

## Poly(vinyl alcohol)/Quaternized Lignin Composite Absorbent: Synthesis, Characterization and Application for Nitrate Adsorption

Ying Li,<sup>1</sup> Xiaoyan Lin,<sup>1,2</sup> Xiurong Zhuo,<sup>1</sup> Xueguang Luo<sup>1,2</sup>

<sup>1</sup>School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang, Sichuan 621010, China

<sup>2</sup>Engineering Research Center for Biomass Materials, Ministry of Education, China

Correspondence to: X. Lin (E-mail: lxy20100205@163.com)

**ABSTRACT:** A new poly(vinyl alcohol) (PVA)/quaternized lignin composite absorbent (PVA/QL) was synthesized from modified lignin and PVA, crosslinked by glutaraldehyde. As-prepared absorbent was characterized by IR, DSC, SEM BET, and DMA. Effects of shaking time, absorbent dose, initial pH, and temperature on  $\text{NO}_3^-$  removal from aqueous solution by the absorbent were comprehensively investigated. The results show that the PVA/QL absorbent comprises quaternary ammonium groups in the form of ether bond. The composite absorbent exhibits remarkable network structure with large numbers of connected holes. The mechanical strength of the absorbent is enhanced by combining of PVA with modified lignin and crosslinkage of glutaraldehyde. The effect of pH on adsorption of  $\text{NO}_3^-$  is apparent and appropriate pH is 2.0. The adsorption process is endothermic, and determined to be consistent with the Langmuir isotherm. Furthermore, it is found that the quaternary ammonium structure and network structure in the surface of PVA/QL are the key factors to remove nitrate. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** adsorption; biomaterials; cellulose and other wood products; crosslinking

Received 26 March 2012; accepted 5 August 2012; published online

DOI: 10.1002/app.38437

### INTRODUCTION

Nitrate pollution in different water and wastewater has become a global problem as a result of industrial and agricultural development and population growth. The nitrate wastewater is generated by some industries. Nitrate is one of nitrogen-containing compound, potentially converted to nitrite in the gastrointestinal tract or to nitrous nitrogen compounds through reduction, which will threat human or animal health.<sup>1</sup> For this reason, nitrate removal from water resources is necessarily explored.

Many studies have demonstrated that substances like nitrate, fluoride, and arsenate can be removed from water by absorbents. Therefore, absorbents are widely applied to water and wastewater treatment.<sup>2</sup> However, the cost of commercial synthetic ion-exchangers is too high to apply in practice. An extensive search for low-cost and efficient ion-exchangers is imperative under the situation. Industrial or agricultural waste products, such as lignin, sawdust, coconut husk, tealeaf and rice hull, are a sort of the low-cost absorbents.<sup>3–5</sup>

Lignin is the second most abundant natural raw material and aromatic polymer. It consists of both aromatic and aliphatic portions containing many active functional groups, such as phenolic, hydroxyl, carboxyl, benzyl alcohol, methoxyl, and

aldehyde groups,<sup>6–8</sup> which suggest some ion exchange and adsorption properties. The study of lignin as absorbent has been increased in the latest years<sup>9,10</sup>; however, it has been considered little about the absorbent for nitrate adsorption and improving the dimensional stability and mechanical properties of the absorbent, which was important when it applied in practice.

Poly(vinyl alcohol) (PVA), a highly polar, water-soluble, biodegradable polymer, has good chemical stability, film forming ability, and high hydrophilicity. Blending lignin with poly(vinyl alcohol) (PVA) has been reported to form miscible homogeneous systems and provide good material performance attributed to the formation of strong intermolecular interaction in them.<sup>11,12</sup> Therefore, PVA is combined with modified lignin followed by crosslinking to enhance the mechanical property and the dimensional stability of the absorbent. Because of natural lignin with only small number of hydroxyl groups (~10%),<sup>13</sup> lignin was phenolated with sulfuric acid catalyst to yield reactive phenolized lignin, greatly increasing the number of hydroxyl groups, i.e., active functional groups, at the side-chain- $\alpha$  position rather than at the condensed aromatic nuclei,<sup>14–16</sup> and aminated by monomeric quaternary ammonium salt synthesized by us in the laboratory to generate quaternized lignin (QL). Finally, the poly(vinyl alcohol)/quaternized lignin absorbent (denoted as PVA/QL), was

prepared by combining PVA with QL followed by crosslinking. The removal of  $\text{NO}_3^-$  from aqueous solution with PVA/QL was investigated. The aim is to explore the synthesis of PVA/QL materials and absorption properties of nitrate on PVA/QL.

## EXPERIMENTAL PROCEDURE

### Materials

Lignin which was used of alkaline pulping by spray drying was from Shanghai Paper, China. The content of lignin is  $>88\%$ . The percentage composition of moisture, metal ion ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ) and ash is, respectively, 7, 1, and 4%, and the density is  $0.29 \text{ g cm}^{-3}$ . PVA, glutaraldehyde (50% content in water), trimethylamine, epichlorohydrin, phenol, sulfuric acid, and hydrochloric acid (35% content) were purchased from Ke Long Chemical Company (Chengdu, China). The degree of polymerization of PVA was 1788. The Coconut-shell activated carbon was provided by Tangshan United Carbon Technology and the density is  $0.53 \text{ g cm}^{-3}$ . All other reagents were of analytical grade. The water used was distilled water.

### Measurements

Infrared spectra of pure lignin, QL, and PVA/QL were determined on KBr pellets with a sample concentration of 1%. FT-IR spectra were recorded using a Nicolet 6700 FTIR spectrometer in the range  $400\text{--}4000 \text{ cm}^{-1}$ .

The surface areas were detected with  $\text{N}_2$  adsorption at liquid nitrogen temperature (77 K) using a surface analyzer (NOVA3000, Quanta Chrome, America). Before measuring the isotherm, all the samples were degassed at  $120^\circ\text{C}$  for 4 h in vacuum ( $10^{-6} \text{ atm}$ ).

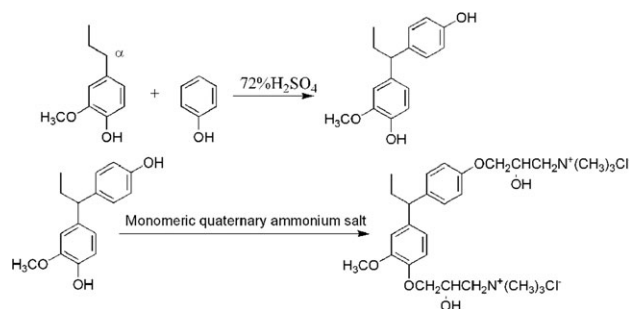
Differential scanning calorimetry (DSC) was performed on a TA Instruments Q200 under flowing nitrogen ( $50 \text{ mL min}^{-1}$ ) atmosphere at  $10^\circ\text{C min}^{-1}$  over the temperature range of  $-50$  to  $190^\circ\text{C}$ . Samples of 5 mg were placed into aluminum pans.

The morphologies of PVA/QL were observed on a JEOL model JSM 5900 scanning microscope operated at an acceleration voltage of 20 kV. All specimens were sputter coated with gold prior to examination.

The mechanical property and fracture behavior were studied using a TA instrument Q800 DMA in the compressed mode. In the time scanning tests for the determination of the mechanical properties, the deformation displacement ( $d$ ) of the samples was determined at a ramp force of  $0.5 \text{ N min}^{-1}$  to  $18\text{N}$  as a function of temperature at  $25^\circ\text{C}$ . The sample sizes were  $2 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$ .

### Preparation of PVA/QL

There is the insufficient number of reactive sites in lignin molecules. To increase the reactivity towards quaternizing reagent (monomeric quaternary ammonium salt), lignin is first phenolized by phenol. In the phenolation reaction, the first step involves the protonation of the benzyl hydroxyl group, followed by dehydration at the  $\alpha$ -carbon, to give a carbonium ion. The phenol molecule undergoes an electrophilic attack by carbonium ion giving rise to a phenol condensation product.<sup>17</sup> These steps result in increase of the number of phenolic hydroxy in the lignin. Phenolic hydroxyl is a significant functional group which is a reactive site acted by quaternizing reagent. The



**Figure 1.** Mechanism of lignin reacting with phenol and phenolized lignin reacting with quaternary ammonium salt.

increasing number of phenolic hydroxy in the lignin leads to increase of reactive sites. Prephenolation of lignin enhances its reactivity toward quaternizing reagent. The reaction mechanism and experiment of lignin phenolized and quaternized is demonstrated as Figure 1 shows.

A mixture of lignin (4.0 g) and phenol (10.0 g) in 20 mL sulfuric acid (72%) was stirred at  $60^\circ\text{C}$  for 6 h. After quenching by dilution with 500 mL of water, the suspension was boiled for 2 h, and then filtered, washed thoroughly with warm water to give phenolized lignin. Synthesis of monomeric quaternary ammonium salt was carried out at mole ratio of trimethylamine and epichlorohydrin 1 : 0.7, temperature from  $-3$  to  $-6^\circ\text{C}$ . Phenolized lignin (4.0 g) and monomeric quaternary ammonium salt (20 g) were mixed in 50 mL water at  $70^\circ\text{C}$  water bath and stirred continuously for 4 h. The final product was filtered, washed with water, and then freeze-dried to give the quaternized lignin (QL). QL (15.0 g) and PVA (3.0 g) were mixed in 30 mL hot water (pH 3.0) to form dense slurry. The flask with the mixture was tightly closed and placed in a water bath case at  $60^\circ\text{C}$ , and agitated for about 2 h until a homogenous suspension was formed. After then, glutaraldehyde (2 mL) was added slowly into the mixture and stirred for 2 h in order that QL and PVA were crosslinked adequately, and the final product was filtered, washed with de-ionized water twice, and then dried to give PVA/QL composite absorbent.

### Preparation of Crosslinked Lignin and Crosslinked QL

Lignin (15.0 g) was dispersed in the  $60^\circ\text{C}$  hot water at pH 3 adjusted with diluted sulfuric acid solution, and then poured into paraffin (100 mL) containing 0.3% surfactants of dodecyl sulfonate, stirred at  $60^\circ\text{C}$  for 2 h. Glutaraldehyde (2 mL) was added slowly into the suspension, reacted for 2 h, filtered and dried, crosslinked lignin was obtained. Preparation of crosslinked QL is the same process as crosslinked lignin.

### Batch Adsorption

Adsorption capacity was determined by adsorption experiments. The designated adsorption materials were mixed with 25 mL of  $\text{NO}_3^-$  solution ( $10 \text{ mg L}^{-1}$ ) and shaken at 200 rpm. Nitrate concentration was determined by spectrophotometric method with phenol disulfonic acid. The removal efficiency ( $E$ ) was calculated as follows:

$$E(\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

where  $C_0$  and  $C_e$  are the concentrations of  $\text{NO}_3^-$  ions before and after adsorption ( $\text{mg L}^{-1}$ ), respectively.

### Desorption Experiment

Removal of the adsorbed nitrate ions from PVA/QL was studied in a batch system. About 0.3 g of PVA/QL with different volumes of 0.1M NaOH, ranging from 10 to 25 mL, was stirred for 10 min, the PVA/QL suspension was centrifuged at 10,000 rpm for 5 min and the concentration of nitrate released into the supernatant was measured by spectrophotometric method. Desorption ratio was calculated using the following equation:

$$\text{Desorption ratio} = \frac{\text{amount of nitrate ions desorbed}}{\text{amount of nitrate ions adsorbed}} \times 100\% \quad (2)$$

The regeneration efficiency experiments were carried out by stirring 0.3 g of PVA/QL with different volumes of 0.1M NaOH, ranging from 10 to 25 mL.

## RESULT AND DISCUSSION

### Characterization of PVA/QL

**FT-IR Spectra Analysis.** Figure 2 shows the FTIR spectra of lignin, QL and PVA/QL. From Figure 2, it can be seen that QL and PVA/QL retains the basic structure of lignin. The broad band at  $3424 \text{ cm}^{-1}$  was dominated by the stretching vibrations of aromatic and aliphatic  $\text{—OH}$  groups. The peaks at  $2926 \text{ cm}^{-1}$  predominantly arose from C—H stretching in methyl and methylene groups of side chains and aromatic methoxyl groups. Stretching at about  $1712$  and  $1715 \text{ cm}^{-1}$  are attributed to conjugated carboxyl and carbonyl. Three peaks at  $1612$ ,  $1505$ , and  $1462 \text{ cm}^{-1}$  could be assigned to typical aromatic skeletal vibrations.<sup>18,19</sup> However, the peak at  $1505 \text{ cm}^{-1}$  covered respectively by the strong absorption peak at  $1476$  and  $1440 \text{ cm}^{-1}$  was not obvious in the IR spectra of QL and PVA/QL compared with pure lignin. And the band around  $1476$  and  $1440 \text{ cm}^{-1}$  provides the evidence of the bending vibration of the quaternary ammonium ion, which reveals that QL and PVA/QL have been introduced quaternary ammonium groups. The band at  $1440 \text{ cm}^{-1}$  of PVA/QL FTIR was obviously shifted to lower wave number

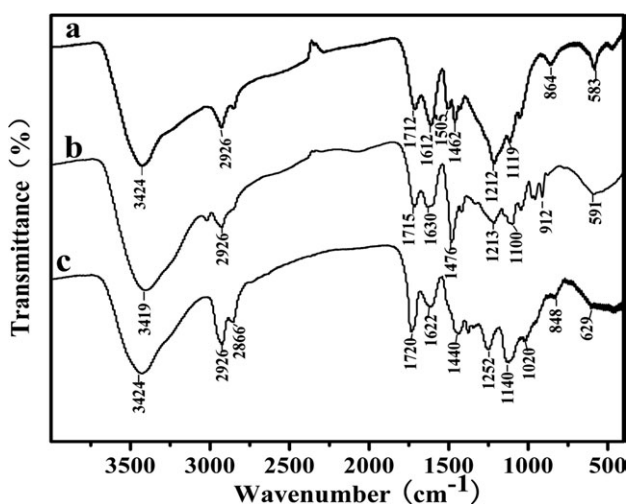


Figure 2. FT-IR spectra of (a) lignin, (b) QL, and (c) PVA/QL.

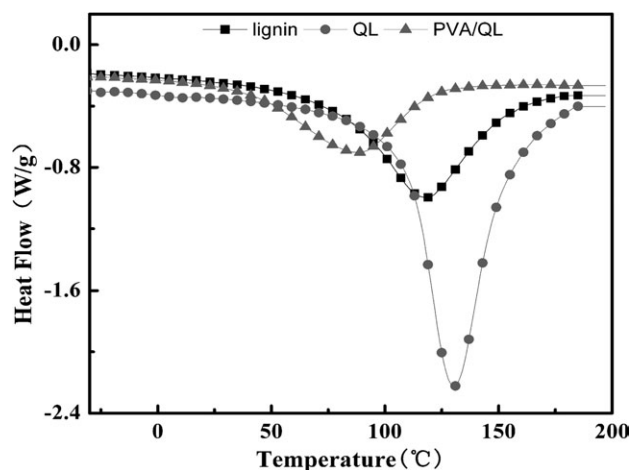


Figure 3. DSC curves of lignin, QL, and PVA/QL.

compared with that of QL. This shift may be resulted from more crosslink between PVA and QL. The peak of  $1140 \text{ cm}^{-1}$  of PVA/QL which is characteristic of ether linkage suggests the crosslink reaction between the hydroxyl group of PVA and lignin and the aldehyde group of glutaraldehyde.<sup>20</sup>

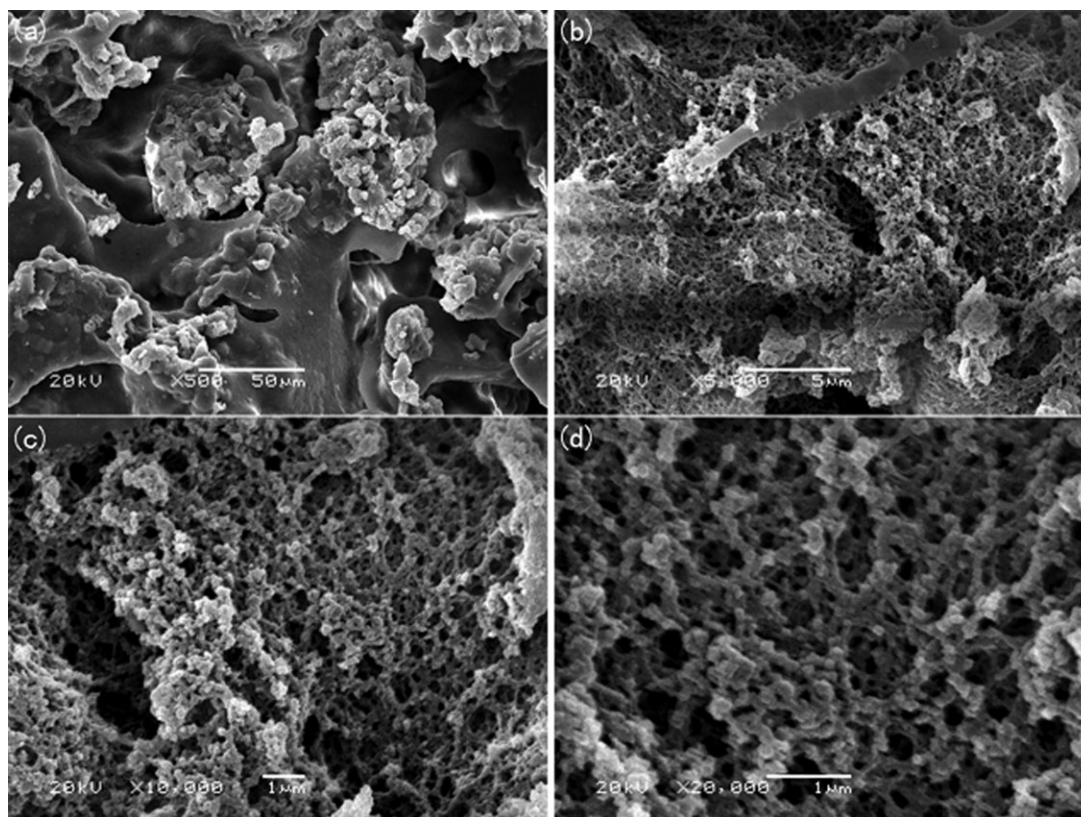
**DSC Analysis.** DSC curves of lignin, QL, and PVA/QL composites absorbent are shown in Figure 3. Thermal parameters of the composites are summarized in Table I. The peak temperatures for lignin, QL, and the PVA/QL are  $118.23$ ,  $130.74$ , and  $87.97^\circ\text{C}$ , respectively. The QL exhibits a higher peak temperature and thermal degradation onset as compared with that of lignin, indicating that the thermal stability is improved by grafting quaternary ammonium groups onto lignin. When PVA is incorporated into QL, it can be seen that the thermal degradation onset and the peak temperature are shifted to a lower temperature, which means PVA/QL has been formed.

**SEM Analysis.** The scanning electron micrograph (SEM) images of PVA/QL composite absorbent at a magnification of  $500\times$ ,  $5000\times$ ,  $10,000\times$  and  $20,000\times$  are shown respectively in Figure 4(a–d). The surface of the composite absorbent shows remarkable network structure with large numbers of connected holes. It may base on a crosslinked structure which is obtained from a reaction between hydroxyl groups of PVA and QL and aldehyde groups of glutaraldehyde in the presence of a strong acid. Because of existence of the holes in the absorbent, the PVA/QL has large surface area which facilitates the adsorption of nitrate.<sup>21</sup>

**BET Analysis.** The surface area was measured by BET method using the adsorption isotherm of  $\text{N}_2$ . The pore structures of lignin and PVA/QL are demonstrated in the Table II. It can be

Table I. Thermal Characteristics of Lignin, QL, and PVA/QL

Sample	Onset ( $^\circ\text{C}$ )	$T_{\text{peak}}$ ( $^\circ\text{C}$ )	End ( $^\circ\text{C}$ )	$\Delta H$ ( $\text{J g}^{-1}$ )
Lignin	52.41	118.23	170.37	222.0
QL	83.98	130.74	182.81	361.2
PVA/QL	19.78	87.97	132.29	151.9



**Figure 4.** SEM images obtained at (a) 500 $\times$ , (b) 5000 $\times$ , (c) 10,000 $\times$ , and (d) 20,000 $\times$  magnification for PVA/QL. Acceleration voltage = 20 kV. Scale = 50, 5, and 1  $\mu\text{m}$ , respectively.

seen that PVA/QL shown larger surface area, pore volume, and average pore size than lignin. The porosity was manifest by low value of surface.

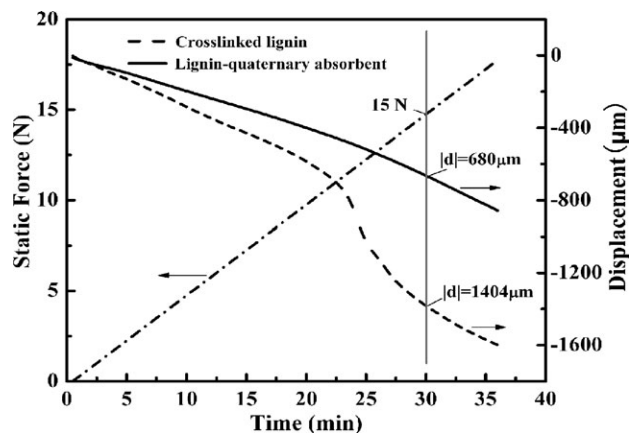
**Mechanical Properties.** As can be seen from Figure 5, it is obvious that the PVA/QL composite exhibited a slow not a sharp decrease curve in comparison to crosslinked lignin. However, the curve of crosslinked lignin greatly deviated from linearity up to the maximum force. For example, the deformation displacement of crosslinked lignin is 1404  $\mu\text{m}$  while the PVA/QL is only 680  $\mu\text{m}$  as the static force is 15 N. The less deformation displacement led to the conclusion that the mechanical strength was enhanced in the presence of PVA. Combining PVA with modified lignin induced the crosslink between PVA and glutaraldehyde and exhibited network structure, as indicated by FTIR and SEM. Crosslink of PVA and glutaraldehyde, formation of network structures and enhanced interfacial bond in the PVA/QL composite resulted in the increase of mechanical properties compared with that of the crosslinked lignin.

**Table II.** Pore Characteristics of Lignin, QL/PVA, and Activated Carbon

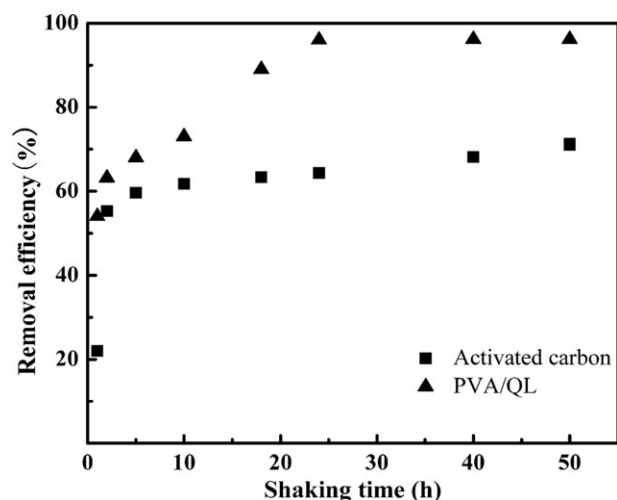
Sample	Surface area ( $\text{m}^2 \text{g}^{-1}$ )	Total pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Average pore size (nm)
Lignin	5.28	0.0053	13.14
QL/PVA	11.10	0.0098	14.58
AB	743.98	0.364	19.561

### Nitrate Adsorption on PVA/QL

**Effect of Shaking Time.** Figure 6 illustrates the effect of shaking time on the removal efficiency. The removal efficiency for nitrate on PVA/QL absorbent increased with the increase of the shaking time. More than 50% removal efficiency occurred within an hour for PVA/QL absorbent. After adsorption time of 24 h, the adsorption tended saturation for PVA/QL absorbent. The removal efficiency reached 96% at 24 h and remained constant when the adsorption time exceeded 24 h. Compared with activated carbon absorbent, the PVA/QL absorbent exhibited the higher removal efficiency for nitrate in whole absorption process.



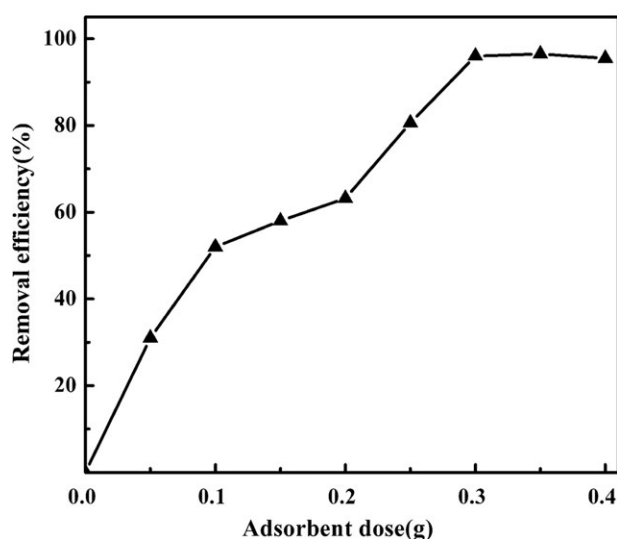
**Figure 5.** DMA spectra of crosslinked lignin and PVA/QL.



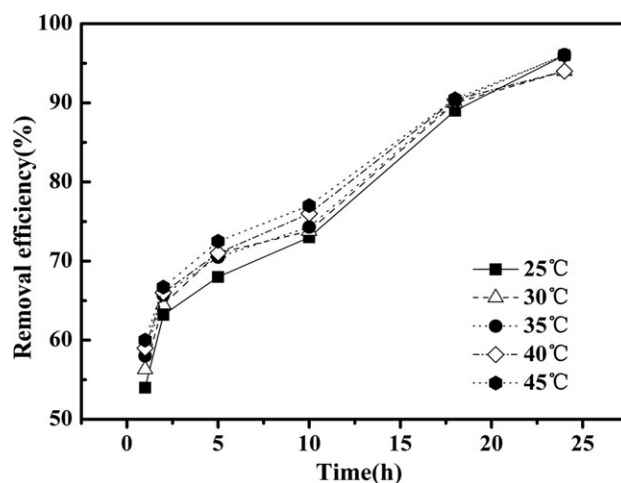
**Figure 6.** The effect of shaking time on adsorption of nitrate at pH 2.0 and 25°C with 0.2 g of adsorbents for 24 h.

From Table II and Figure 6, it can be seen that active carbon had more pores and larger surface than PVA/QL; however the removal efficiency at any shaking time is lower than PVA/QL. Therefore, we deduce that the high removal efficiency for the PVA/QL is ascribed to adequate functional groups in the surface of the adsorbent, which provided more binding site for the adsorption.

**Effect of Adsorbent Dose.** Effect of PVA/QL dosage on  $\text{NO}_3^-$  adsorption was investigated by changing the sorbent dose from 0.05 to 0.4 g with the initial  $\text{NO}_3^-$  concentration at  $10 \text{ mg L}^{-1}$ . Figure 7 shows the removal efficiency of  $\text{NO}_3^-$  increased with increasing of adsorbent dose. The removal efficiency of  $\text{NO}_3^-$  increased rapidly when PVA/QL dose increased from 0.05 to 0.3 g and then reached the maximum with >90% of  $\text{NO}_3^-$  in solution was removed. But the removal efficiency changed little when the adsorbent weight was beyond 0.3 g. At a higher PVA/



**Figure 7.** The effect of adsorbent dose on adsorption of nitrate on PVA/QL at pH 2.0 and 25°C for 24 h.

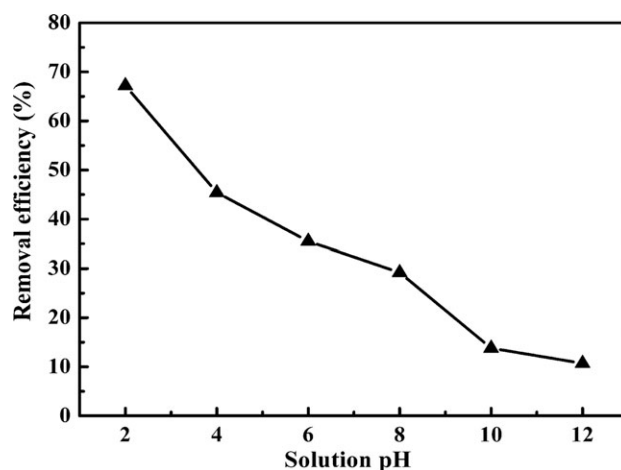


**Figure 8.** The effect of temperature on adsorption of nitrate on PVA/QL at pH 2.0 with 0.3 g of the adsorbent.

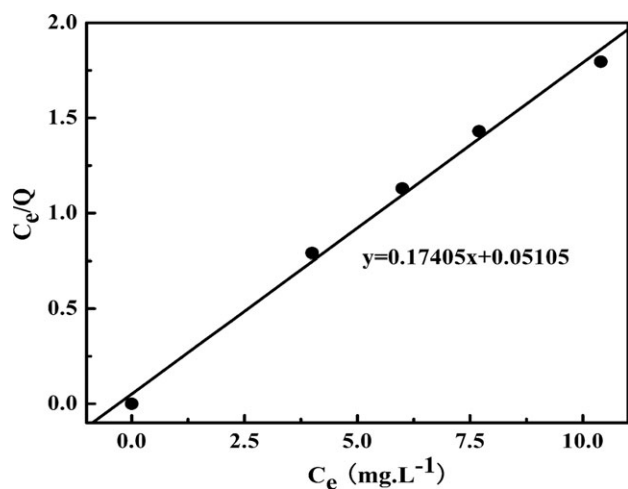
QL dose, e.g., 0.4 g, the sorption sites were sufficient and a further increase in sorbent dose did not lead to a significant increase in the  $\text{NO}_3^-$  removed from aqueous solution. Therefore, when the initial concentration of nitrate was  $10 \text{ mg L}^{-1}$ , the adsorbent dose of 0.3 g was more appropriate.

**Effect of Temperature.** Figure 8 gives the adsorption of  $\text{NO}_3^-$  on PVA/QL at 25, 30, 35, 40, and 45°C. The removal efficiency of the adsorbent for  $\text{NO}_3^-$  increased with the increase of the temperature from 25 to 45°C in the first 10 h, indicating that the adsorption process to be endothermic. Nevertheless, little difference in removal efficiency of nitrate was observed with the increase of the temperature, so the adsorption temperature was conducted at 25°C to save energy. The increase in remove efficiency of  $\text{NO}_3^-$  with temperature may be due to the changes in the size of the pores or the increasing in molecule movement rate.

**Effect of Solution pH.** The effect of solution pH on the adsorption of nitrate on PVA/QL is presented in Figure 9. Nitrate adsorption is known to be dependent on the pH of



**Figure 9.** The effect of solution pH on adsorption of nitrate on PVA/QL at 25°C for 24 h with 0.2 g of the adsorbent.



**Figure 10.** The adsorption isotherm for nitrate is at pH 2.0. Absorbent dose = 0.3g, shaking time = 24 h, temperature = 25°C.

solution. Solution pH is an important controlling parameter in the adsorption process, and thus the role of solution pH is examined at different pH value covering a range of 2.0–12.0. Figure 9 shows that with an increase in solution pH ranging from 2.0 to 12.0, the removal efficiency of  $\text{NO}_3^-$  decrease from 67.2 to 13.8%. The removal efficiency is higher in the acidic conditions than those in the neutral and alkaline solutions. Moreover, because when the solution pH above 6 the nitrate generates nitrophenol disulfonic which is yellow compound, the color of the nitrate solution changes evidently. Change in the solution color interferes with the evaluation for data validity of the adsorption. Therefore, the solution pH was adjusted to 2.0 to conduct the adsorption experiments.

**Adsorption Isotherms.** The adsorption isotherm experiments were performed with the initial nitrate concentrations varied from 10 to 80  $\text{mg L}^{-1}$ . For the Langmuir model, the linear equation has the following form:

$$\frac{C_e}{Q} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (3)$$

where  $Q$  is the adsorbed amount at equilibrium and  $C_e$  is the concentration at equilibrium, and  $Q_m$  and  $b$  are Langmuir constants. The adsorption data were applied to Langmuir isotherm equation and its contents were calculated, where  $Q_m$  was 5.75,  $b$  was 3.41, and  $R^2$  was 0.99696. From the slope of the Langmuir curve, the maximum adsorption capacity of PVA/QL was evaluated as 5.75  $\text{mg g}^{-1}$ . Figure 10 shows that the equilibrium

**Table III.** Desorption of Nitrate Ions

0.1M NaOH volume (mL)	Recovery percentage (%)
10	51
15	75
20	87
25	82

sorption data fits well Langmuir model, indicating to monolayer adsorption on the surface.

#### Regeneration of PVA/QL

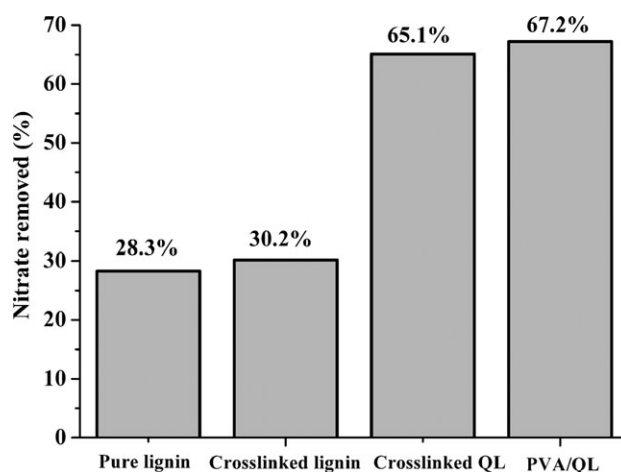
The regeneration efficiency for PVA/QL at different volumes of 0.1M NaOH is shown in Table III. It was found that nearly 87% of the adsorbed nitrate ions were desorbed from PVA/QL by using 20 mL 0.1M NaOH. It means that the high desorption percentage could led to PVA/QL be repeatedly used in nitrate adsorption study with slight losses in the initial adsorption capacities.

#### Mechanism of Adsorption

In this work, lignin was first phenolated to give high reactivity, aminated by monomeric quaternary ammonium groups, then the modified lignin were immobilized onto PVA followed by crosslink, greatly increasing the intensity and surface area of PVA/QL absorbent and the active functional groups of adsorption for  $\text{NO}_3^-$ . The mechanism involved is simply inferred as anion exchange chemical adsorption owing to dissociation of hydroxide ion. Grafting of quaternary ammonium groups onto lignin may increase electronic charge density of the molecule and enhance the charge neutralization as well. The adsorption mechanism of PVA/QL may be mainly charge neutrality action and adsorption bridging action.

Furthermore, by comparing the nitrate removal efficiency of pure lignin, crosslinked lignin, crosslinked QL and PVA/QL composite, the mechanism of adsorption for  $\text{NO}_3^-$  is estimated.

Figure 11, it can be seen that nitrate removal efficiencies of PVA/QL and QL are higher than that of pure lignin and cross-linked lignin under the same conditions. The crosslinked lignin without amination shows the low nitrate removal efficiency as well as pure lignin, and QL shows almost the same high removal efficiency as PVA/QL. These results indicate that quaternary ammonium groups are the main reactive groups on the absorbent for adsorption of nitrate. It can be concluded that amino group of quaternary ammonium is the major functional group responsible for the nitrate removal in QL and PVA/QL, and crosslink plays a small role on nitrate removal. However,



**Figure 11.** Removal efficiency of various absorbents for nitrate (%), at pH 2.0 and 25°C with 0.2 g of absorbents for 24 h.

the nitrate removal efficiency of PVA/QL is slightly higher than QL. This may be attributed to crosslink of PVA and QL producing network structure resulted in the increase of surface area of PVA/QL absorbent.

## CONCLUSION

A new poly(vinyl alcohol) (PVA)/quaternized lignin composite absorbent was prepared from lignin after phenolization and then quaternization (QL), and combined PVA with QL followed by crosslinking of glutaraldehyde. IR spectroscopy of the new composite absorbent reveals that lignin in the absorbent is grafted with quaternary ammonium groups and crosslink reaction between the hydroxyl group of PVA and lignin and aldehyde group of glutaraldehyde occurs. The quaternary ammonium structure and network structure in the surface of PVA/QL are the key factors to remove nitrate. The nitrate adsorption was strongly dependent on pH and absorbent dose, but influenced little by temperature and shaking time. The adsorption process was found to comply with the Langmuir isotherm. Furthermore, PVA/QL absorbent exhibits effectiveness in the removal of nitrate from aqueous solution and be regenerated by using NaOH solution. The effective application of the PVA/QL absorbent in the removing of nitrate from aqueous solution demonstrates that the new composite absorbent has a great potential to be an economical and efficient absorbent.

## ACKNOWLEDGMENTS

This work was supported by National Key Technology R&D Program of China (No.2007BAB18B08) and Key program of Sichuan education department (No.[2007] 604).

## REFERENCES

- Ghafari, S.; Hasan, M.; Aroua, M. K. *Bioresour. Technol.* **2008**, *99*, 3965.
- Orlando, U. S.; Okuda, T.; Baes, A. U.; Nishijima, W.; Okada, M. *React. Funct. Polym.* **2003**, *55*, 311.
- Mall, I. D.; Srivastava, V. C.; Agarwal, K. N. *Dyes. Pigments.* **2006**, *69*, 210.
- Babel, S.; Kurniawan, T. A. *J. Hazard. Mater.* **2003**, *97*, 219.
- Demirbas, A. *J. Hazard. Mater.* **2004**, *109*, 221.
- Suhas Carrott, P. J. M.; Carrott, M. M. L. R. *Bioresour. Technol.* **2007**, *98*, 2301.
- Guo, X. Y.; Zhang, S. Z.; Shan, X. Q. *J. Hazard. Mater.* **2008**, *151*, 134.
- Wu, Y.; Zhang, S. Z.; Guo, X. Y.; Huang, H. L. *Bioresour. Technol.* **2008**, *99*, 7709.
- Dizhbite T.; Zakis G.; Kizima A.; Lazareva, E.; Rossinskaya, G.; Jurkiane, V.; Telysheva, G.; Viesturs, U. *Bioresour. Technol.* **1999**, *67*, 221.
- Orlando, U. S.; Baes, A. U.; Nishijima, W.; Okada, M. *Chemosphere* **2002**, *48*, 1041.
- Kubo, S.; Kadla, J. F. *Biomacromolecules* **2003**, *4*, 561.
- Fernandes, D. M.; Hechenleitner, W. A. A.; Job, A. E.; Radovanovic, E. *Polym. Degrad. Stab.* **2006**, *91*, 1192.
- Parajuli, D.; Inoue, K.; Ohto, K.; Oshima, T.; Murota, A.; Funaoka, M.; Makino, K. *React. Funct. Polym.* **2005**, *62*, 129.
- Matsushita, Y.; Imai, M.; Iwatsuki, A.; Fukushima, K. *Bioresour. Technol.* **2008**, *99*, 3024.
- Matsushita, Y.; Yasuda, S. *Bioresour. Technol.* **2005**, *96*, 465.
- Matsushita, Y.; Iwatsuki, A.; Yasuda, S. *J. Wood. Sci.* **2004**, *50*, 540.
- Nada, A. M. A.; El-Saied, H.; Ibrahim, A. A.; Yousef, M. A. *J. Appl. Polym. Sci.* **1987**, *33*, 2915.
- Perezdrienko, I. V.; Molodozhnyuk, T. B.; Shermatov, B. E.; Yunusov, M. P. *Appl. Chem.* **2001**, *74*, 1650.
- Sharma, R. K.; Wooten, J. B.; Baliga, V. L.; Lin, X. H.; Chan, W. G.; Hajaligol, M. R. *Fuel* **2004**, *83*, 1469.
- Yeom, C. K.; Lee, K. H. *J. Membr. Sci.* **1996**, *109*, 257.
- Luo, X. G.; Liu, F.; Lin, X. Y.; Zhou, J. *Mater. Sci. Forum.* **2008**, *569*, 217.