Preparation of Lignin-Based Quaternary Amine Anion Exchangers in NaOH Solutions and their Characteristics

Nana Bo [a] and Zhen Wang [a,b,]*

A lignin-based quaternary amine anion exchanger (LQAE) modified from raw lignin was synthesized after the reaction with epichlorohydrin and triethylamine using an NaOH solution as the basic solvent. The reaction mechanism of the experiment was explored and validated. Effect of reaction conditions on the preparation of LQAE were investigated. The performance of the LQAE was characterized by FTIR, SEM, and elemental analysis. The adsorption rate and yield were the measurable indicators, and when the NaOH concentration was 6 M, the nitrate adsorption capacity and the yield were 36.7 mg nitrate/g anion exchanger lignin and 123.6%, respectively.

Keywords: Lignin; Nitrate adsorption; LQAE

*Contact information: a: Key Laboratory of Pulp & Paper Science and Technology, Ministry of Education, Qilu University of Technology, Jinan, Shandong province, China, 250353; b: Key Laboratory of Cleaner Production and Industrial Waste Recycling and Resourcization, Qilu University of Technology, Jinan, Shandong province, China, 250353;*Corresponding author: wangzhenyft@126.com*

INTRODUCTION

As the second most abundant natural raw material (Gosselink *et al*. 2004), lignin is the most abundant aromatic (phenolic) polymer (Lora and Glasser 2002) in nature. Its content usually depends on the plant species (roughly 15 to 30%) (Dence 1992). There are more than 50 million tons of lignin being produced annually worldwide as a residue (low value by-product) from pulp and paper and ethanol production processes (Gosselink *et al.* 2004); however, only a small portion (1 to 2%) of it is commercially used to partially replace petrochemicals, while the rest is used as fuel to heat the pulping boilers (El Mansouri *et al.* 2011a). Recently, considerable interest has been shown in their utilization in several industrial applications, mainly based on more environmentally friendly and natural compounds.

Lignin can be used to prepare polymeric materials, such as polyurethanes (Bonini *et al.* 2005; Liu *et al.* 2009), phenolic resins (Cavdar *et al.* 2008; Wang *et al.* 2009), and epoxy resins (Nieh and Glasser 1989; Zhao *et al.* 2000). Researchers have developed several methods to synthesize lignin-based epoxy resins. Sun *et al.* (2007) used water-soluble lignin (prepared from calcium lignosulfonate treated with sulfuric acid and phenol) mixed with epichlorohydrin and sodium hydroxide to obtain lignin-based epoxy resin. Ismail *et al.* (2010) used sodium lignosulfonate as a matrix to form two series of crosslinked epoxy resins; the crosslinked epoxy resins obtained presented high potential to be used as adhesives and to be used to produce polymers with high biomass contents. Malutan *et al.* (2008), El Mansouri *et al.* (2011a; 2011b), and Feng and Chen (2012) used different methods to obtain epoxidized lignin. However, there have not been many studies exploring lignin as a polymer matrix for anion exchangers, especially in aqueous systems.

In this study, a lignin-based epoxy resin intermediate was synthesized based on previous studies (El Mansouri *et al.* 2011a); furthermore, lignin-based quaternary anion exchangers (LQAE) were synthesized from the epoxy resin intermediate. The main objective was to better understand the preparation and reaction mechanism of LQAE from lignin after its reactions with epichlorohydrin and triethylamine in NaOH solutions containing no other catalysts. Lignin and the products were characterized structurally by FTIR spectroscopy and scanning electron microscopy (SEM).

MATERIALS AND METHODS

Materials

All the chemicals used in this study were of analytical grade and purchased from Damao Company, Tianjin, China. The 1000 mg L^{-1} nitrate stock solutions were prepared by dissolving the required quantities of KNO_3 (Damao, China) in distilled water. All solutions for sorption and analysis were prepared by appropriate dilution of freshly prepared stock solution. The raw lignin was obtained from Shanfeng Biomass Materials Co. Ltd., Jiangsu, China; it was extracted from the black liquor of wheat straw by an acid precipitation method and was purified according to the method reported by El Mansouri *et al*. (2011a).

Preparation of LQAE

The procedure for LQAE synthesis is presented in Fig. 1. Batch experiments were conducted using 4 g of raw lignin with 17 mL of epichlorohydrin and 60 mL of 1-8M NaOH solution added to a three-necked round-bottom flask at 40 to 80 °C for 2 to 8 h. Then, the solution pH was adjusted to about 7 with NaH_2PO_4, and the precipitated epoxy lignin was suction filtrated and washed with plenty of distilled water (El Mansouri *et al.* 2011a; Malutan *et al.* 2008).

The epoxide lignin product and 30 mL of 0.3 M NaOH solution were added to the three-necked flask and stirred well, followed by the drop-wise addition of 15 mL of triethylamine (99.5% w/w) for the graft reaction at 65 °C for 3 to 5 h. The solution pH was acidified with 0.1 M HCl, and the solution was soaked for some time. The final products were washed with a large amount of distilled water to remove residual chemicals, and the precipitate was dried at 60 °C for 12 h. The dried precipitate products were then stored until required.

Performance Indicators of LQAE

In this paper, the performance indicators of the final product LQAE were determined through the data of nitrate removal efficiency of LQAE. The nitrate removal experiments were operated as follows: A series of 125 ml flask were filled with LQAE at mass loadings 2 g L^{-1} for nitrate solution (60 mg L^{-1}) at room temperature (20 ± 1 ^{o}C). The conical flasks were then agitated in an orbital shaker at 120 rpm, and liquid samples were taken out at a given time interval for nitrate analyses with an UV–visible spectrophotometer (model UV754GD, Shanghai).

Characterization of LQAE

The yield of LQAE

The yields of LQAE were calculated according to Eq. 1,

$$Yield(\%) = \frac{m_{(\text{mod})}}{m_{(\text{un mod})}} \times 100\% \qquad (1)$$

where $m_{(\text{mod})}$ is the dry weight of LQAE and $m_{(\text{un mod})}$ is the dry weight of raw lignin.

Infrared (IR) spectra analysis and SEM analysis

The functional groups of the LQAE and the initial raw lignin were investigated using FTIR (IRPretige-21, Shimadzu, Japan). The samples were prepared by mixing 1 mg of material with 100 mg of spectroscopic grade KBr. The spectra were recorded from 500 to 3000 cm^{-1} at 32 scans per sample. SEM micrographs of the samples were obtained with a Quanta 200 (FEI) scanning electron microscope. The sample was coated with a conducting resin, and the conductive treatment consisted of sprayed gold prior to obtaining the SEM micrograph (Wang *et al.* 2013).

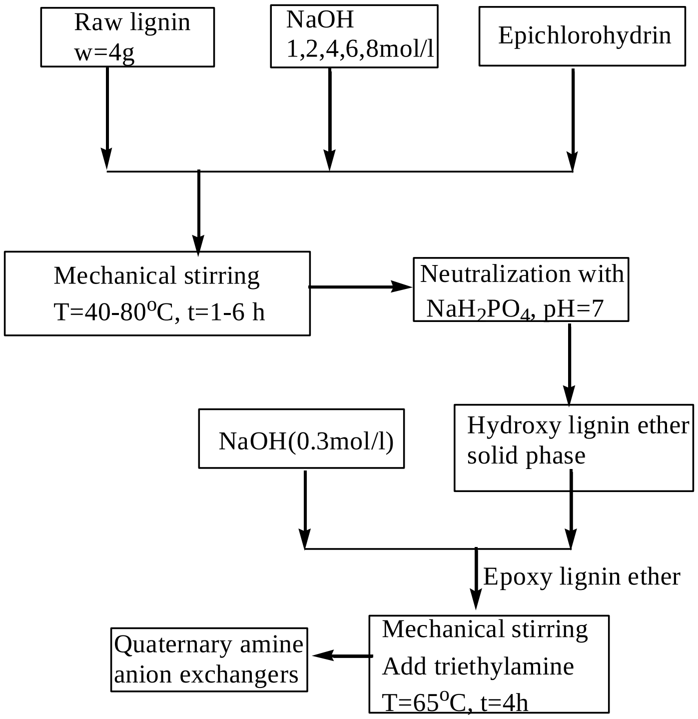

Fig. 1. Diagram of the preparation of LQAE

Elemental analysis

The nitrogen, carbon, and hydrogen contents of LQAE was measured using an elemental analyzer (Elementar Vario EL III, Germany) to evaluate the amount of grafted amine groups in the LQAE.

Zeta potential

Zeta potential measurements were carried out using a microelectrophoresis apparatus (JS94H, Shanghai Zhongchen Digital Technical Apparatus Co., Ltd., China).

The samples were prepared with 0.2 g material in 100 mL of 0.01 M NaCl, and vibrated at 25 °C for 2 h. The sample particles were dispersed into distilled water over the pH range of 1.0 to 10.0 to determine the zeta potential of the LQAE and the raw lignin at different pH values.

Adsorption experiment

Nitrate solution with a concentration of 300 mg L^{-1} was prepared by dissolving 30.0 g of KNO_3 into 1000 mL of distilled water, and the solution was stocked in a 1000-mL volumetric flask. The solution was diluted into various concentrations (from 50 mg L^{-1} to 300 mg L^{-1}) before use.

To determine the maximum exchange capacities of LQAE for nitrate, batch exchange experiments were carried out at 20 ± 1 °C using a 100-mL Erlenmeyer flask containing 50 mL of nitrate solution at different concentrations. The optimum amount of LQAE was immersed in the solutions, which were agitated for 3 h. Residual anionic concentrations in solutions were determined according to the brucine-sulfanilic colorimetric method (APHA 1989) using a UV-vis spectrophotometer (model UV754GD, Shanghai). The maximum exchange capacity (Q_{max}) was evaluated with the Langmuir isotherm equation.

RESULTS AND DISCUSSION

Mechanism Analysis

Reaction mechanism

The synthesis of LQAE using raw lignin as a starting material is shown in Fig. 2. In strong alkali solutions, the reaction between epichlorohydrin and lignin was induced after the hydroxyl groups in the lignin molecule were activated. The reaction occurs between the epoxy group of epichlorohydrin and the hydroxyl group of lignin, which grafts the halogen group onto the lignin structure (McCormick and Dawsey 1990; Gao *et al*. 2009).

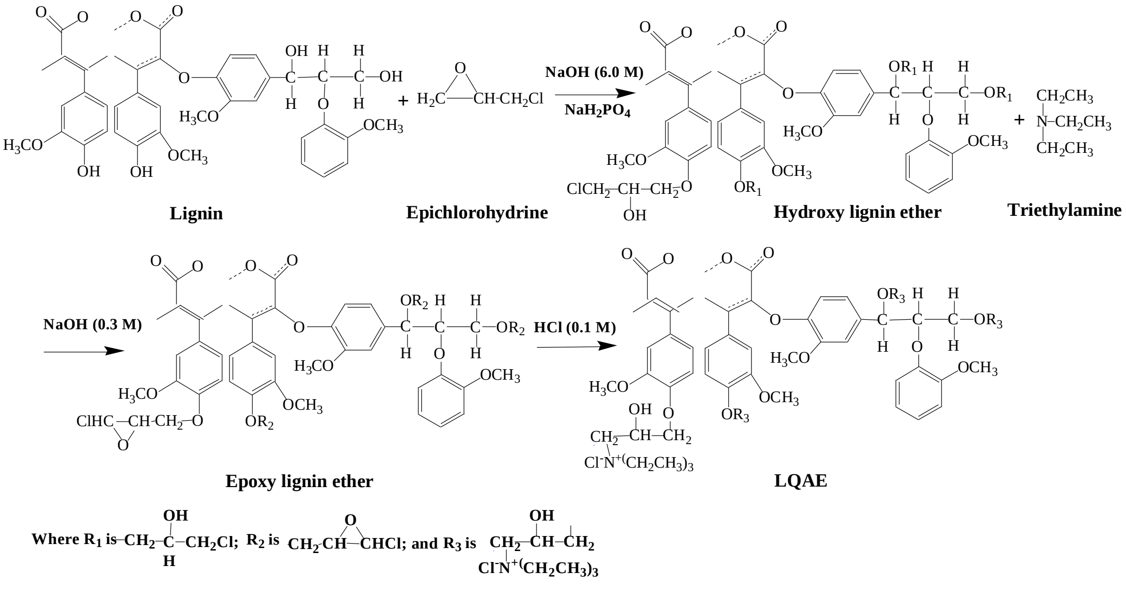

Fig. 2. Synthesis of LQAE

The hydroxy lignin ether was then neutralizated and washed by deionized water and was used as the intermediate in the reaction. During the amination reaction, the hydroxy lignin ether was cyclized by the catalyst existing in the alkaline condition to produce the epoxy lignin ether. Reaction with triethylamine is believed to occur after ring opening of the epoxide group and condensation through chloromethyl group in an excess of epichlorohydrin (Biçak and Şenkal, 1998; Orlando *et al*. 2002b; Gao *et al*. 2009). The free electrons of the N atom of triethylamine can attack the C atom in the epoxy group of the epoxidized lignin, triethylamine and epoxidized are then covalently together. LQAE was obtained after the graft reaction between epoxy lignin ether and triethylamine (Gao *et al*. 2009).

Effect of Reaction Conditions on the Preparation of LQAE

Effect of medium concentration on the reaction

Data of nitrate removal efficiency were used as the performance indicators of the prepared LQAE. The presumed conditions for the synthesis in this work were selected as 4 g of lignin, 17 mL of epichlorohydrin, and 60 mL of NaOH solution. The experimental temperature was selected as 60 ºC, and the reaction time was set as 5 h.

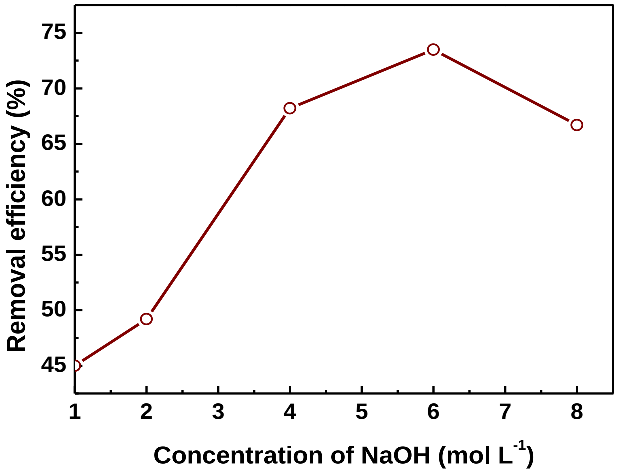

Fig. 3. Effect of NaOH concentration on the preparation of LQAE

Figure 3 illustrates the effect of NaOH concentration on the performance of prepared LQAE. Parallel experiments were carried out using 1M, 2 M, 4 M, 6 M, and 8 M NaOH. As the NaOH concentration was increased from 1 to 6 M, the nitrate removal of LQAE increased from 45.0% to 73.5%, and the performance of LQAE was almost constant with further increase in NaOH concentration from 6 to 8 M. This indicates that 6 M of NaOH was the optimal concentration for the preparation of LQAE.

Under the alkaline conditions, partial hydrolysis of epichlorohydrin to glycerol occurred, and the hydrolysis rate of epichlorohydrin was markedly enhanced when the concentration of NaOH at low decreased (Wang *et al*. 2010). This will decrease the graft reaction between epoxy lignin ether and triethylamine. The produced glycerol may result in other side reactions (Ismail *et al*. 2010), and finally decrease the performance of the LQAE. On the other hand, the hydrolysis of the epichlorohydrin can be stabilized to a certain extent when the concentration of NaOH is increased to a certain level (Wang *et al.* 2010). In this experiment, the optimum concentration of NaOH was found to be 6 M.

Effect of reaction temperature on the preparation of LQAE

Effect of reaction temperature on the preparation of LQAE is shown in Fig. 4(a). As the reaction temperature was increased from 40 to 60 °C, the percentages of nitrate sorbed onto the series of LQAE increased from 47.5% to 72.5%. However, a gently decreasing trend was observed in the nitrate removal of LQAE prepared with further increase in reaction temperature from 60 to 80 °C. This decrease was probably due to secondary reactions occurring between the formed hydroxyl lignin ether and the free hydroxyl groups.

The same behavior was reported by Malutan *et al.* (2008) when they studied the epoxidization reaction different alkaline lignins with epichlorohydrin under alkaline conditions. Therefore, optimal reaction temperature for the preparation of LQAE was selected at 60 °C in this work.

Effect of reaction time on the preparation of LQAE

The effect of reaction time on the performance of prepared LQAE is shown in Fig. 4(b). With the increase of reaction time from 1 to 3 h, nitrate removal of LQAE increases from 42.0% to 72.5%. The removal efficiency of nitrate showed a gently decreasing tendency in the nitrate removal of LQAE prepared in later period from 3 to 4 h. This is because the ring opening in epoxide group, caused by the hydrolysis and crosslinking reactions occurred in the epoxy lignin ether, which will decrease the efficiency of amination reaction, and finally weaken the performance of LQAE. Therefore, 3 h of reaction time was selected in the preparation of LQAE.

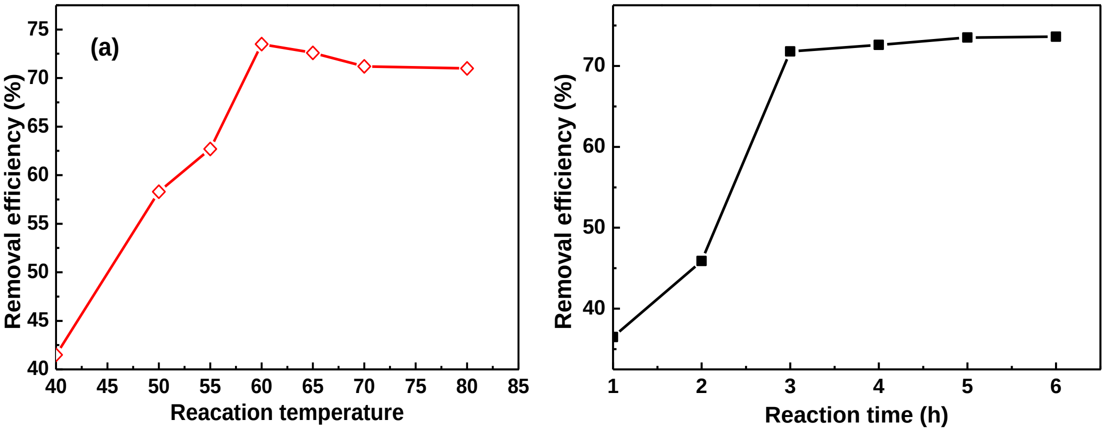

Fig. 4. Effect of reaction temperature and reaction time on the preparation of LQAE

Yield Analysis

The LQAE were synthesized in accordance with the above method. The final optimum synthesis conditions were determined through single factors analysis and multi-level orthogonal design (not shown in this paper) as follows: the concentration of NaOH was 6 M, reaction temperature was 60 °C and the reaction time was 3 h. The yield reached 123.6% (from Eq. (1)) under the optimum reaction conditions. The resulting product was reddish-brown powder; this powder was used in all the adsorption experiments.

FTIR Analysis

The FTIR spectra of the raw lignin, epoxy lignin, and LQAE are shown in Fig. 5. For the raw lignin (Fig. 5(a)), the peak at 2924 cm^{-1} is associated with the special vibration of the aliphatic C-H bond in lignin. The carbonyl groups in lignin molecule are denoted by the intensity of the band at 1709 cm^{-1}. The aromatic skeletal vibration occurred at 1600 and 1515 cm^{-1}. The C-H deformations band of asymmetric methyl and methylene appeared at 1460 cm^{-1}. The band at 1370 and 1328 cm^{-1} are due to the bending vibration of the phenolic OH groups (El Mansouri *et al*. 2011a). Bands at 1210 and 1035 cm^{-1} are the characteristic of secondary and primary aliphatic OH groups (Malutan *et al*. 2008; El Mansouri *et al*. 2011a). Compared with raw lignin, the disappeared peak at 1035 and 1130 cm^{-1} corresponds to the decrease of aliphatic OH groups in hydroxy lignin ether (Fig. 5(a)). As can be seen in Fig. 5(c), the intense vibration at 1320-1380 cm^{-1} indicates the existence of grafted amine groups in the structure of the LQAE (Gao *et al*. 2009). As a result, the adsorption of nitrate anions onto LQAE can be ascribed to the significant increase of cationic quaternary amine groups, which are used as exchanger sites for sequestering nitrate anions.

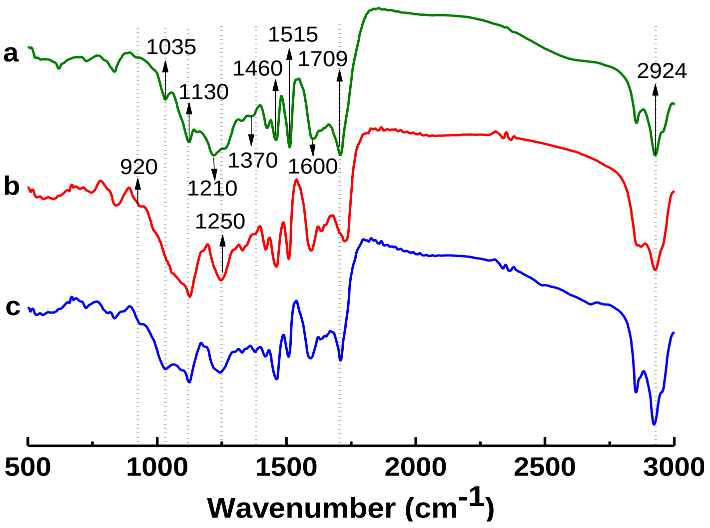

Fig. 5. IR analysis of (a) raw lignin (b) epoxy lignin and (c) LQAE

SEM Analysis

The results of SEM measurements of the structures of raw lignin and LQAE are shown in Fig. 6.

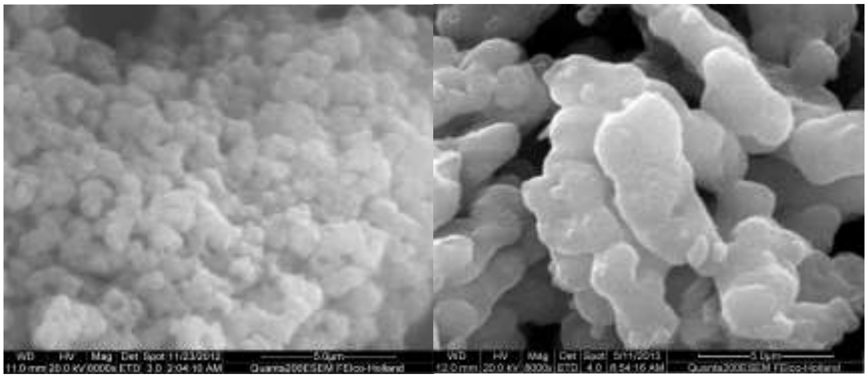

Fig. 6. SEM micrographs of raw lignin (left) and LQAE (right)

More micropores were observed on the surface of the LQAE when compared to the surface of the raw lignin. This indicated that the specific area of the lignin increased during the process of modification. It also indicated that more gaps existed in the microporous surface of the LQAE, which could be beneficial for nitrate removal.

Elemental Analysis

Table 1 displays the elemental changes of carbon, hydrogen, and nitrogen in LQAE in comparison with raw lignin. A slight increase is observed in the carbon content and hydrogen content after a comparison between LQAE and raw lignin. The nitrogen content of LQAE, however, increases significantly, from 0.58% to 6.0%, indicating that the reactions proceeded efficiently and that quite a number of amino groups from triethylamine had been introduced into the LQAE.

Table 1. Change in Elemental Content of Raw Lignin

	N (%)	C (%)	H (%)
Raw lignin	0.58	44.6	5.9
LQAE	6.0	56.2	6.6

Zeta Potential at Various pH values

Figure 7 shows that the zeta potentials of the LQAE were in the range of +2.5 to +41.3 mV, while the raw lignin was in the range of -13 to +14.6 mV over the designated pH range. This indicated the existence of cationic functional groups on the LQAE structure.

It was also observed that the zeta potentials of the LQAE gradually decreased as the pH was increased from 1 to 10 this could be attributed to the pH-dependent functional groups existing in LQAE, such as hydroxyl and carboxyl groups. These groups will exhibit a greater negative charge when the pH is increased, which results in the decrease in the positive charge of LQAE. Similar results have been reported in the work of Huang *et al*. (2009) and Wang *et al*. (2013).

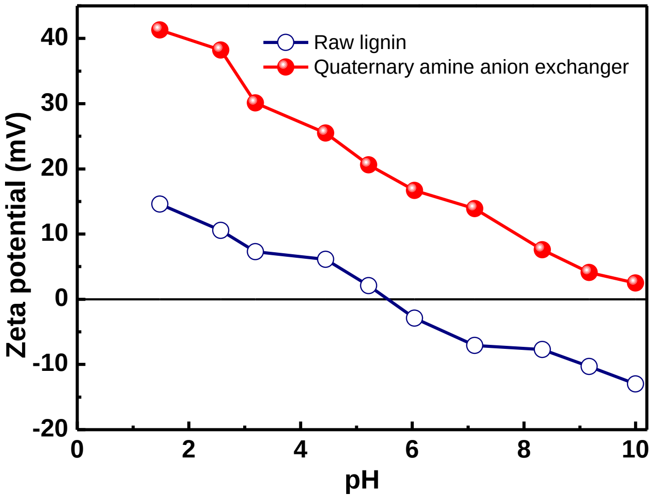

Fig. 7. Zeta potential of LQAE and raw lignin as a function of pH

Sorption Capacity of LQAE

To evaluate the sorption capacities of LQAE, batch sorption tests were conducted on the LQAE for the sorption of nitrate. The initial concentrations of nitrate were selected in the range of 5 to 300 mg L^{-1} (Fig. 8).

The related parameters were analyzed with the Langmuir model to evaluate the maximum exchange capacity (Q_{max}). A Langmuir-type isotherm is an indication of surface homogeneity of the exchangers and ion exchange phenomena (Weber 1972). The Langmuir isotherm equation in the linear form is as follows:

$$q_e = \frac{Q_{\max} \cdot b \cdot C_e}{1 + b \cdot C_e} \tag{2}$$

In Eq. 2, q_e is the amount of sorbed nitrate on the LQAE (mg g^{-1}); C_e is the equilibrium nitrate concentration in solution (mg L^{-1}); Q_{max} is the maximum value of sorption capacity (mg g^{-1}); and b is the Langmuir constant (L mg^{-1}). The related parameters for the fitting of the Langmuir equation were determined using Origin 8.5. The results indicate that the Q_{max} for nitrate is 36.7 mg g^{-1} and the constant b is 0.095 (R^2=0.995).

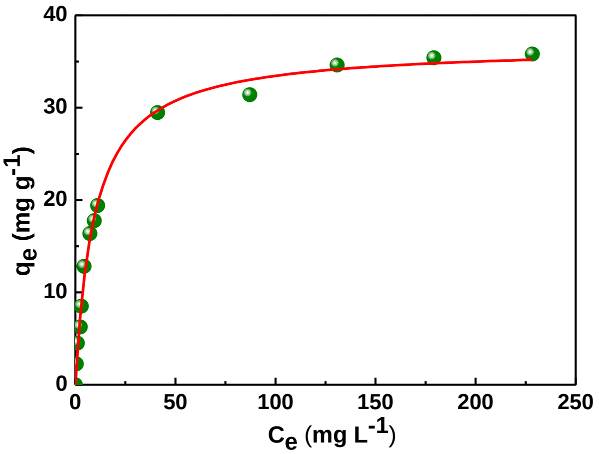

Fig. 8. Sorption capacities of NO_3^- *vs.* equilibrium concentrations

Some commercially available anion exchange resins, activated carbon, and reported modified adsorbents have been selected and their nitrate adsorption capacities have been evaluated (Orlando *et al*. 2002a; Park and Na 2006; Chabani *et al*. 2007; Wang *et al*. 2013; Katal *et al.* 2012; Wan *et al*. 2012). The results are presented in Table 2 for comparison with LQAE.

Table 2. Q_{max} of NO_3^- on Different Ion Exchangers

Ion Exchangers	Q_{max} (mg g^{-1})	Reference
LQAE	36.7	In this work
Activated carbon	5.8	Park and Na 2006
DiaionWA10	117.8	Orlando *et al.* 2002a
Amberlite IRA 400	65.36	Chabani *et al.* 2007
Hydrotalcites	34.36	Wan *et al*. 2012
Lignin based anion resin	74.53	Wang *et al.* 2013
Modified rice husk	55.5	Katal *et al.* 2012

The nitrate adsorption capacity of LQAE (36.7 mg g^{-1}) was found to be similar to the commercial anion exchange resins (36.0 to 65.36 mg g^{-1}) but higher than the activated carbon (5.8 mg g^{-1}), and lower than the reported modified biomass adsorbents (52.8 to 117.8 mg g^{-1}). Comparing these results with the $Q_{\max}$ obtained from commercial anion exchange resin, activated carbon and other modified biomass adsorbents, the lignin matrix anion exchangers developed in this study can be considered to be alternative materials for nitrate removal in aqueous solution.

CONCLUSIONS

1. Optimal synthesis conditions for the preparation of LQAE in NaOH solutions were determined, and the characteristics of the LQAE synthesized at optimal conditions were evaluated. The reaction mechanism of this experiment was explored and validated. When the NaOH concentration was 6 M, the nitrate adsorption capacity and yield of LQAE were 36.7 mg g^{-1} and 123.6%, respectively.
2. It was observed that quaternary amine cationic groups were grafted in the structure of LQAE, as determined by IR spectra and zeta potential analyses. It has been further demonstrated that LQAE have excellent nitrate removal rates.

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