Preparation of Lignin-Based Anion Exchangers and their Utilization for Nitrate Removal

Zhen Wang, a, b Nana Bo, a Yu Liu, a Guihua Yang, a Ying Liu, a and Yuan Zhao b

Lignin-based anion exchangers (L-AE) were prepared by reacting lignin with epichlorohydrin and triethylamine in the presence of N,N-dimethylformamide and a catalyst. A multi-factor and multi-level orthogonal design of experiment was carried out in order to obtain the optimal conditions for the preparation of lignin-based anion exchangers. The optimized parameters including the dosages of catalysts, the amounts of triethylamine, graft reaction time, and the graft reaction temperature were defined. Data of nitrate removal and yield were used as performance indicators of the products prepared. The results indicated that the reaction temperature was the primary factor. The optimal synthesis reaction parameters were lignin:pyridine:triethylamine = 2 g:3 mL:12 mL. The optimal experimental temperature was 70 °C, and the reaction time was 7 h. The yield was 188.6% and the nitrate removal was 91.2%. Under some reaction conditions, the yields were found greater than 100%; this was due to the grafted mass from epoxidation with epichlorohydrin and quaternization (through the reaction of epoxide with triethylamine).

Keywords: Adsorption; Nitrate; Lignin-based anion exchanger

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INTRODUCTION

Lignin is the second most abundant natural raw material (Gosselink et al. 2004) and nature’s most abundant aromatic (phenolic) polymer (Lora and Glasser 2002), whose main function is to cement the cellulose fibers in plants. It is generally obtained as the by-product from paper mills in large quantities; however most of the lignin produced by the paper industry is burnt in the recovery boiler during the chemical recovery process. This practice fails to derive the fully potential value from this natural resource. On the other hand, as the production of lignin amounts to more than 50 million tons/year, there has been increasing interest in the development of economically viable new applications.

In earlier published research, lignin has been shown to be a excellent cation adsorbent to remove various heavy metals, such as Cu(II) (Merdy et al. 2002; Acemioğlu et al. 2003; Sciban and Klasnja 2004) and Cd(II) (Mohan et al. 2006; Basso et al. 2004), as well as dyes, bile acids, cholesterol, surfactants, pesticides, and phenols (Dizhbite et al. 1999; Ludvik and Zuman 2000; Allen et al. 2005; Van Beinum et al. 2006). However, there are very limited literature reports exploring lignin as matrix for adsorbing anions.

In previous research work, some investigators reported the preparation of tertiary amino anion exchangers from different biomass materials. In these studies, amine groups were introduced into the biomass materials by the reactions with the alcoholic hydroxyl
groups, carboxylic groups, and reactive aromatic sites present in lignocellulosic materials. These groups can be epoxidized, chlorinated, or sulfchlorinated by chemical reagents such as epichlorohydrin (Orlando et al. 2002a, b; Xu et al. 2009, 2010), glycidylmethacrylate (Anirudhan and Jalajamony 2010), or thionyl chlorides (Baes et al. 1997; Orlando et al. 2003). Amine groups were introduced by quaternization of amines and ammonium hydroxide (Šimkovic and Laszlo 1997). Many biomass materials such as rice hulls, bagasse, coconut husk, pine bark, persimmon leaf, wheat straw, and sawdust have been used as matrices to prepare anion adsorbents; however, there is no information concerning quaternary amino anion exchangers prepared from lignin and used for nitrate removal reported in the present literature.

The main objective of this paper is to discuss the preparation of a lignin-based anion exchanger (L-AE) derived from the reaction of lignin with epichlorohydrin and triethylamine in the presence of \( N,N \)-dimethylformamide and catalyst. The optimal synthesis conditions were determined by a multi-factor and multi-level orthogonal design of experiments, \textit{i.e.} the Taguchi Method of Design of Experiment (Montgomery 1996). The characteristics of L-AE and its propensity for nitrate removal were studied.

**EXPERIMENTAL**

**Materials**

All the chemicals used in this study were of analytical grade. The 1000 mg L\(^{-1} \) of potassium nitrate stock solutions were prepared by dissolving the required weighed quantities of KNO\(_3\) (Damao, China) in distilled water. All solutions for sorption and analysis were prepared by the appropriate dilution of freshly prepared stock solution. Epichlorohydrin, pyridine, methanol, and triethylamine were obtained from Damao, China. Kraft 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 \textit{et al.} (2011).

Two grams of lignin were dispersed in 25 mL of \( N, N \)-dimethylformamide (DMF) in a 250 mL 3-necked round bottom flask for 1 h (Orlando \textit{et al.} 2002b). A 20 mL aliquot of epichlorohydrin was added, and the mixture was stirred for 1 h at 70 °C. Next, 3 to 9 mL of pyridine catalyst was added, and the mixture was stirred for 1 h. Finally, 6 to 12 mL of 99\% (w/w) triethylamine was added and stirred for 3 to 7 h at 50 to 70 °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 \( \mu \)m. The final product was obtained after a second cycle of washing, drying, and sieving. It was used in all adsorption experiments.

The synthesis of the L-AE is schematically shown in Fig. 1. The reaction between epichlorohydrin and lignin occurred with the hydroxyl groups in the lignin. At first, the hydroxyl in lignin was cyclized by the catalyst existing in the alkaline condition to produce the epoxy lignin ether that was used as the intermediate in the reaction; then, the L-AE was obtained after the graft reaction between epoxy lignin ether and triethylamine.

Pyridine acted as a catalyst during the process. The effect of the catalyst was to improve the synthesis of the lignin ether intermediate, which was obtained after the reaction between lignin and epichlorohydrin, and to provide a weak base (pH 8 to 11) to facilitate the reaction between epoxide lignin ether intermediate and triethylamine (Orlando \textit{et al.} 2002a, b; Navarro \textit{et al.} 1996). By increasing the pyridine dosage, the
pyridine is able to more efficiently penetrate into the lignin polymer. However, the nitrate removal efficiency of the resulting L-AE tends to decrease when the pyridine dosages becomes too high. This can be explained by a side reaction (Garkusha-Bozhko and Shvaika 1990), as shown in Fig. 2. This side reaction is caused by the superfluous pyridine, which reacts with the epoxide to form a quaterized ammonium moiety, in a way somewhat similar to the reaction of triethylamine with the epoxide. This reaction decreases the opportunity to graft triethylamine with the epoxy lignin ether.

\[
\text{where } R_1 = \text{H}_2\text{C-CH-CH}_2\text{Cl},
\]
\[
\text{R}_2 = \text{H}_3\text{C-CH-C}^-\text{N}^+\text{C}_2\text{H}_5\text{Cl}
\]

Fig. 1. Synthetic reactions of lignin-based anion exchanger

**Characterization of the Materials**

The epoxy value of epoxy lignin ether was determined in accordance to ISO 3001-1999. All samples were collected before the graft reaction between epoxy lignin ether and triethylamine; the epoxy lignin ether was washed with acetone and deionized water. Then it was analyzed after drying in an oven under vacuum at 30 °C for one day. The analysis was performed in triplicate.

The \textsuperscript{31}P-NMR spectra of the lignin samples were used to determine the phenolic hydroxyl content and the aliphatic hydroxyl content of the lignin. Spectra were obtained with a Bruker 400 MHz spectrometer. Approximately 40 mg of oven-dried lignin sample was placed into a pyridine/chloroform solution (1.6:1, V/V) in a small vial and stirred continuously for several hours to fully dissolve it. \textit{N}-hydroxyl naphthalimide was used as the internal standard, and chromium acetylacetonate was used as the relaxation reagent.
Lastly, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was used as the phosphitylating agent to convert all of the labile lignin hydroxyl groups to phosphate ethers.

\[ \text{Fig. 2. Side reaction between pyridine and epoxy lignin ether. The } R_1 \text{ and } R_2 \text{ are the same as in Fig. 1.} \]

The FTIR spectra were recorded using an FTIR technique (IRPretige-21, Shimadzu, Japan) by the KBr-pellet method. The spectrum was scanned in the range 400 to 4000 cm\(^{-1}\) wavenumbers.

The zeta potential was measured using a Zetasizer (JS94H, Shanghai Zhongchen Digital Technical Apparatus Co., Ltd., China) according to the solid addiction method (Stumm and Morgan 1996). To determine the zeta potential of L-AE and lignin at different pH values, the L-AE and lignin particles in the sediment phase were dispersed into the distilled water with pH range of 1.0 to 9.0.

**Orthogonal Tests**

In this work, an orthogonal design of experiments was chosen to analyze the effect of all the factors on the experimental goals. The dosages of pyridine, dosages of triethylamine, graft reaction times, and reaction temperatures were selected as the independent influential factors. Data of nitrate removal and yield were used as performance indicators of the products prepared.

The nitrate removal experiments were conducted as follows. An aliquot of 0.1 g of L-AE was added to 100 mL of 100 mg L\(^{-1}\) KNO\(_3\) solution at room temperature (20±2 °C); this mixture was then shaken at 120 rpm for 60 min. The nitrate concentration was determined spectrophotometrically according to the brucine-sulfanilic colorimetric method (APHA 1989), using a UV-vis spectrophotometer (model UV754GD, Shanghai).

**RESULTS AND DISCUSSION**

**Orthogonal Tests for the Determination of the Optimal Reaction Conditions**

An orthogonal design of experiments is the primary approach for a fractional factorial design that can comprehensively reflect effects of all factors selected in a test. It has been widely used across research fields due to its high efficiency and practical economic value (Montgomery 1996). In this study, orthogonal tests were applied to validate the optimal reaction conditions and the key influential factor in the preparation of L-AE.
Orthogonal tests with four factors and three levels were designed. Nine synthesis conditions were carried out at pyridine dosages of 3, 6, and 9 mL, triethylamine dosages of 6, 9, and 12 mL, graft reaction times of 3, 5, and 7 h, and reacting temperatures of 50, 60, and 70 °C. All selected factors were examined using an orthogonal L9 (3⁴) test, as presented in Table 1, to determine their impact on nitrate removal and yield.

Table 1. Optimal Reaction Conditions Determined by Orthogonal Test

<table>
<thead>
<tr>
<th>No.</th>
<th>Pyridine dosage (mL)</th>
<th>Triethylamine dosage (mL)</th>
<th>Graft reaction time (h)</th>
<th>Graft reaction temperature (°C)</th>
<th>Nitrate removal (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>6</td>
<td>3</td>
<td>50</td>
<td>43.9</td>
<td>72.6</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>9</td>
<td>5</td>
<td>60</td>
<td>45.8</td>
<td>74.5</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>12</td>
<td>7</td>
<td>70</td>
<td>91.2</td>
<td>188.6</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>6</td>
<td>5</td>
<td>70</td>
<td>74.3</td>
<td>145.9</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>9</td>
<td>7</td>
<td>50</td>
<td>47.3</td>
<td>73.1</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>12</td>
<td>3</td>
<td>60</td>
<td>61.7</td>
<td>117.3</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>6</td>
<td>7</td>
<td>60</td>
<td>65.5</td>
<td>122.1</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>9</td>
<td>3</td>
<td>70</td>
<td>86.5</td>
<td>165.0</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>12</td>
<td>5</td>
<td>50</td>
<td>48.6</td>
<td>97.2</td>
</tr>
</tbody>
</table>

* The yield is calculated by the formula: yield = m₁/m₂; where m₁ is the mass of L-AE and m₂ is the mass of lignin.

The results from the experiments listed in Table 1, evident among all 9 designed orthogonal tests, indicate that the parameters corresponding to the highest yield and nitrate removal of L-AE were 188.6% and 91.2% (No. 3), respectively. As can be seen in Table 1, the yields of NO. 3, NO. 4, NO. 6, NO. 7, and NO. 8 were found to be greater than 100%. This can be attributed to the grafted mass from epoxidation with epichlorohydrin and quaternization (through the reaction of epoxide with triethylamine).

Therefore, we concluded that the optimal synthesis conditions for L-AE preparation occurred when the proportion of lignin-to-pyridine-to-triethylamine was 2 g:3 mL:12 mL, and when the reaction time was 7 h and the reaction temperature was 70 °C.

To determine the key influential factor, a further orthogonal analysis was performed. The calculated k and R values, which are widely used in the range analysis of orthogonal tests, are listed in Table 2, 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 represent the effects of various factor levels on the preparation of L-AE, and the R values reflect the effects of various factors on the synthesis reaction. The high value of R value demonstrates the major impact of the corresponding indicators (Montgomery 1996).

As indicated in Table 2, the prominent k value was obtained at 70 °C reaction temperature, which indicated that the preparation of L-AE will be operated more efficiently at 70 °C of graft reaction temperature in comparison with other conditions. The ranges of R values for the four factors (pyridine dosage, triethylamine dosage, reaction time, reaction temperature) were 6.3, 7.3, 11.8, 37.4, and 16.2, 30.2, 22.1, 85.5 by taking the nitrate removal and the yield as the indicators, respectively. The relatively high R values of the reaction temperature compared to the other factors indicate that graft reaction temperature is the most important factor determining the preparation of L-AE.
Table 2. Analysis of Orthogonal L₉(3⁴) Test

<table>
<thead>
<tr>
<th></th>
<th>Pyridine dosage</th>
<th>Triethylamine dosage</th>
<th>Graft reaction time</th>
<th>Graft reaction temperature</th>
<th>Nitrate removal (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁</td>
<td>60.3</td>
<td>61.2</td>
<td>64.0</td>
<td>46.6</td>
<td>58.0</td>
<td>-</td>
</tr>
<tr>
<td>k₂</td>
<td>61.1</td>
<td>59.9</td>
<td>56.2</td>
<td>57.7</td>
<td>58.7</td>
<td>-</td>
</tr>
<tr>
<td>k₃</td>
<td>66.9</td>
<td>67.2</td>
<td>68.0</td>
<td>84.0</td>
<td>71.5</td>
<td>-</td>
</tr>
<tr>
<td>R</td>
<td>6.6</td>
<td>7.3</td>
<td>11.8</td>
<td>37.4</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>k₁'</td>
<td>111.9</td>
<td>113.5</td>
<td>118.3</td>
<td>81.0</td>
<td>-</td>
<td>106.2</td>
</tr>
<tr>
<td>k₂'</td>
<td>112.1</td>
<td>104.2</td>
<td>105.9</td>
<td>104.6</td>
<td>-</td>
<td>106.7</td>
</tr>
<tr>
<td>k₃'</td>
<td>128.1</td>
<td>134.4</td>
<td>127.9</td>
<td>166.5</td>
<td>-</td>
<td>139.2</td>
</tr>
<tr>
<td>R</td>
<td>16.2</td>
<td>30.2</td>
<td>22.1</td>
<td>85.5</td>
<td>33.0</td>
<td></td>
</tr>
</tbody>
</table>

a \( k_i = \frac{\sum \text{the nitrate removal of single factor}}{3} \)

b \( R_i = \max k_i - \min k_i \)

c \( k_i' = \frac{\sum \text{the yield of single factor}}{3} \)

d \( R_i = \max k_i - \min k_i \)

Characteristics of L-AE Prepared under the Optimal Conditions

The lignin sample and its modification products prepared under the optimal conditions were characterized using \(^{31}\text{P}\) NMR, zeta potential, FTIR, and epoxy value.

\(^{31}\text{PNMR analysis}\)

The \(^{31}\text{P}\)-NMR spectra of the phosphorous-derivatized lignin samples are shown in Fig. 3.

Fig. 3. \(^{31}\text{P}\)-NMR spectra of lignin samples before modification

The spectra made it possible to quantify the aliphatic, phenolic, and carboxylic acid groups. The integration fields corresponding to the various hydroxyl moieties of lignin that were examined in this study are listed in Table 3 (Liu et al. 2012).

<table>
<thead>
<tr>
<th>Chemical shift (ppm)</th>
<th>Functional groups</th>
<th>Content (mol/kg lignin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>149.3-144.9</td>
<td>Aliphatic OH</td>
<td>1.75</td>
</tr>
<tr>
<td>144.0-143.1, 142.0-140.2</td>
<td>Condensed phenolic OH</td>
<td>1.32</td>
</tr>
<tr>
<td>143.1-142.0</td>
<td>Guaiacyl and demethylation OH</td>
<td>0.81</td>
</tr>
<tr>
<td>140.2-138.4</td>
<td>Syringyl OH</td>
<td>1.41</td>
</tr>
<tr>
<td>138.4-136.3</td>
<td>p-hydroxyphenyl OH</td>
<td>1.38</td>
</tr>
<tr>
<td>136.3-133.8</td>
<td>COOH</td>
<td>2.73</td>
</tr>
</tbody>
</table>

As can be seen in Table 3, the content of aliphatic hydroxyl groups was 1.75 mol/kg lignin. The total amount of phenolic hydroxyl groups, which was comprised by condensed phenolic hydroxyl, guaiacyl, demethylation hydroxyl, syringyl, and p-hydroxyphenyl groups, was 4.92 mol/kg lignin. And the content of the carboxylic acid was 2.73 mol/kg lignin. So the total amount of hydroxyl groups was 6.67 mol/kg lignin. The epoxy value was 1.46 mol/kg lignin, so the highest conversation rate of hydroxyl was judged to be about 21.9%.

**FTIR analysis of L-AE**

The FTIR spectral changes between the raw lignin and the L-AE are shown in Fig. 4.

![FTIR analysis for lignin and L-AE](image)

**Fig. 4.** FTIR analysis for lignin and L-AE

For the raw lignin, a large vibration band at 3380 cm\(^{-1}\) indicates the existence of hydroxyl groups in the lignin. The peak at 2924 cm\(^{-1}\) is associated with the special vibration of the aliphatic C-H bond in lignin. Aromatic cyclic groups are denoted by the
intensity of the band at 1709 cm\(^{-1}\). The IR analysis of the L-AE showed a change in structure between the L-AE and the raw lignin. As shown in Fig. 4, changes in the peak details at 1375 cm\(^{-1}\) suggests the grafted amine groups in the structure of the L-AE. Similar results were also reported in our previous work, with grafted amine groups observed at a band of 1350 cm\(^{-1}\) (Xu et al. 2009).

**Zeta potential**

Zeta potentials of the samples were evaluated using an electro-kinetic analyzer over a pH range of 1 to 9 (Fig. 5). Results showed that the zeta potentials of the L-AE were in the range of −1.2 to +35.4 mV in comparison with the raw lignin of −10 to +14.6 mV over the designated pH range, which indicated the existence of cationic functional groups on the L-AE structure.

It was also observed that the zeta potentials of the L-AE gradually decreased as the pH was increased from 1 to 9; this could be attributed to the pH-dependent functional groups of the L-AE, such as hydroxyl and carboxyl groups. These groups will exhibit a greater negative charge when the pH is increased, which will decrease the impact of the grafted cationized quaternized ammonium group. It was observed in Fig. 5 that there was a marked difference in the isoelectric point (IEP) between the raw lignin (pH IEP = 5.22) and the L-AE (pH IEP = 8.85). Raw lignin contains more acidic carboxyl groups, which will dissociate at higher pH values and result in a lower IEP pH value. What is more, the more positive-charge functional groups with a high dissociation pH in L-AE might have caused a higher isoelectric point when compared with raw lignin. Similar results have been reported in the work of Huang et al. (2009).

![Fig. 5. Zeta potential of L-AE and lignin as a function of pH](image)

**SEM analysis of L-AE**

The results of SEM measurements of the structures of raw lignin and L-AE are shown in Fig. 6. More micropores were observed with the surface of the L-AE when compared to the surface of the raw lignin, which suggests that the specific area of the lignin increased during the process of modification. It also suggests that a large number...
of adsorption sites existed in the microporous surface of the L-AE, which could be beneficial for nitrite removal.

Fig. 6. SEM micrographs of (a) raw lignin and (b) L-AE

Adsorption isotherm
To evaluate the adsorption capacities of L-AE, batch adsorption tests were conducted for the adsorption of nitrate. The initial concentrations of nitrate were selected in the range of 50 and 500 mg L\(^{-1}\). The experimental isotherm data were interpreted by the non-linear forms of Langmuir, Freundlich, and Redlich-Peterson isotherm models (Tsai et al. 2006).

![Experimental vs. Isotherm Models](image)

**Fig. 7.** Comparison of different isotherm models to the experimental data for nitrate adsorption by L-AE at 20 °C

The Langmuir adsorption isotherm is governed by the following equation,

\[
q_e = \frac{Q_{\text{max}} F_i C_e}{1 + F_i C_e}
\] (1)
the Freundlich adsorption isotherm equation is,

\[ q_e = K_F C_e^{\frac{1}{n}} \]  

(2)

and the Redlich-Peterson adsorption isotherm equation is,

\[ q_e = \frac{K_R C_e^{1+a_R C_e^2}}{1} \]  

(3)

where \( q_e \) and \( C_e \) are the equilibrium concentrations of the nitrate on the adsorbent and solution respectively. \( Q_{\text{max}} \) and \( K_L \) are the Langmuir constants, \( K_F \) and \( 1/n \) are the Freundlich constants, and \( K_R, C_e^s \) and \( a_R \) are the Redlich-Peterson constants. The experimental and model curves for the nitrate adsorption are shown in Fig. 7.

The values of isotherm constants were calculated using non-linear regression analysis, and the results are listed in Table 4. The low value of \( \chi^2 \) and high value of \( R^2 \) for the Redlich-Peterson isotherm indicated a very good mathematical fit of the Redlich-Peterson isotherm and experimental data. \( K_R \) was found to be 7.69, \( C_e^s \) was fitted as 0.106, and \( a_R \) was determined as 0.996. As reported, the experimental data also fit well with the Langmuir model in experiment conditions (Xu 2009). This can be attributed to the fact that the adsorption follows a monomolecular layer adsorption mechanism.

**Table 4. Isothermal Data of Nitrate Adsorption onto L-AE, Calculated on the Basis of Non-linear Curve Fitting**

<table>
<thead>
<tr>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Redlich-Peterson</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_{\text{max}} ) (mg g(^{-1}))</td>
<td>( K_L ) (mg L(^{-1}))</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>74.53</td>
<td>0.087</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Some commercially available anion exchange resins, activated carbon, and other reported biomass adsorbents have been selected to compare their nitrate adsorption capacities on the basis of reported literature (Orlando *et al.* 2002a; Park and Na 2006; Chabani *et al.* 2007; Xu *et al.* 2010; Katal *et al.* 2012; Wan *et al.* 2012). The results are presented in Table 5 in comparison to those of L-AE.

**Table 5. \( Q_{\text{max}} \) of NO\(_3\)\(^-\) on Different Ion Exchangers**

<table>
<thead>
<tr>
<th>Ion Exchangers</th>
<th>( Q_{\text{max}} ) (mg g(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-AE</td>
<td>74.53</td>
<td>In this work</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>5.8</td>
<td>Park and Na 2006</td>
</tr>
<tr>
<td>Commercial anion exchange resins</td>
<td>36.0</td>
<td>Orlando <em>et al.</em> 2002a</td>
</tr>
<tr>
<td>Amberlite IRA 400</td>
<td>65.36</td>
<td>Chabani <em>et al.</em> 2007</td>
</tr>
<tr>
<td>Hydrotalcites</td>
<td>34.36</td>
<td>Wan <em>et al.</em> 2012</td>
</tr>
<tr>
<td>Wheat straw-anion resin</td>
<td>52.8</td>
<td>Xu <em>et al.</em> 2010</td>
</tr>
<tr>
<td>Modified rice husk</td>
<td>55.5</td>
<td>Katal <em>et al.</em> 2012</td>
</tr>
</tbody>
</table>
The nitrate adsorption capacity of L-AE (74.53 mg g\(^{-1}\)) was found to be higher than those of commercial anion exchange resins (36.0 to 65.36 mg g\(^{-1}\)), activated carbon (5.8 mg g\(^{-1}\)), and reported modified biomass adsorbents (52.8 to 55.5 mg g\(^{-1}\)). Comparing these results with the \(Q_{\text{max}}\) obtained from commercial anion exchange resin, activated carbon and other modified biomass adsorbents, the lignin matrix exchangers developed in this study can be considered as alternative materials for nitrate removal in aqueous solution.

CONCLUSIONS

1. Optimal synthesis conditions for the preparation of L-AE were determined by orthogonal design of experiment tests; the reaction temperature was found to be the key influential factor.

2. The characteristics of the L-AE prepared by the optimal synthesis conditions were evaluated. The total amount of hydroxyl was found to be about 6.67 mol/kg lignin based on analysis by \(^{31}\)P NMR; the highest conversation rate of hydroxyl groups in lignin was about 21.9%.

3. A large number of quaternary ammonium groups with positive charge were found in the structure of L-AE after the IR spectra and zeta potential analyses. It has been further demonstrated that the excellent nitrate removal of the L-AE was due to the higher specific area of L-AE versus the raw lignin.

4. The optimal synthesis reaction parameters of dosages were lignin:pyridine: triethylamine = 2 g:3 mL:12 mL. Optimal experimental temperature was 70\(^{\circ}\)C, and reaction time was 7 h. The yield was 188.6%, and the nitrate removal was 91.2%.

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