellulose ether that was used as the intermediate in the reaction; the WR-QE was obtained after the graft reaction between epoxy cellulose ether and triethylamine [5,12].

2.3. Characteristics of WR-QE

2.3.1. The yield (%) and zeta potential (mV)

The yield of WR-QE can intuitively reflect the reaction efficiency of the preparation of WR-QE by comparing the dry weight of WR-QE and WR. The yield was determined gravimetrically using the following equation:

$$\text{Yield (\%)} = \frac{m_1}{m_0} \quad (1)$$

where m_1 and m_0 are the dry weight of WR-QE and WR, respectively. The lower bound of the yield is about 80% with the impurity in WR extracted after an unsuccessful synthesis, and the theoretic upper bound of the yield is evaluated at about 600–700% after the sufficient reaction of organic chemicals with WR.

The new anion exchanger prepared from WR is used for the removal of anionic pollutant. As a result, it is significant to determine the change of surface charge of WR-QE in comparison with WR. Zeta potential of WR-QE and WR were determined by electrokinetic analyzer (JS94H, Shanghai Zhongchen Digital Technical Apparatus Co., Ltd., China).

Table 1
Effect of catalyst types on the preparation of WR-QE.

Catalyst types	Catalyst added		No catalyst	
	Pyridine (15 ml)	NaOH solution (15 ml)	Control experiment	WR
Nitrate removal (%)	89.1	35.3	21.3	8.2
Yield (%)	556.3	84.5	90.2	–

2.3.2. Nitrogen content and total exchange capacity (TEC, mEq g^{-1})

The nitrogen content of WR-QE was measured by element analyzer (Elementar Vario EL III, Germany). TEC was estimated from the nitrogen content and calculated using the following equation [5,15].

$$\text{TEC}(\text{mEq g}^{-1}) = \frac{N\%}{1.4} \quad (2)$$

2.3.3. Infrared (IR) spectra analysis

IR spectra were recorded on a PerkinElmer “Spectrum BX” spectrometer in the $4000\text{--}400\text{ cm}^{-1}$ region.

2.4. Single influential factor experiments and orthogonal tests

In this work, it is very difficult to use factorial experiment designs to determine the optimal synthesis conditions, because too many factors and levels should be selected to determine. The combination of single influential factor experiments and orthogonal experiment designs can greatly reduce the workload of the experiments. Orthogonal experiment can also enhance the precision between all of the factors. First, the single influential factor experiments were designed to determine the single optimal synthesis conditions step by step. Then, orthogonal experiments were chosen to analyze the effect of all the factors on the experimental goals.

Single influential factor experiments and orthogonal tests were designed to determine the conditions including types of catalysts, dosages of triethylamine, and experimental temperatures (activating temperature, catalytic temperature and reacting temperature). Data of nitrate removal and yield were used as performance indicators of the products prepared.

The nitrate removal experiments were operated as follows: An aliquot of 0.1 g of WR-QE was added to 100 ml of 100 mg l^{-1} KNO_3 solution at room temperature ($20 \pm 2^\circ\text{C}$) and then shaken at 120 rpm for 60 min. The nitrate concentration was determined spectrophotometrically according to the Brucine-sulfanil colorimetric method [17], using a UV-vis spectrophotometer (model UV754GD, Shanghai).

3. Results and discussion

3.1. Optimal synthesis conditions determined by single influential factor

The single influential factor experiments were performed under optimal conditions, described by the works of Orlando [12], by varying a single selected factor, while simultaneously holding constant all other factors. The presumed optimal conditions for the synthesis in this work were selected as 2 g of WR, 15 ml of pyridine, 30 ml of triethylamine, and the optimal experimental temperatures (activating temperature, catalytic temperature and reacting temperature) were assumed at 100°C .

3.1.1. Effects of catalyst types on the preparation of WR-QE

In this study, catalyst was used to improve the synthesis of intermediate, which was transformed from the hydroxy cellulose ether, and to provide a weak-base (pH 8–11) reaction condition to facilitate the graft reaction between triethylamine and intermediate [5,18]. Therefore, weak-base catalysts can be considered for the use of this reaction. A control experiment was designed without adding a catalyst: because triethylamine itself is a weak-base reactant, it is hypothesized that it may have a catalytic effect on the reaction. The effects of the types of catalyst (sodium hydroxide solution and pyridine) on the performance of prepared WR-QE are shown in Table 1.

As shown in Table 1, the data of nitrate removal of raw WR and the WR-QE prepared from the control experiment are only 8.2% and 21.3%, respectively. Nitrate removal of the product using 0.01 mol l^{-1} of NaOH solution as catalyst is 35.3%, lower than that of the product (89.1%) using pyridine as catalyst. The pH value of the synthetic mixture after the addition of pyridine is about 8.0–9.0, compared with the pH value (5.0–6.0) of the synthetic mixture before the addition of pyridine; this indicates that pyridine can provide a suitable pH value range for the synthesis process. In addition to providing alkaline condition, pyridine can also penetrate into cellulose molecules and induce the hydroxy cellulose ether cyclized which may significantly enhance the graft reaction in the next step [5,12]. This has also been confirmed by the high yield (556.3%) of the product with pyridine as catalyst. Therefore, pyridine was selected as the catalyst in this work.

3.1.2. Effect of pyridine dosage on the preparation of WR-QE

The effect of pyridine dosage on the performance of prepared WR-QE is shown in Fig. 2. With the addition of 5 ml of pyridine, the nitrate removal of WR-QE increases rapidly from 21.0% to 69.5%; with an increase in pyridine dosage from 5 to 25 ml, a slow increase is observed in nitrate removal from 69.5% to 89.1%. The highest removal (89.1%) is obtained at 15 ml and no increase is found with more pyridine added. Pyridine's effect on yield produces a trend similar to that of nitrate removal. By increasing the pyridine dosage,

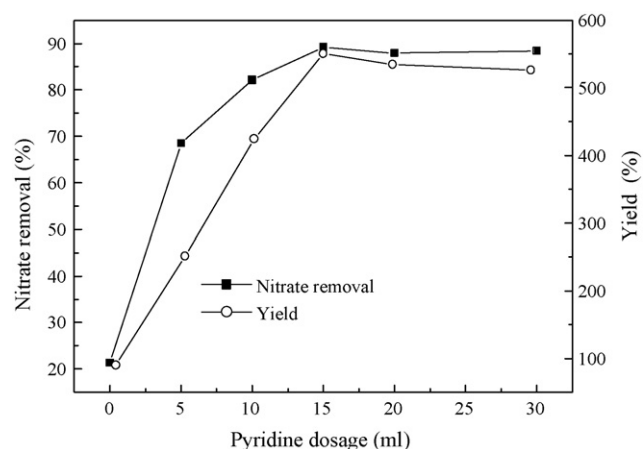


Fig. 2. Effect of pyridine dosage on the preparation of WR-QE.

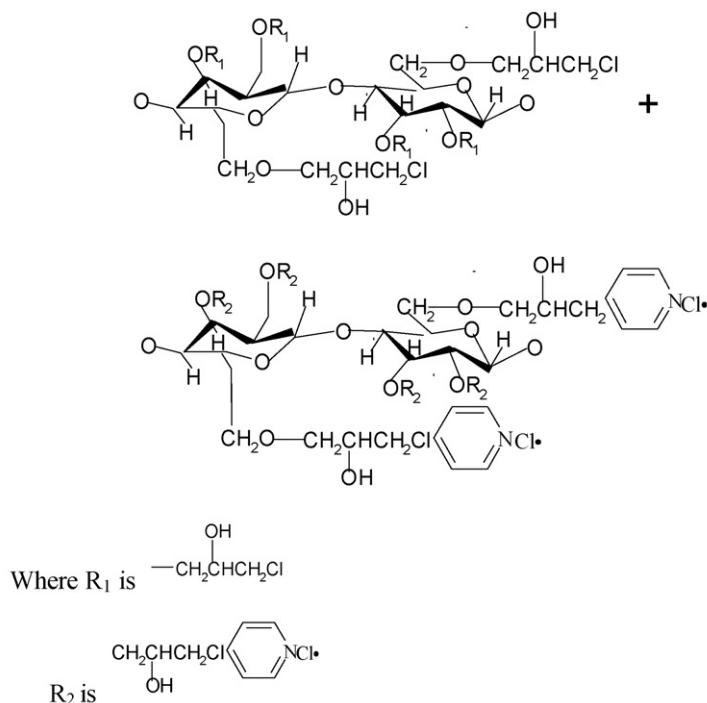


Fig. 3. Side reaction between pyridine and hydroxy cellulose ether.

it is able to more efficiently penetrate into cellulose molecules. It is found, however, that WR-QE yield decreases slightly at dosages higher than 15 ml. This can be explained by a side reaction [19], shown in Fig. 3, caused by the superfluous pyridine: it produces the byproduct heterocyclic cellulose ether, which in turn reduces the hydroxy cellulose ether.

3.1.3. Effect of WR dosage on the preparation of WR-QE

The effect of WR dosage on the performance of prepared WR-QE is shown in Fig. 4. During the preparation of WR-QE, the highest nitrate removal is obtained at 2 g of WR dosage, however, a decrease of nitrate removal is observed as the dosage of WR is increased from 2 g to 6 g. When there exists in the system an excess of WR, an insufficiency of epichlorohydrin causes a decrease of functional groups for nitrate removal. Although the highest yield is obtained at 1 g of WR dosage (Table 2), the highest dry weight (11.13 g of

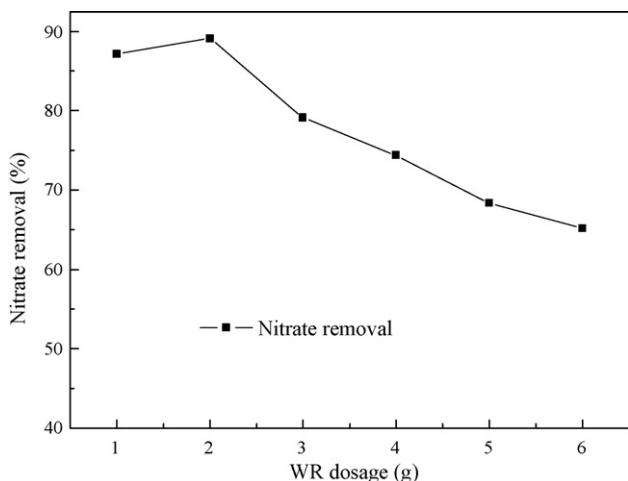


Fig. 4. Effect of WR dosage on the preparation of WR-QE.

WR-QE is still obtained using 2 g of WR (Table 2). For purposes of this work, 2 g of WR dosage seems more economical than 1 g of WR dosage. The dry weight of WR-QE decreases with the further increase of WR dosage, indicating that WR could not be utilized on a large-scale; this problem merits a further investigation. Therefore, 2 g of WR dosage was selected in this work.

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

In contrast to WR-TE, which was prepared using dimethylamine as the graft reactant, WR-QE was prepared using triethylamine. Fig. 5 shows the effect of the dosages of triethylamine and dimethylamine on the performance of prepared WR-QE and WR-TE, respectively.

As shown in Fig. 5(a), nitrate removal increases from 69.0% to 89.1% with the increase of triethylamine dosage from 15 to 30 ml, and the highest nitrate removal (89.1%) is obtained at 30 ml of triethylamine. A slight decrease, however, in nitrate removal is observed with a further increase of triethylamine dosage from 30 to 40 ml; this is due to the decrease of functional groups in WR-QE. The reaction between triethylamine and epoxy cellulose ether requires an excess of epichlorohydrin, which induces cross-linking in the reaction [20]. At triethylamine dosages higher than 30 ml, the cross-linking reaction stops due to an insufficiency of epichlorohydrin, and as a result the functional groups in WR-QE for nitrate removal decrease. The effect of dimethylamine dosage on nitrate removal is similar to that of triethylamine dosage, but at all dosages, nitrate removal in WR-TE is 6–10% lower than in WR-QE; its highest nitrate removal is only 78.0%. WR-QE's higher nitrate removal

Table 2
Dry weight of WR-QE changed with the dosage of WR.

Dry weight of WR (g)	1	2	3	4	5	6
Dry weight of WR-QE (g)	8.02	11.23	9.64	9.03	8.98	7.95
Yield (%)	802.0%	561.5%	321.3%	225.8%	179.6%	132.5%

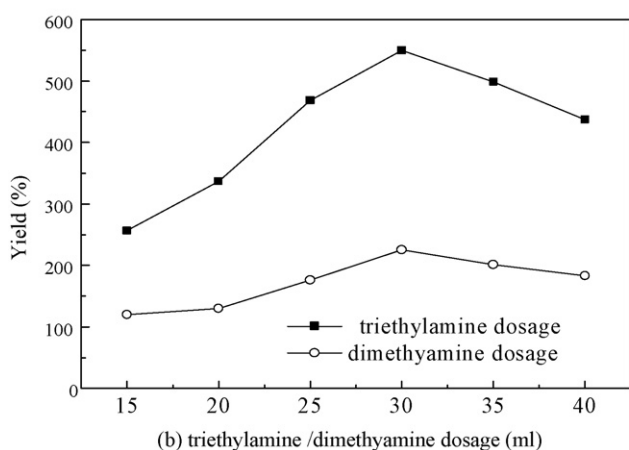
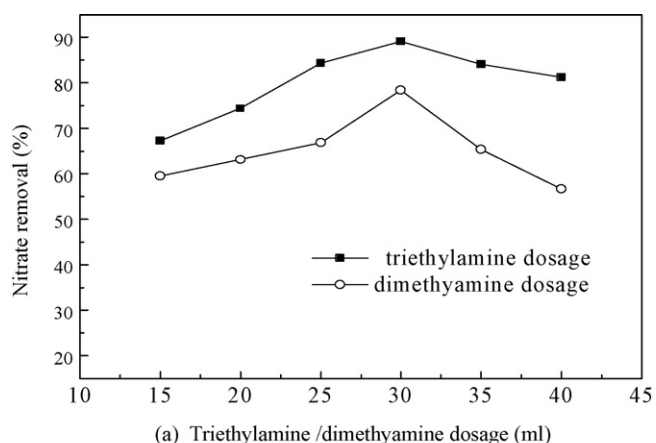


Fig. 5. Effect of triethylamine/dimethylamine dosage on the preparation of WR-QE/WR-TE.

adsorption effect could be explained by the high speed of quaternary amine adsorption, which exceeds that of tertiary amine and hydroxyl [21,22].

Fig. 5(b) presents the effects of triethylamine and dimethylamine dosages on the yields of WR-QE and WR-TE, respectively. Though their yields and nitrate removal show similar trends, a remarkable difference is observed in the yield between WR-QE and WR-TE. Compared with the yield of WR-TE, which ranges between 130.1% and 225.0%, the yield of WR-QE increases from 255.1% to 556.3% with increasing triethylamine dosage, with the highest yield (556.3%) obtained at 30 ml of triethylamine. The higher yield of WR-QE indicates that the use of triethylamine could lower the activation energy of the graft reaction [22].

3.1.5. Effect of temperature on the preparation of WR-QE

The synthesis process for WR-QE is divided into three steps; the experimental temperatures for these steps are the activating temperature, the catalytic temperature and the reacting temperature. The activating temperature is defined as the experimental temperature in the first synthesis process that activates the hydroxyl existing in the WR, and then induces the synthesis of hydroxy cellulose ether through the reaction between epichlorohydrin and hydroxyl. The experimental temperature in the second synthesis step was the activating temperature; in this second step, epoxy cellulose ether was produced after the hydroxyl cellulose ether cyclized by the catalyst pyridine. The reacting temperature is used to describe the graft reaction between epoxy cellulose ether and triethylamine.

Fig. 6 shows the effects of experimental temperatures on the preparation of WR-QE in the single influential factor experiments. As indicated in Fig. 6(a), the optimal experimental temperature that yields the highest nitrate removal for the synthesis of WE-QE is 100 °C. Nitrate removal is less than 50% at catalytic temperatures less than 90 °C, however it sharply increases from 49.1% to 89.1% as the catalytic temperature is increased from 90 to 100 °C. The effects of the activating temperature and reacting temperature on the nitrate removal performance of WR-QE are relatively less than the effect of the catalytic temperature (shown in Fig. 6(a)). Similar trend is observed in the yield (Fig. 6(b)). As a result, the catalytic temperature could be considered to be the key factor in experimental temperatures.

3.2. Orthogonal tests for the determination of the optimal reaction conditions

Orthogonal experimental design is the primary approach of fractional factorial design, which can comprehensively reflect the effects of all factors selected in a test. It has been widely used across research fields for its high efficiency and practical economic value [23,24]. In this study, orthogonal tests were applied to validate the optimal reaction conditions and the key influential factor in the preparation of WR-QE.

Though pyridine dosage, triethylamine dosage, and temperatures are considered to be the most important factors in the single influential factor experiments, a composite analysis is required for

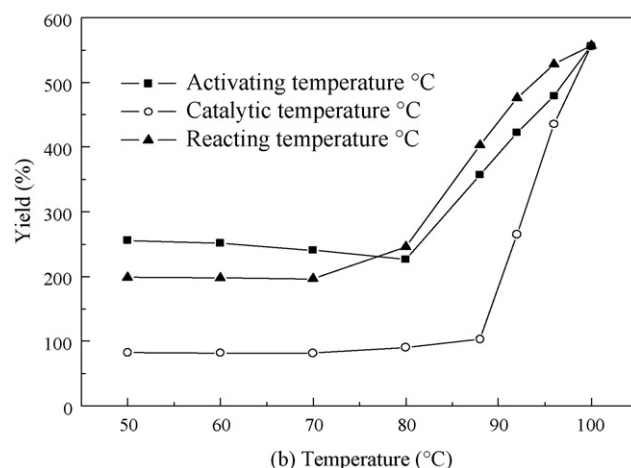
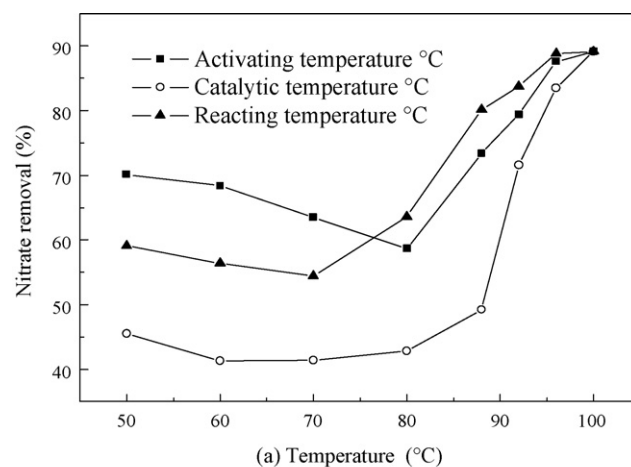


Fig. 6. Effect of experimental temperature on the preparation of WR-QE.

Table 3
Optimal reaction conditions determined by orthogonal tests.

No.	(A) Activating temperature (°C)	(B) Pyridine dosage (ml)	(C) Catalytic temperature (°C)	(D) Triethylamine dosage (ml)	(E) Reacting temperature (°C)	Nitrate removal (%)	Yield (%)
1	A1 100	B1 15	C1 100	D2 30	E1 100	89.1	556.3
2	A1 100	B2 10	C2 80	D3 20	E2 80	45.3	89.2
3	A1 100	B3 5	C3 60	D1 40	E3 60	42.8	91.2
4	A2 80	B1 15	C1 100	D3 20	E2 80	65.5	179.4
5	A2 80	B2 10	C2 80	D1 40	E3 60	43.2	86.2
6	A2 80	B3 5	C3 60	D2 30	E1 100	41.2	93.2
7	A3 60	B1 15	C2 80	D2 30	E3 60	46.8	90.5
8	A3 60	B2 10	C3 60	D3 20	E1 100	45.6	87.6
9	A3 60	B3 5	C1 100	D1 40	E2 80	70.1	214.7
10	A1 100	B1 15	C3 60	D1 40	E2 80	43.9	86.1
11	A1 100	B2 10	C1 100	D2 30	E3 60	62.4	193.2
12	A1 100	B3 5	C2 80	D3 20	E1 100	47.2	98.2
13	A2 80	B1 15	C2 80	D1 40	E1 100	41.7	86.2
14	A2 80	B2 10	C3 60	D2 30	E2 80	42.5	85.2
15	A2 80	B3 5	C1 100	D3 20	E3 60	63.5	203.6
16	A3 60	B1 15	C3 60	D3 20	E3 60	43.7	88.6
17	A3 60	B2 10	C1 100	D1 40	E1 100	72.5	252.1
18	A3 60	B3 5	C2 80	D2 30	E2 80	41.5	92.4

Table 4
Analysis of orthogonal $L_{18} (3)^5$ test.

	Activating temperature (°C)	Pyridine dosage (ml)	Catalytic temperature (°C)	Triethylamine dosage (ml)	Reacting temperature (°C)	Nitrate removal (%)	Yield (%)
k_1^a	55.1	55.1	70.5	55.6	56.7	58.4	–
k_2	49.6	52.0	44.6	49.8	49.5	45.3	–
k_3	52.1	51.0	43.5	52.6	50.8	50.0	–
R^b	5.5	4.0	26.9	5.8	7.1	13.1	–
k_1^c	185.8	181.1	266.3	185.1	195.5	–	202.9
k_2^c	122.3	132.3	88.8	124.5	124.6	–	118.6
k_3^c	137.5	132.1	88.7	109.0	110.2	–	115.2
R^d	63.5	49.0	177.5	76.1	85.3	–	86.1

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

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

^c $k_i^c = \sum \text{the yield of single factor}/6$.

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

further understanding of the optimal reaction conditions. Due to its failure in large-scale utilization, the dosage of WR is not considered in the orthogonal tests. Orthogonal tests with five factors and three levels were designed. Eighteen synthesis conditions were carried out at activating temperatures of 60, 80 and 100 °C, pyridine dosages of 5, 10 and 15 ml, catalytic temperatures of 60, 80 and 100 °C, triethylamine dosages of 20, 30 and 40 ml and reacting temperatures of 60, 80 and 100 °C. All selected factors were examined using an orthogonal $L_{18} (3)^5$ test presented in Table 3, with nitrate removal and yield as indicators. The orthogonal tests were designed and analyzed by Orthogonality Experiment Assistant II 3.0 (software) [25].

The results of experiments listed in Table 3, evident among all 18 designed orthogonal tests, indicate that the parameters of the highest yield and nitrate removal of WR-QE are 556.3% and 89.1% (No. 1), respectively. The synthesis conditions of orthogonal test No.1 are the same as the optimal synthesis conditions determined by the single influential factor experiments. Therefore, we conclude that the optimal synthesis conditions for WR-QE preparation are at the ratios of wheat residue:epichlorohydrin:pyridine:triethylamine = 2 g:20 ml:15 ml:30 ml, and experimental temperature of 100 °C.

To determine the key influential factor, a further orthogonal analysis was performed [24]. The calculated k and R values which are widely used in the range analysis of orthogonal tests are listed in Table 4, where k is the average of the data in one level of the single factor, and R is the difference between the maximal value and minimal value of k .

The values of k present the effects of various levels on the preparation of WR-QE and the R values reflect the effects of various factors on the synthesis reaction. The high R value of the factor demonstrates the major factor on the impact of indicators. As indicated in Table 4, the prominent k value is obtained at 100 °C of catalytic temperature, which indicates that the preparation of WR-QE will be operated more efficiently at 100 °C of catalytic temperature

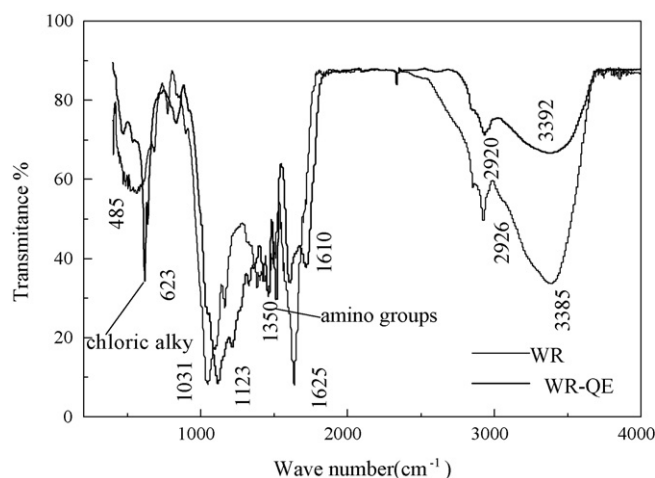


Fig. 7. IR analysis of WR-QE and WR.

Table 5
Change of element content of WR.

	N (%)	C (%)	H (%)	TEC (mEq g ⁻¹)
WR	0.4	41.1	6.1	0.3
WR-QE	6.0	47.3	6.7	4.3

in comparison with other conditions. Range *R* values of the five factors (activating temperature, pyridine dosage, catalytic temperature, triethylamine dosage, reacting temperature) are 5.5, 4.0, 26.9, 5.8, 7.1, and 63.5, 49.0, 177.5, 76.1, 85.3 by taking nitrate removal and yield as the indicators, respectively. The significantly high *R* values of catalytic temperature than the other factors indicate that catalytic temperature is the most important factor that determines the preparation of WR-QE. This result has confirmed the data of the single influential factor experiments.

3.3. Characteristics of WR-QE prepared by the optimal synthesis conditions

WR-QE prepared under the optimal synthesis conditions described above has shown an excellent nitrate removal capacity and high yield. Further investigation is needed in order to evaluate the characteristics of WR-QE as compared with those of WR, including zeta potential, nitrogen content and IR analysis.

3.3.1. Zeta potential (mV) analysis

Sample's zeta potentials were performed using electro-kinetic analyzer. Results show that the zeta potentials of WR-QE and WR are +45 and -35 mV, respectively, indicating the existence of positive-charge functional groups on the WR-QE structure.

3.3.2. Nitrogen content (%) analysis

Table 5 displays the elemental changes of carbon, hydrogen and nitrogen in WR-QE in comparison with WR. A slight increase is observed in the carbon content and hydrogen content after a comparison between WR-QE and WR. Nitrogen content of WR-QE, however, increases significantly from 0.4% to 6.0%, indicating that the reactions proceed efficiently and quite a number of amino groups from triethylamine have been introduced into the WR-QE. TEC estimated from the nitrogen contents of WR-QE and WR are given in Table 5. The excellent nitrate removal of WR-QE is validated by the significant higher TEC values of WR-QE over those in the raw WR.

3.3.3. IR analysis of WR-QE

The IR spectral change of WR and WR-QE is shown in Fig. 7. The band intensity at 3380 cm⁻¹ indicates a mass of hydroxyl groups; ketone groups are observed by the band intensity at 2920 cm⁻¹, and the band at 1625 cm⁻¹ is associated with the special vibration of aromatic cyclic groups. IR analysis of WR-QE shows a change in the structure between WR-QE and WR. Fig. 7 shows chloric alky in WR-QE by the intense vibration of band at 623 cm⁻¹. The intense vibration at 1350 cm⁻¹ further indicates that a large number of amino groups have been grafted into the WR-QE structure.

The IR spectrums of WR-QE and WR indicate that the largest changes in WR-QE are the decrease in hydroxyl reactive groups and the increase of amino groups as adsorption sites for nitrate removal.

4. Conclusions

Optimal synthesis conditions for the preparation of WR-QE were determined by single influential factor experiments and orthogonal tests; the catalytic temperature was found to be the key influential

factor. The high nitrate removal (89.1%) and yield (556.3%) of WR-QE prepared from the optimal synthesis reactions indicated that lower activation energy was required in the graft reaction between epoxy cellulose ether and triethylamine.

The characteristics of WR-QE prepared in the optimal synthesis conditions were evaluated. A large number of amino groups with positive charge were found in the structure of WR-QE after the IR spectrums analysis and zeta potential analysis. It has been further demonstrated that the excellent nitrate removal of WR-QE was confirmed by the significant high TEC value of WR-QE.

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