Graft copolymerization of acrylic acid on kraft lignin to enhance aniline adsorption from aqueous solution

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ABSTRACT: Kraft lignin from bamboo was modified by grafting with acrylic acid to improve its capacity to adsorb aniline, a typical aromatic organic pollutant. Characterization of the copolymer structure and morphology indicated that lignin was successfully grafted by acrylic acid. Batch experiments showed that after graft copolymerization, the modified lignin had an enhanced aniline adsorption capacity (89.89 mg/g) as compared with the original lignin (6.61 mg/g). A kinetics study showed that the adsorption process followed pseudo-second-order kinetics, and the activation energy (*Ea*) was 10.22 kJ/mol. The equilibrium data were consistent with the Langmuir equation. The maximum monolayer capacity was 108.7 mg/g, which is higher than those of most reported lignin-based adsorbents. Thermodynamic values indicated that adsorption of aniline on the modified lignin is an exothermic process and spontaneous in nature due to the negative value of ΔH and ΔG. Consequently, graft copolymerization of acrylic acid on lignin appears to be a promising modification process to enhance the aniline adsorption capacity from aqueous solution.

Application: Information from this study can help mills prepare a better lignin adsorbent.

Aniline is an important organic chemical, extensively used in medicine, pesticides, dyestuffs and other industries [1]. However, aniline is also a recognized persistent pollutant with highly harmful influences on human health [2,3]. At present, some progress has been made in the treatment of aniline wastewater by physical, chemical, and biological methods, such as aerobic biodegradation, chemical oxidation, ion exchange, and membrane separation [4]. Among these approaches, adsorption is one of the most effective methods for separation and removal of this organic impurity from wastewater [5,6], owing to its high efficiency, low cost, easy operation, and non-secondary-pollution characteristics. Various adsorbent materials have been tested for the removal of aniline, including modified bentonite [7], diatomite [8], and crosslinking polymers [9]. Currently, investigations on the removal of organic pollutants from aqueous solutions by adsorption are focused on using renewable adsorbents from biomass, such as saw dust [10] and rice husks [11]. Therefore, one challenge faced by aniline adsorption technologies is to find a low-cost, renewable, and efficient adsorption material to remove the organic pollutant from wastewater [12].

Lignin is the third largest natural macromolecular organic substance in the world [13]. It is generally considered to be a three-dimensional network of polymers formed by the connection of ether bonds and carbon bonds. The network contains a number of functional groups, such as phenolic hydroxide, alcoholic hydroxide, carboxyl, methoxyl, and aldehyde groups [14]. Currently, lignin is widely used in adhesives [15], flocculants [16], and surfactants [17,18] because of its molecular structure characteristics. Because of its negatively charged functional groups, unmodified lignin itself can be used as an adsorbent to remove various heavy metal ions and organic pollutants from wastewater [19-21]. Moreover, grafting polymerization of lignin with some monomers [22] is an effective way to introduce functional groups to lignin to improve its adsorption performance.

New attempts are needed to find sustainable and economical materials with high adsorption capacity to remove aniline from wastewater [23]. In this work, an efficient adsorbent for aniline removal was synthesized by grafting acrylic acid onto bamboo lignin. Batch experiments of aniline adsorption from simulated wastewater by the original and modified lignins were compared under optimized conditions of adsorbent dosage, pH, and contact time. The kinetic, equilibrium isotherm, and thermodynamic models were further explored to determine the behavior and mechanism of aniline adsorption on the acrylic acid grafted lignin.

MATERIALS AND METHODS

Materials

Bamboo lignin was obtained by acid precipitation of black liquor from a laboratory-scale pre-hydrolysis kraft process using bamboo (*Phyllostachys pubescens*) as the raw material. According to the analysis method described by Liu et al. [24],

the dried lignin sample had 90.67% Klason lignin (w/w), 4.82% acid-soluble lignin (w/w), 1.66% carbohydrates (glucosan and xylan, w/w), and 1.99% ash (w/w).

Preparation of modified bamboo lignin

We added 5 g acrylic acid and 5 mL 30% sodium hydroxide solution (to maintain neutralization degree at around 60%) to a flask with a stirring device. The flask was then placed in a thermostatic water bath at 65°C. After heating the mixture for 15 min, 20 mL 0.2 g/mL potassium persulfate solution and 5 g kraft lignin were slowly added to the flask. After a 2-h reaction, the crude product was collected and dried in an electric oven at 105°C for 12 h. The dried crude product was ground to go through a 60-mesh screen. The resulting powders were dissolved in water by adding sodium hydroxide (1 mol/L) to pH 11 and then precipitated by adding hydrochloric acid (1 mol/L) to pH 3. The product was centrifuged at 10000 rpm for 15 min to remove the supernatant and dried in an oven at 105°C for 12 h. Four different modified lignins (LAA-1, LAA-2, LAA-3, and LAA-4) were prepared by controlling the mass ratio of bamboo lignin and acrylic acid. LAA-1 means the ratio of acrylic acid to bamboo lignin is 1:1, LAA-2 means the ratio of acrylic acid to bamboo lignin is 2:1, and so on.

Characterization of adsorbents

Fourier transform infrared spectroscopy (FTIR) spectra of the original and modified lignin were obtained using the FTIR spectrophotometer (FTIR-650, Guangdong Sci. & Tech. Development Co. Ltd.; Tianjin, China) in the range of 400-4000 cm^{-1} [25]. A scanning electron microscope (SEM, Japan Electronics Corp. Ltd.; Tokyo, Japan) was used to observe the morphology of the adsorbents. The dried samples were coated with gold before the examination.

Aniline adsorption experiments

Adsorption studies about the evaluation of the adsorbents for the removal of aniline from aqueous solutions were carried out in triplicate using 100 mL Erlenmeyer flasks containing 40 mL simulated wastewater. The pH, ranging from 4 to 8 of aniline aqueous solution, was adjusted by adding 0.1 mol/L sodium hydroxide and 0.1 mol/L hydrochloric acid. A fixed amount of the adsorbent was added to 40 mL aniline solution with known concentration and the mixture was shaken in an electrically thermostatic reciprocating shaker at 120 rpm and a predetermined temperature. After the adsorption, the solid and liquid were separated by centrifuging at 10000 rpm for 10 min. After filtration through a 0.45 μm membrane, the absorbance of the supernatant solution was measured by an ultraviolet-visible spectrophotometer at 280 nm to determine the residual aniline concentration using a previously established calibration curve. The adsorption capacity Q_t (mg/g) and aniline removal efficiency E (%) were calculated based on the following equations [26]:

$$Q_t(mg/g) = \frac{C_0 - C_t}{m} \times V \quad (1)$$

$$E(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

where C_o (mg/L) and C_t (mg/L) are the initial and concentration of aniline solution at time t, respectively; V (mL) is the volume of aniline solution used; and m (g) is the weight of the adsorbent used.

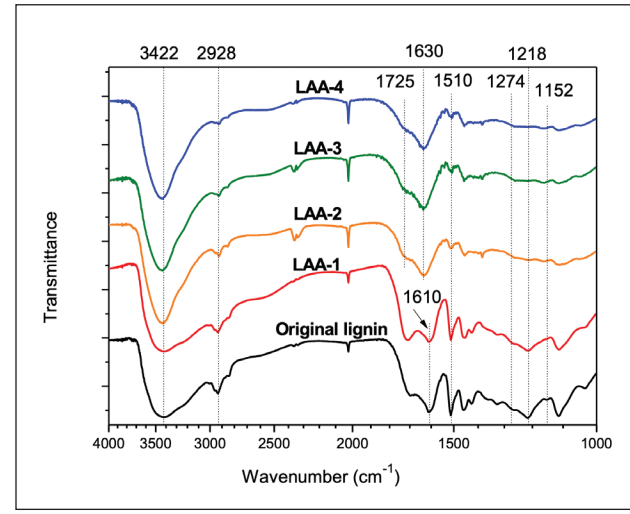
RESULTS AND DISCUSSION

Characterization of modified bamboo lignin

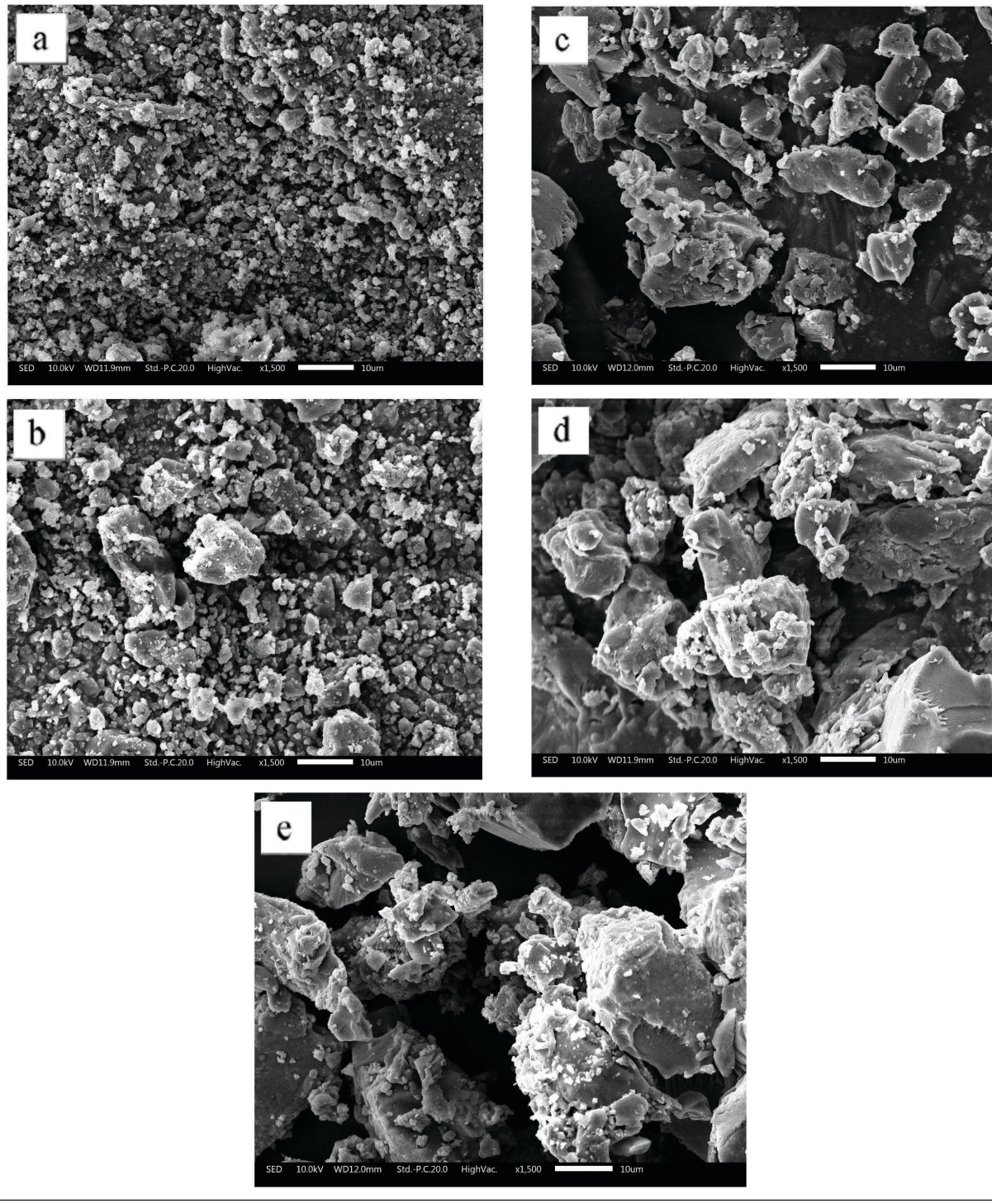
FTIR analysis

We used a simple chemical modification to introduce carboxyl groups into bamboo kraft lignin by grafting with acrylic acid. Because of the large amount of carboxyl groups in the modified lignin, the hydrogen bonds and the electrostatic interactions between adsorbent and aniline were stronger, resulting in a higher adsorption capacity. **Figure 1** shows the FTIR spectra of bamboo lignin and four different graft copolymers. Some of the basic absorption peaks of lignin were observed from the spectra of original bamboo lignin. The peak at the wave number of 3422 cm^{-1} was attributed to the stretching of phenol hydroxyl or alcohol hydroxyl groups. The peak at 2928 cm^{-1} was induced by methyl and methylene on the side chain or methoxyl in the benzene ring [27]. The strong absorption peaks of benzene ring framework vibration appeared at 1610 cm^{-1} and 1510 cm^{-1}, which represented the basic structure of lignin [28]. The typical bands at 1274 cm^{-1} (guaiacyl unit, G), 1218 cm^{-1} (syringyl unit, S), and 1152 cm^{-1} (*p*-coumaryl unit, H) were all present, which proved that the bamboo kraft lignin belonged to GHS lignin [29].

For the spectra of the graft copolymers, the basic characteristic peak of lignin remained almost unchanged, but their intensities were visibly decreased after grafting acrylic acid.



1. Fourier transform infrared spectroscopy (FTIR) spectra of original lignin and modified lignins by graft copolymerization with acrylic acid (LAA-1, LAA-2, LAA-3, and LAA-4).

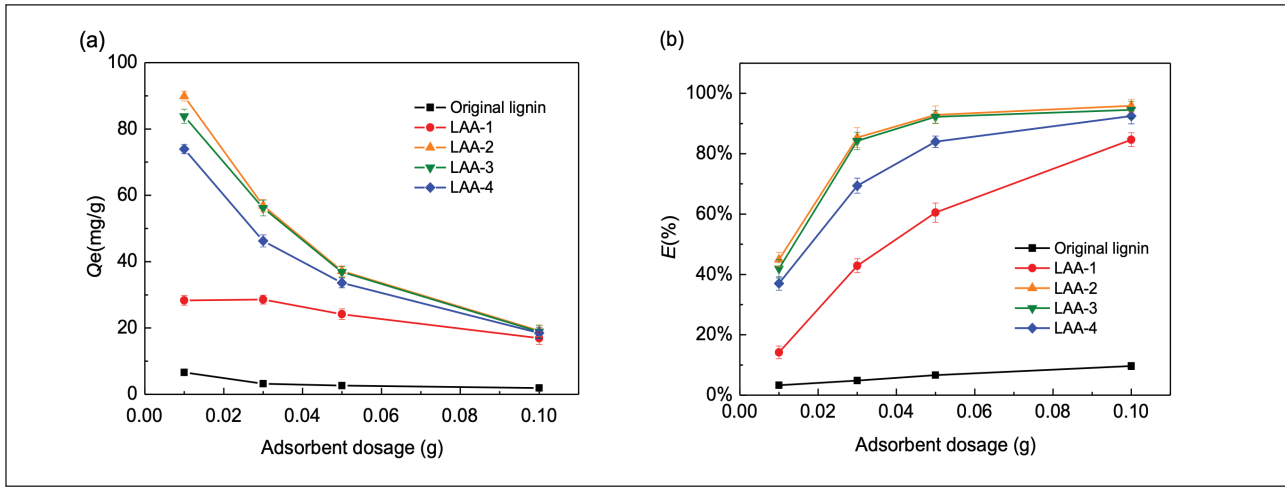


2. Scanning electron microscope (SEM) images of (a) original lignin and lignins modified by graft copolymerization with acrylic acid: (b) LAA-1, (c) LAA-2, (d) LAA-3, and (e) LAA-4.

Compared with the unmodified lignin, the main changes in the FTIR spectra were the enhanced absorption intensities at 1725 cm^{-1} and 1630 cm^{-1}, which were assigned to carbonyl groups. It indicated that carboxyl groups from acrylic acid were successfully grafted onto lignin [30]. A large number of carboxyl groups is critical for the effective adsorption of aniline by modified bamboo lignin.

SEM analysis

Figure 2 shows SEM micrographs of the original lignin, LAA-1, LAA-2, LAA-3, and LAA-4. The size of the modified lignin particles increased with the increase of the acrylic acid dos-



3. Effect of adsorbent dosage on (a) aniline adsorption capacity and (b) efficiency (aniline: 50 mg/L, pH: 5.5, contact time: 120 min, temperature: 30°C).

age. The small particle size of LAA-1 is probably because the lignin content is too high to be completely grafted with acrylic acid, resulting in LAA-1 containing unmodified lignin. Compared with the surface morphology of the original lignin, some changes were also observed for the modified lignins (Fig. 2b, c, and d). With the increasing of the acrylic content, the roughness of the surface was decreased. This might be because acrylic acid has the properties of water absorption and film formation, which make the sample surface smooth.

Removal of aniline using modified bamboo lignin

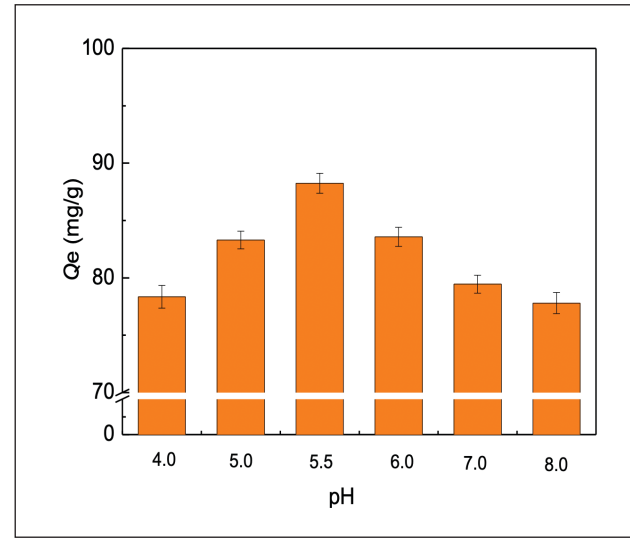
Effect of adsorbent dosage

Figure 3 shows the effect of grafted copolymer dosage on aniline adsorption. As the adsorbent dosage increased, the removal efficiency gradually increased and the adsorption capacity decreased. The adsorption capacity of the grafted copolymers (LAA-1, LAA-2, LAA-3, and LAA-4) were 28.33, 89.89, 83.85, and 73.95 mg/g, respectively (Fig. 3a). The adsorption capacity of grafted copolymers was much higher than that of the original bamboo lignin (6.61 mg/g), indicating that the graft copolymerization significantly enhances the aniline adsorption capacity of lignin. This is mainly because the modified bamboo lignin has a large number of carboxyl groups, which can form hydrogen bonds with amino groups in aniline molecules and improve the adsorption efficiency.

Effect of pH on adsorption performance of LAA-2

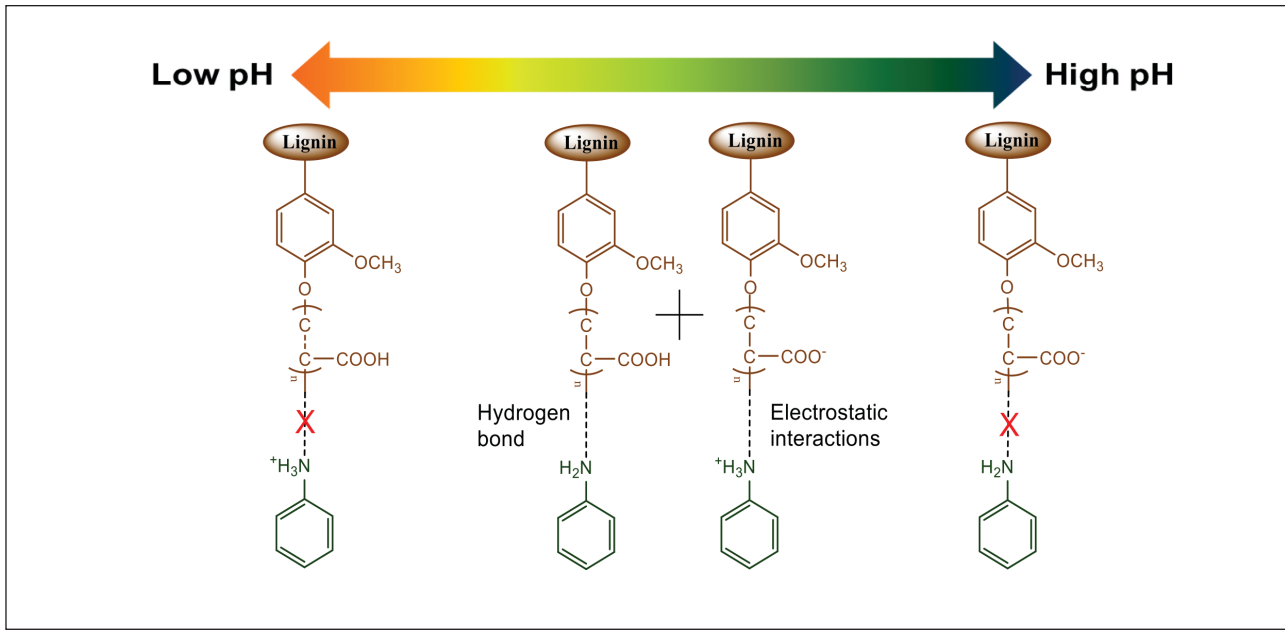
Compared with the other three graft copolymers, LAA-2 had the best adsorption capacity on aniline. Therefore, LAA-2 was used as the only adsorbent for the further adsorption studies. One of the important factors influencing the removal efficiency of aniline by modified bamboo lignin is pH.

Figure 4 shows that LAA-2 had a high adsorption performance for aniline under weak acidity (pH = 5.5). **Figure 5** shows the interaction between LAA-2 and aniline during the adsorption process under different pH values. At lower pH,

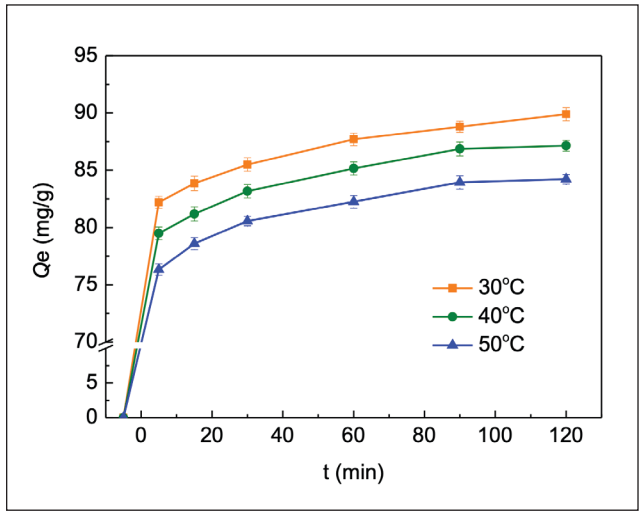


4. Effect of pH on the adsorption capacity of aniline on LAA-2 (adsorbent dosage: 0.01 g/40 mL, aniline: 50 mg/L, contact time: 120 min, temperature: 30°C).

hydrogen (H^+) in the solution reacts with the carboxyl group in LAA-2, and more aniline molecules are protonated. These prevent the generation of hydrogen bonding (O-H···N hydrogen bond and N-H···O hydrogen bond) between LAA-2 and aniline [31], and decrease the adsorption efficiency of aniline on the modified lignin. With the increasing of pH values, the carboxyl groups exist in the form of -COOH and $-COO^-$, and the aniline exist in the form of $C_6H_5NH_2$ and $C_6H_5NH_3^+$. The formation of the hydrogen bonds and the electrostatic interactions ($-H_3N^+-OOC^-$) increase sharply, resulting in a high adsorption capacity. When the solution alkalinity is strong, the carboxyl group in LAA-2 is deprotonated, and the aniline is mostly in the form of $C_6H_5NH_2$, which is not conducive to adsorption. Therefore, high pH decreases the aniline adsorption capacity of the modified lignin adsorbent.



5. Schematic diagram of the interactions between modified lignin and aniline during the adsorption process under different pH values.



6. Effect of contact time on the adsorption capacity of aniline on LAA-2 at different temperatures (adsorbent dosage: 0.01 g/40 mL, aniline: 50 mg/L, pH: 5.5).

Effect of contact time and adsorption kinetics

Figure 6 shows the effect of contact time on the adsorption of aniline on LAA-2 at different temperatures. As can be seen from Fig. 6, the adsorption capacity reached 95% of the saturated adsorption capacity within 15 min at 30°C. After 60 min, the adsorption capacity increased slowly. At the initial stage of the reaction, the concentration of aniline in the solution is high, and there are sufficient active reaction sites on the surface of LAA-2. Thus, the adsorption rate is high. As the reaction time extends, the number of reactivity sites provided by LAA-2 gradually decrease. Hence, the adsorption capacity increases slowly when the reaction approaches adsorption equilibrium.

Adsorption kinetics theory aims at studying the absorption capacity varying with time, including the adsorption rate and dynamic equilibrium during the adsorption process. The pseudo-first-order and pseudo-second-order kinetics models were fitted to the experimental data for the determination of potential rate-controlling steps of the aniline adsorption kinetics. The linear form of the pseudo-first-order and pseudo-second-order kinetics models are expressed as follows:

T, °C	Q_e, mg/g	Pseudo-first-order Kinetics		Pseudo-second-order Kinetics	
		k^2, min^{-1}	R_1^2	k^2, g/(mg·min)	R_2^2
30	90.09	0.0294	0.9345	0.00913	0.9998
40	87.72	0.0240	0.9864	0.00949	0.9999
50	84.75	0.0247	0.9881	0.00988	0.9999

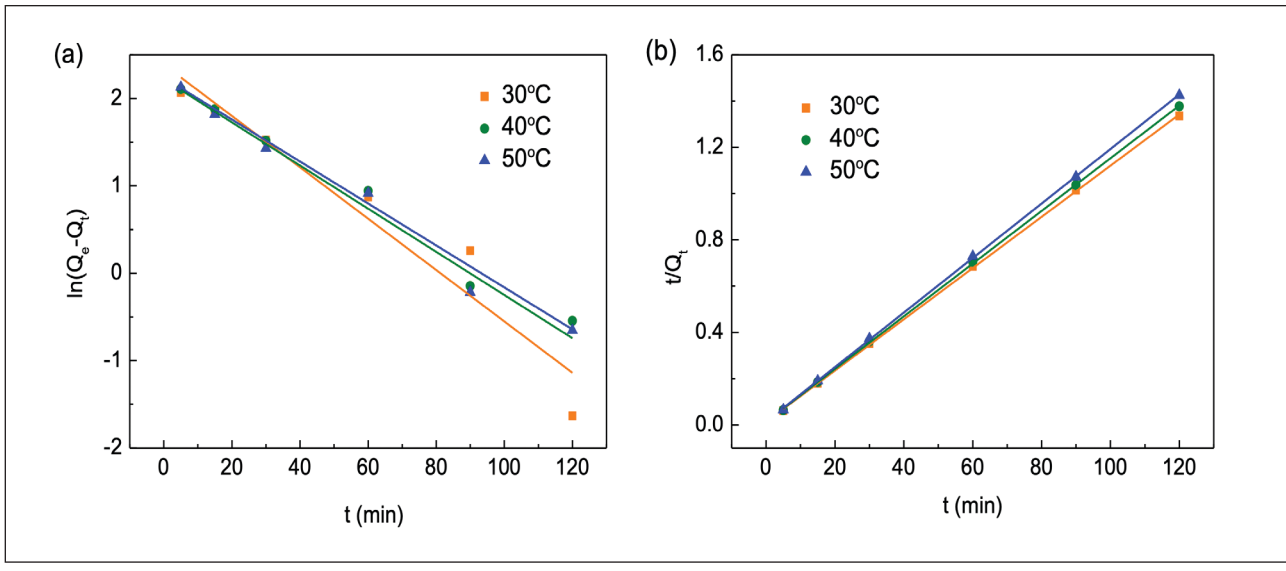
I. Kinetic parameters for the adsorption of aniline on LAA-2.

$$\ln(Q_e - Q_t) = -k_1 t + \ln Q_e \quad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^{\,2}} + \frac{t}{Q_e} \quad (4)$$

where Q_e (mg/g) is the amount of adsorption at equilibrium; Q_t (mg/g) is the amount of adsorption at any time t; t (min) is the adsorption time; k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption; and k_2 (g/(mg·min)) is the rate constant of pseudo-second-order adsorption.

Table I gives the parameters for the kinetics models, as derived from Eqs. 3 and 4, together with the fitted pseudo-first-order and pseudo-second-order kinetics models (**Fig. 7**). At different temperatures, the experimental value of the



7. Kinetics models for adsorption of aniline on LAA-2 at different temperatures: (a) pseudo-first-order kinetics model and (b) pseudo-second-order kinetics model.

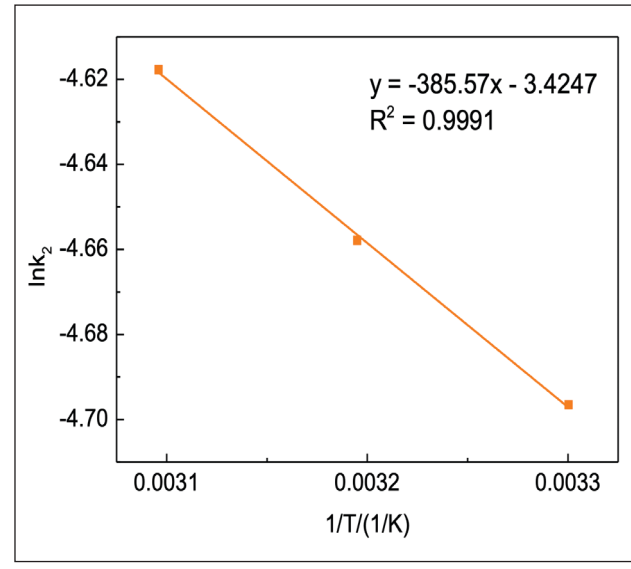
adsorption capacity was close to the calculated value of the pseudo-second-order kinetics equation. The determination coefficient R^2 of the pseudo-second-order kinetics model was also higher than that of the pseudo-first-order kinetics model. Moreover, the theoretical equilibrium adsorption capacity (Q_e) was 84.75–90.09 mg/g according to the pseudo-second-order kinetics model, which was not much different from the obtained experimental results. Therefore, the aniline adsorption on LAA-2 was in good agreement with the pseudo-second-order kinetics model, indicating that the speed control of adsorption is mainly the interactions of functional groups, including the formation of hydrogen bonds and electrostatic interactions.

The rate constant of pseudo-second-order adsorption k_2 was substituted into the Arrhenius equation [32]. The activation energy of the adsorption of aniline on the modified lignin adsorbent can be obtained by Eq. 5 [26]:

$$\ln k_2 = \ln A - \frac{Ea}{RT} \quad (5)$$

where E_a (kJ/mol) and A are the activation energy and the pre-index factor, respectively; R (8.31451 J/(K·mol)) is the universal gas constant; and T (K) is the adsorption temperature in Kelvin.

Activation energy refers to the minimum energy required to reach the activated molecule from the reactant molecule in a chemical reaction, which can be obtained from the slope by plotting a graph of lnk_2 versus *1/T* (**Fig. 8**). The magnitude of the activation energy might give an idea about the type of adsorption (i.e., physical or chemical adsorption). In this work, the value of *E*a for the adsorption was found to be 10.22 kJ/mol, suggesting that the adsorption of aniline onto the modified lignin adsorbent is a physical adsorption type (<40 kJ/mol).



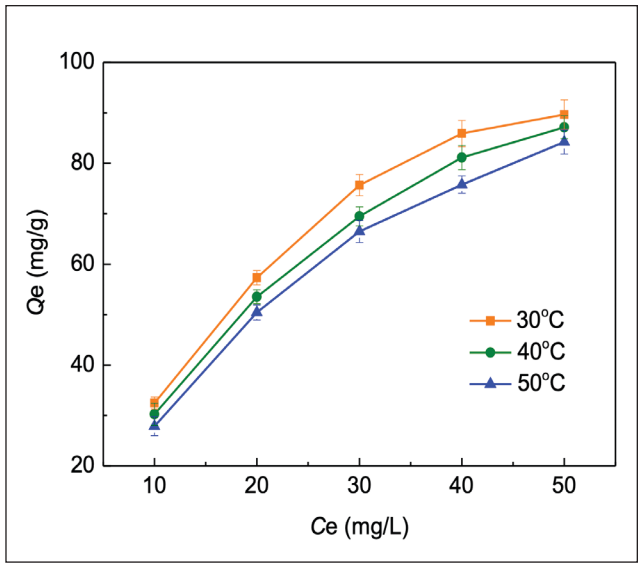
8. Relationships of lnk_2 *and 1/T.*

Effect of equilibrium concentration and isotherm models

Figure 9 shows the effect of different initial concentration of aniline on the adsorption capacity at different temperatures. The capacity of LAA-2 for adsorption of aniline increased as the aniline equilibrium concentration increased at all three temperatures (30°C, 40°C, and 50°C).

In the adsorption isotherm experiments, the equilibrium data were fitted to the well-known and widely used isotherm equations of Langmuir and Freundlich models. The linear equations are as follows [26]:

$$\text{Langmuir:} \quad \frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \quad (6)$$



9. Adsorption isotherms of aniline on LAA-2 at different temperatures (adsorbent dosage: 0.01 g/40 mL, pH: 5.5, contact time: 120 min).

Freundlich: $$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (7)$$

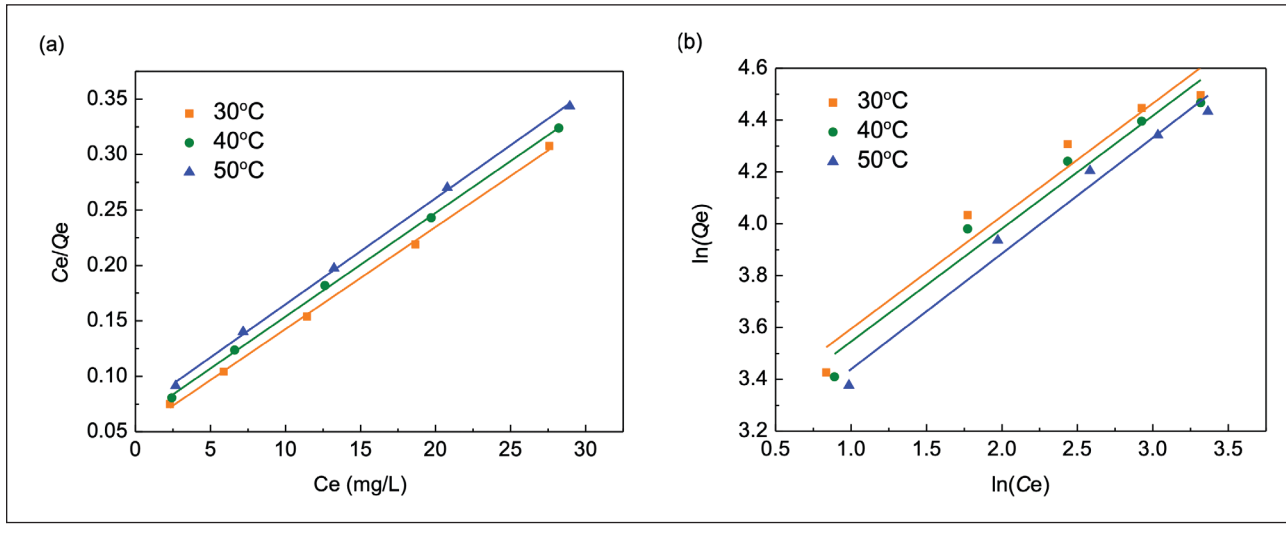
where C_e (mg/L) is the concentration of adsorbate at the equilibrium, Q_e (mg/g) is the solid phase concentration of adsorbent at equilibrium, Q_m (mg/g) is the maximum capacity of adsorbent, K_L (L/mg) is the Langmuir isotherm constant, K_F [(mg/g)(L/mg)$^{1/n}$] is the Freundlich constant, and *1/n* is the heterogeneity factor.

The equilibrium data were analyzed according to the Freundlich and Langmuir equations. **Table II** shows the fitted parameters of the Langmuir and Freundlich equations. **Figure 10** shows the fitted plots for the adsorption at different temperatures by the (a) Langmuir and (b) Freundlich models. The coefficient R^2 of Langmuir isotherm was greater than or equal to 0.99 under different temperatures, which was much higher than that of the Freundlich isotherm. This indicates that the adsorption is better fitted by the Langmuir isotherm. The maximum monolayer adsorption capacity calculated by the Langmuir model was 108.7 mg/g, which is much higher than those of the lignin-based bio-adsorbents reported in the literature (**Table III**) [33-40]. The result suggests that use of the lignin-based adsorbent modified by grafting acrylic acid is an effective method for removing aniline from aqueous solution.

In the Langmuir isotherm equation, K_L is the adsorption equilibrium constant, and its value is related to the characteristics of the adsorbent, adsorbent itself and temperature. The higher the value of K_L, the stronger the adsorption capacity

	Langmuir			Freundlich		
T, °C	Q_m	K_L, L/mg	R^2	*1/n*	K_F, mg/g	R^2
30	108.70	1.81	0.9990	0.435	27.40	0.9491
40	106.38	1.56	0.9994	0.437	21.80	0.9765
50	104.17	1.39	0.9993	0.446	19.94	0.9799

II. Characteristic parameters obtained by the Freundlich and Langmuir equations.



10. The linear (a) Langmuir and (b) Freundlich isotherms of aniline adsorption on LAA-2.

Adsorbents	Adsorption Capacity, mg/g	Literature Cited
Bamboo lignin grafted acrylic acid	108.7	This work
Lignin extracted from water hyacinth	16.1	[33]
Alkali lignin by grafting methacrylic acid	38.5	[34]
Na-bentonite modified with cetyltrimenthyl ammonium bromide and quaternized chitosan	29.7	[35]
Pyromellitic dianhydride modified jute fiber	91.5	[36]
Activated carbon fiber	75.19	[37]
Quaternary ammonium salt cellulose	63.29	[38]
Carbonized wheat straw	112.36	[39]
Corn straw biochar	37	[40]

III. Comparison of adsorption capacity of aniline on various adsorbents.

[31]. As can be seen from Table III, the value of K_L decreased with the increasing of temperature, indicating that the sorption process of aniline on LAA-2 was more favorable at lower temperatures.

Effect of temperature and adsorption thermodynamics

Figures 6 and 9 give the effect of temperature on aniline adsorption. As the temperature increased, the adsorption capacity gradually decreased. This indicates that the adsorption of aniline by LAA-2 is an exothermic reaction. The adsorption thermodynamics are mainly based on the adsorption amount of adsorbent under various temperature conditions so as to obtain various thermodynamic data. Through these thermodynamic data, we could determine the Gibb's free energy (ΔG, kJ/mol), enthalpy (ΔH, kJ/mol), and entropy (ΔS, kJ/[mol·K]) of the adsorption process. The thermodynamic parameters are calculated by the following equations [26]:

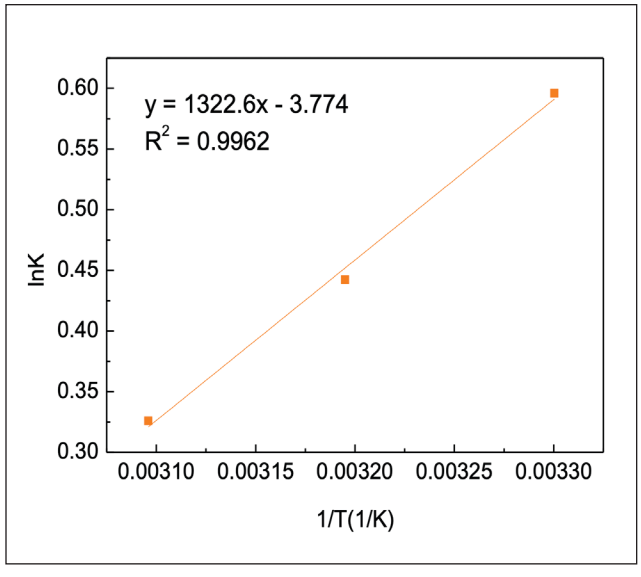
$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (8)$$

$$\Delta G = \Delta H - T \cdot \Delta S \quad (9)$$

where K is the adsorption equilibrium constant, R (8.3145 J/[K·mol]) is the universal gas constant, and T (K) is the adsorption temperature in Kelvin.

The study of adsorption thermodynamics is conducive to an in-depth understanding of the adsorption behavior of adsorbents on aniline. Meanwhile, the thermodynamic parameters play an important role in studying the thermal energy changes during the adsorption process and determining whether the adsorption is spontaneous [36]. As shown in **Fig. 11**, the ln$K$ had a good linear relationship with 1/T, and the linear equation was y = 1322.6x - 3.774. Through the mathematical conversion, **Table IV** shows the results of Gibbs free energy (ΔG), enthalpy change (ΔH), and entropy (ΔS).

As shown in Table IV, the negative value of ΔH indicates that the adsorption of aniline on LAA-2 is an exothermic process. The negative value of ΔS suggests that the chaos of the system is reduced after LAA-2 interacts with aniline. The values of Gibb's free energy are below zero, which reveal that the adsorption is a spontaneous reaction in the temperature



11. Relationships of lnK and 1/T.

T, °C	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, J/mol K	Ea, kJ/mol
30	-1.49	-11.00	-31.38	3.21
40	-1.18			
50	-0.86			

IV. Thermodynamic parameters of aniline adsorption on LAA-2.

range. And the value of ΔG increased with the temperature rising, illustrating that low temperature is beneficial to adsorption.

CONCLUSIONS

Four kinds of graft copolymers were obtained by acrylic acid grafting modification of bamboo kraft lignin. In comparing results for the adsorption capacity of aniline on the different adsorbents, the LAA-2 had the best adsorption efficiency among the modified bamboo lignins. The adsorption process highly depended on the pH and temperature and the highest adsorption capacity was found at 30°C and pH 5.5. Furthermore, the adsorption data fit well with pseudo-second-order kinetics and the Langmuir isotherm adsorption. The thermodynamic parameters indicated that the aniline adsorption by LAA-2 is an exothermic process and spontaneous in nature. The adsorption of aniline onto the modified lignin is mainly formed by hydrogen bonds and the electrostatic interactions between the adsorbent and aniline. The graft copolymerization of acrylic acid on lignin significantly enhances the aniline adsorption capacity, which provides a feasible application for lignin as an effective adsorbent. **TJ**

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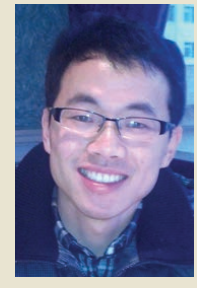

Wang

Liu

Si

We chose this topic because unmodified lignin itself can be used as an adsorbent to remove various heavy metal ions and organic pollutants from wastewater, because the lignin has negatively charged functional groups. Pollution of aniline organic wastewater also is becoming more and more serious.

Previous studies have only used lignin to adsorb pollutants in organic wastewater. Few studies have considered adsorption of aniline on modified lignin.

The most difficult aspect of this research was how to control the mass ratio of acrylic acid and lignin to prepare a better adsorbent. This was achieved by constantly adjusting the mass ratio of acrylic acid and lignin.

The graft copolymerization of acrylic acid on lignin was a promising modification process to enhance the aniline adsorption capacity from aqueous solution. We found it interesting that more acrylic acid was not always better, although the addition of acrylic acid can help lignin to adsorb aniline.

The next step is to further improve the adsorption capacity and scale up the process.

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