Synthesis of Chitosan–Ignosulfonate Composite as an Adsorbent for Dyes and Metal Ions Removal from Wastewater

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ABSTRACT: Sodium lignosulfonate is a polymer with extensive sources and abundant functional groups. Therefore, it has potential value for research and wide utilization. In this study, the adsorption material was prepared by blending sodium lignosulfonate and chitosan, which could adsorb anionic and cationic dyes and metal ions. The composite was characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and thermogravimetry (TG). The results showed that the composite was cross-linked mainly by the strong electrostatic interaction between the protonated amino group in chitosan and the sulfonate group in sodium lignosulfonate. Moreover, the effects of initial concentration, adsorption time, initial pH, and mass ratio of chitosan to sodium lignosulfonate on the adsorption performance of the composite were investigated. Meanwhile, the adsorption processes were agreed well with the pseudo-second-order kinetic model and Langmuir isotherm model. The adsorption mechanism was that the electrostatic interaction between the protonated amino and hydroxyl groups of the composite with anionic (SO3−) and HCrO4− groups of Congo red and Cr(VI), respectively. In addition, the electrostatic interaction between SO3− of the composite and positively charged group of Rhodamine B played an important role in the adsorption of Rhodamine B.

1. INTRODUCTION

The wastewater from dyestuff, electroplating, textile, and other industries contain dyes, heavy-metal ions, and other harmful chemicals, causing water contamination.1,2 The dyes in wastewater are harmful to aquatic organisms and affect the aesthetics because of their high toxicity and high visibility.3,4 Rhodamine B and Congo red as typical dyes are widely used in many industries, which have to be removed from wastewater due to their carcinogenic and mutagenic effects.5,6 Similarly, Cr(VI), derived from various industries such as electroplating, textile, storage batteries, and leather tanning, is non-biodegradable and highly toxic, posing a serious threat to human health.7,8 To remove these contaminants, various techniques have been developed, including adsorption,9,10 membrane filtration,11 catalytic degradation,12,13 electrochemical process,14 advanced oxidation process,11 etc. Among them, adsorption has potential application prospect due to its high efficiency, economic feasibility, and convenient operation. Various adsorption materials have been reported for the removal of pollutants such as polymers,15 inorganic materials,16 biomaterials,17–19 and macromolecular materials.20 In recent years, biomaterials have become the concern of materials, owing to environmental protection, renewability, and high removal efficiency for pollutants.

Lignin, the second most abundant organic compound, is a kind of macromolecular polymer with three-dimensional network structure.21,22 Although lignin is abundant, it is rarely used as a raw material in industrial production due to its complex molecular structure.23 Therefore, the effective utilization of lignin is very meaningful and promising. Due to its phenolic hydroxyl, alcoholic hydroxyl, and carboxyl, lignin could be used as an adsorbent to adsorb dyes and metal ions.24,25 However, it has been shown that the adsorption property of lignin was poor in previous researches.26 Therefore, many studies focused on its modification to improve its adsorption capacity.26 Chitosan, the only natural polysaccharide with amino group, is obtained from deacetylation of chitin, which widely exists in nature.27 It is a linear natural polymer composed of β(1,4)-2-amino-2-deoxy-D-glucopyranose units. Chitosan could adsorb pollutants on account of its active sites including amino and hydroxyl groups.28 It could improve the adsorption performance of other materials by cross-linking. Therefore, development of chitosan–lignin composites is a good way to improve the adsorption properties of lignin.

Some studies prepared chitosan–lignin composites by solvent evaporation,29 blending method,30 and layer-by-layer self-assembly.31 Due to their excellent properties, the composites have a wide range of applications in the fields of...
cosmetics, biomedicine, biology, and others. However, only a few studies have reported its application in sewage treatment. Sohni et al. fabricated a chitosan/nanolignin composite material as a highly efficient adsorbent, and its adsorption results demonstrated efficient removal ratio (about 83%) of methylene blue dye. Nair reported the adsorption of the chitosan–alkali lignin composite for Remazol Brilliant Blue R and Cr(VI) and found that it had the highest removal percentage of pollutants compared to chitosan and alkali lignin. Wysokowski et al. developed the chitin–lignin adsorbent with high adsorption efficiency of nickel(II) and cadmium(II) (88.0 and 98.4%, respectively). The findings from these studies illustrated that the composites had the ability to adsorb dyes and metal ions. However, a composite that can adsorb heavy-metal ions, anionic dyes, and cationic dyes has not been fully investigated in previous studies.

As the main form of lignin, lignosulfonate has sulfonate groups, derived from sulfite pulping process, which is a polyanionic electrolyte with good water solubility. The present study prepared the chitosan–lignosulfonate composite and explored its molecular structure, synthesis mechanism, thermal stability, and surface morphology. Also, it was the first time to comprehensively investigate its adsorption performance of Congo red (anionic dye), Rhodamine B (cationic dye), and Cr(VI) (metal ion). Moreover, the change of adsorption percentage of pollutants compared to chitosan and alkali lignin.

2. RESULTS AND DISCUSSION

2.1. Characterization of Chitosan–Lignosulfonate Composites

2.1.1. Fourier Transform Infrared Spectroscopy (FT-IR) Analysis. The FT-IR spectra of sodium lignosulfonate, chitosan, and the composite are shown in Figure 1. For sodium lignosulfonate, the peaks at 3420 and 2932 cm$^{-1}$ were due to the stretching vibrations of $\text{O} \cdot \text{H}$ and $\text{N} \cdot \text{H}$ bonds. The peaks at 2890 and 1614 cm$^{-1}$ were assigned to stretching vibrations of $\text{C} \cdot \text{H}$ in the alkyl group and $\text{N} \cdot \text{H}$ in the amino group, respectively. The peak at 1169 cm$^{-1}$ was related to the $\text{C} \equiv \text{O}$ stretching. The peak at 667 cm$^{-1}$ was due to the out-of-plane bending of the $\text{O} \cdot \text{H}$ group.

After compounding sodium lignosulfonate with chitosan, it could be observed that the FT-IR spectra of the composite had all the key characteristics of sodium lignosulfonate and chitosan with some small changes due to the weak interaction between the two materials. In composite, the peaks of $\text{N} \cdot \text{H}$ stretching moved from 1614 cm$^{-1}$ (in chitosan) to 1594 cm$^{-1}$ and the peak at 1036 cm$^{-1}$, similar to that of sodium lignosulfonate, was attributed to $\text{S} \equiv \text{O}$ stretching. It could be inferred that $\text{NH}_2$ was protonated into $\text{NH}_3^+$, and there was electrostatic interaction between $\text{NH}_3^+$ and $\text{SO}_3^-$. The shifts of $\text{C} \equiv \text{O}$ stretching peak from 1169 cm$^{-1}$ (in chitosan) to 1155 cm$^{-1}$ and $\text{C} \equiv \text{O} \cdot \text{C}$ peak from 1113 cm$^{-1}$ (in sodium lignosulfonate) to 1064 cm$^{-1}$ were clearly observed. The results suggested that the hydrogen bonding existed between the hydroxyl group in sodium lignosulfonate and the glucosidic bond in chitosan, and there was the interaction between the hydroxyl group in chitosan and the ether bond in sodium lignosulfonate.

According to the FT-IR characterization, the interactions in the chitosan–lignosulfonate composite are depicted as Scheme 1, including weak hydrogen bonds and electrostatic interaction. A weak bond was formed between hydroxyl group of chitosan and methoxy group of sodium lignosulfonate (shown as dashed line 1 in Scheme 1). Also, the hydroxyl group in the phenolic ring of sodium lignosulfonate could also interact with $\beta$-1,4-glicosidic oxygen in chitosan (dashed line 2). It could be seen

Scheme 1. Preparation of Chitosan–Sodium Lignosulfonate Composite

Figure 1. FT-IR spectra of sodium lignosulfonate, chitosan, and chitosan–lignosulfonate composite.
that the electrostatic interaction existed between the protonated amino group in chitosan and the sulfonate group in the sodium lignosulfonate (dashed line 3).

2.1.2. Thermogravimetric Analysis. Thermalgravimetric analysis (TGA) curves describe the trend of material degradation with an increase in temperature and characterize the thermal stability of materials. The thermogravimetric curves of chitosan, sodium lignosulfonate, and chitosan–lignosulfonate composite are shown in Figure 2. The thermal degradation of chitosan, sodium lignosulfonate, and the composite proceeded in two stages. In the first stage, chitosan was obviously weightless around 100 °C, while the weight loss of sodium lignosulfonate and chitosan–lignosulfonate composite occurred at around 150 °C, indicating the evaporation of water absorbed in materials. In the second stage, there was the degradation of three materials. It was clear that chitosan degraded in the range of 250–410 °C owing to the breaking of the molecular chain, and sodium lignosulfonate decomposed in a wide temperature range of 150–500 °C due to the volatilization of low-molecular-weight lignin fragments. The composite degraded in the temperature range of 250–410 °C, which might be related with pyrolysis of chitosan molecular chains and lignosulfonate.

Comparing the degradation ranges of the three materials, it was found that the weight loss of the composite was merely about 40% in the temperature range of 250–410 °C and the weight loss rate of the composite was higher than that of chitosan and lower than that of sodium lignosulfonate. It was indicated that the degradation rate of the composite was reduced by the addition of sodium lignosulfonate. The weight loss of composite was higher than that of sodium lignosulfonate and lower than that of chitosan at 800 °C, proving that the composite had the corresponding binding region of sodium lignosulfonate and chitosan.

2.1.3. Surface Morphology Analysis. The surface morphologies of sodium lignosulfonate, chitosan, and the composite are shown in Figure 3. It could be found from Figure 3a that the surface of sodium lignosulfonate was rough with some folds and holes. As seen from Figure 3b, chitosan presented an uneven network structure and had many pores with different sizes, which were mainly due to the interlacing of the molecular chains of chitosan. As seen in Figure 3c, these cross sections of molecular chains were arranged neatly and distributed evenly, which might be the molecular chains of chitosan cross-linking with sodium lignosulfonate. It was speculated that the ordered arrangement of chitosan molecular chains was due to the strong electrostatic interaction between sodium lignosulfonate and chitosan.

The surface morphology of the Cr(VI)-adsorbed composite is shown in Figure 3d. It was found that the composite after adsorption for Cr(VI) had a more dense surface and was caked, which indicated that Cr(VI) was fully adsorbed by the composite. Also, it could be observed from Figure 3e that the surface of composite was smoother and some clumps appeared, which manifested that the composite adsorbed Rhodamine B. Figure 3e shows that the composite after adsorption for Congo red had a more uniform surface with small holes, which illustrated that Congo red could be adsorbed by the composite and was mainly adsorbed on the surface of the composite.

2.1.4. Elemental Analysis. Energy-dispersive X-ray spectroscopy (EDS) of chitosan–lignosulfonate composite and pollutants-adsorbed chitosan–lignosulfonate composite is shown in Figure 4. Cr element was found in the Cr-adsorbed composite, indicating that Cr was adsorbed by composite. After the adsorption of Rhodamine B, the atomic percentages of C and O in the composite changed from 54.77 to 59.72 and from 37.36 to 33.28, respectively, which validated that the composite adsorbed Rhodamine B. The atomic percentages of N and S had a noticeable increase after adsorbing Congo red.
by composite, which fully proved that the composite had the ability to absorb Congo red.

2.2. Effect of Mass Ratio. The mass ratio of sodium lignosulfonate and chitosan had a great effect on the adsorption performance of the composite. The adsorption capacity of the composites with different proportions for pollutants is shown in Figure 5. The adsorption amount of Congo red showed a gradual increasing trend with an increase in chitosan (with amino group). Congo red (anionic dye) could be adsorbed through electrostatic interaction between its anion group and the protonated amino group in the composite.3 The result indicated that the reason for the rising adsorption amount of Congo red was the increase of protonated amino groups in the composite. It also could be observed that the adsorption amount of Rhodamine B decreased with the increase in chitosan. Absorption of Rhodamine B (cationic dye) on the composite was due to the electrostatic interaction and the formation of hydrogen bonds.4,5 It could be inferred that the decreased adsorption amount of Rhodamine B was due to the reduction of sulfonic groups and hydroxyl groups in the composite.

In addition, the adsorption amount of Cr(VI) tended to decline with the reduction of mass ratio. At a pH of 2, Cr(VI) existed predominantly in the form of HCrO$_4^-$ and the amino and hydroxyl groups in the composite were fully protonated to form the positively charged groups, resulting in the electrostatic interaction between HCrO$_4^-$ and the composite.47,48 It was speculated that the reduction of the hydroxyl group was higher than the increase of the amino group as the chitosan increased.

As seen in Figure 5, it is clear that the adsorption amount of the composite for the pollutants followed the order: Congo red > Cr(VI) > Rhodamine B. However, the adsorption sites of the composite for Cr(VI) were more than that for Congo red from the inset in Figure 5. It was because (i) the molecular weight of Cr(VI) was lower than that of Congo red and (ii) the adsorption of Cr(VI) included not only the electrostatic interaction but also hydrogen bonding interaction. With an increase in chitosan, the amount of free amino groups increased and the number of the free sulfonic groups and hydroxyl groups declined in the composite. It proved that the preparation mechanism of the composite was consistent with the result of FT-IR.

2.3. Adsorption Dyes and Cr(VI) on the Pollutants. 2.3.1. Effect of pH. The pH of the solution is an important parameter affecting the adsorption amount of pollutants. It determines the level of electrostatic adsorption between adsorbent and adsorbate. Under different initial pH conditions,
The adsorption amounts of the composite for Cr(VI), Congo red, and Rhodamine B are shown in Figure 6. As seen from Figure 6a, the adsorption amount of the composite for Cr(VI) decreased drastically with increase in the pH value within the range of 2–8. When the pH value was higher, the trend of decrease tended to be stable. It was clear that the adsorption of the composite was pH dependent. Cr(VI) exists predominantly in the form of HCrO$_4^-$ ions in the aqueous solution below pH of 4, while this form transfers to CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ anions with an increase of pH. The adsorption capacity showed a decreasing trend at higher pH, which could be clarified by the fact that the negative charge on the surface of the composite was not conducive to the adsorption of Congo red due to electrostatic repulsion. Therefore, the adsorption system with a pH of 7 was chosen for further adsorption experiments for Congo red.

As shown in Figure 6c, the adsorption amount went up with an increase of the pH and reached the maximum at pH 7. It was indicated that the surface of composite was positively charged owing to the protonation of amine and hydroxyl groups and the electrostatic attraction occurred between the composite and Congo red at a low pH value. The adsorption capacity showed a decreasing trend at higher pH, which could be clarified by the fact that the negative charge on the surface of the composite was not conducive to the adsorption of Congo red due to electrostatic repulsion. Therefore, the adsorption system with a pH of 7 was chosen for further adsorption experiments for Congo red.

Figure 6. Effect of the initial pH on the adsorption of (a) Cr(VI), (b) Rhodamine B, and (c) Congo red.

2.3.2. Adsorption Kinetics. The effect of contact time on the adsorption of pollutants by the composite is shown in Figure 7a. The adsorbed amount of Cr(VI) increased rapidly within 25 min, and then the upward tendency was steady until reaching an equilibrium state. In addition, the adsorbed amount of Rhodamine B on the composite showed a rapidly rising trend within 40 min, and then the uptake rate decreased.

Figure 7. (a) Effect of adsorption time on the adsorption amount of chitosan–lignosulfonate composite for Cr(VI), Rhodamine B and Congo red; (b) pseudo-second-order kinetic model.
distinctly after 100 min. Among the three pollutants, the adsorption capacity of Congo red on composite was the highest. The adsorption amount increased obviously within 100 min, and then the increasing rate decreased slowly.

The pseudo-first-order model and the pseudo-second-order model were used to describe the adsorption process. The equations are given as follows (eqs 1 and 2, respectively):

First-order kinetic model:
\[
\ln(q_e - q_t) = \ln q_e - k_1t
\]

Second-order kinetic model:
\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \( q_e \) (mg/g) and \( q_t \) (mg/min) are the amounts adsorbed at equilibrium and at the time \( t \) (min), respectively; \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/mg/min) are the pseudo-first-order and pseudo-second-order constants, respectively.

From Figure 7b, it is observed that the kinetics of adsorption for different pollutants was best described by the pseudo-second-order kinetic model. The kinetic model parameters and the correlation coefficients are shown in Table 1. It could be found that the correlation coefficient of the second-order kinetic model was higher than that of the first-order kinetic model, and the maximum adsorption in the second-order kinetic model was matched well with the experimental data. It was indicated that the second-order kinetic model was more consistent with the adsorption process of the three pollutants and the adsorption rates of pollutants were controlled by chemical adsorption.

### Table 1. Kinetic Model Parameters for the Adsorption of Cr(VI), Rhodamine B, and Congo Red

| Pollutant | \( q_e \) (mg/g) | \( k_1 \) (min\(^{-1}\)) | \( R^2 \) | \( q_e \) (mg/g) | \( k_2 \) (g/mg/min) | \( R^2 \) |
|-----------|----------------|----------------|---------|----------------|----------------|---------|
| Cr(VI)    | 64.51          | 0.2378         | 0.9466  | 68.97          | 0.0027         | 0.9994  |
| Rhodamine B | 34.69          | 0.0850         | 0.9372  | 38.17          | 0.0027         | 0.9987  |
| Congo red | 240.33         | 0.0229         | 0.9496  | 285.71         | 0.0001         | 0.9927  |

2.3.3. Adsorption Isotherm. It is well known that the adsorption capacity is greatly affected by the concentration of the pollutants. The effect of the concentration on the adsorption of the composite for pollutants is shown in Figure 8. It could be found that the adsorption amount of pollutants enhanced with an increase in the initial concentration. And then, it tended to be a stable state after a certain concentration. The reason was mainly that the amplification of the concentration would facilitate the diffusion of pollutants to the surface of the adsorption material. Eventually, the adsorption of pollutants reached a saturated state at a certain concentration.

Three equilibrium isotherm models were used to describe the adsorption process successfully. The Langmuir isotherm model assumes that the adsorption takes place on a single molecular layer and there is no interaction between the adsorbate and the adsorbent. The Freundlich isotherm model is suitable for a heterogeneous multilayer adsorption process. The Tempkin isotherm shows that the increase of heat in the adsorption process is linear when the interaction between adsorbate and adsorbent is not considered, and it is appropriate for heterogeneous multilayer adsorption. The three isotherms are calculated by the following eqs 3–5, respectively:

**Langmuir isotherm:**
\[
\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{k_1 q_{max}}
\]

**Freundlich isotherm:**
\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

**Tempkin isotherm:**
\[
q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e
\]
where $C_e$ (mg/L) is the equilibrium concentration of the adsorbate in the solution; $K_L$ (L/mg) is the Langmuir constant related to the maximum adsorption capacity and the energy of adsorption; $q_{\text{max}}$ (mg/g) is the saturated adsorption capacity; $K_F$ is the Freundlich constant of the adsorption capacity; $1/n$ is a parameter related to the adsorption strength; $b$ (J/mol) is the heat of adsorption; and $A$ is the isothermal constant related to adsorption.

The adsorption isotherm parameters are shown in Table 2. It was observed that the Langmuir model was the best model to simulate the adsorption of the two dyes with the highest correlation coefficient among the three models. It was indicated that adsorbing the two dyes on the composite was a homogeneous adsorption covering a single surface, which was mainly a chemical adsorption process. The Tempkin model best matched the adsorption process of Cr(VI), which indicated that the adsorption heat and temperature of the composite presented a well linear relationship in the adsorption process. Moreover, the correlation coefficient in Langmuir reached 0.99, which is higher than that in Freundlich. This proved that the adsorption was mainly a chemical process and the surface of the composite had adsorption sites with homogeneous adsorption energy. Moreover, the Freundlich constant ($1/n$) represented the intensity of adsorption, which meant $0.1 < 1/n < 0.5$ was quite easy to adsorb; $0.5 < 1/n < 1$ was easy to adsorb; and $1/n > 1$ was difficult to adsorb. Hence, for Rhodamine B and Cr(VI), the values of $1/n$ were lower than 0.7, indicating the adsorption was easy. In addition, the adsorption of Congo red was the easiest with $1/n$ of 0.4053. Combined with the maximum adsorption amount in the adsorption process, it could be concluded that the composite had the best adsorption capacity on Congo red among the three pollutants.

### 2.4. Adsorption Mechanism

According to the above analysis, the adsorption mechanism of the composite on the Congo red, Rhodamine B, and Cr(VI) is proposed and shown as Scheme 2. It was clear that the electrostatic interaction between the protonated amino groups of the composite and the anions ($SO_3^-$) of the Congo red played a main role in Congo red adsorption. The adsorption mechanism of Rhodamine B by the composite was as follows: (i) electrostatic interaction between the anion group ($SO_3^-$) of the composite and the positively charged group of the Rhodamine B and (ii) the weak hydrogen bond between the carboxyl of Rhodamine B and methoxy group of the composite. Cr(VI) existed in the form of $HCrO_4^-$ under acidic conditions, which was adsorbed due to the electrostatic interaction between protonated amine and hydroxyl groups of the composite and the $HCrO_4^-$. Based on the above reactions, it could be seen that the type and number of adsorption sites in chitosan—lignosulfonate had increased significantly. It was indicated that the chitosan—lignosulfonate composite could be an excellent adsorbent for anionic and cationic dyes and metal ions.

### 3. CONCLUSIONS

In this work, the chitosan—lignosulfonate composite was successfully prepared by using a simple blending method. It was found that the composite was cross-linked by weak hydrogen bond and electrostatic interaction. Functional groups, hydrogen bonds, and electrostatic interactions in composites enhanced surface and chemical properties of the composite than chitosan and sodium lignosulfonate. The results showed that the mass ratio of chitosan to sodium lignosulfonate, the initial concentration of pollutants, and the contact time had great effects on the adsorption capacity of the composite. Moreover, it revealed that the pseudo-second-order kinetic model was matched well with the adsorption kinetics of pollutants on the composite and the adsorption isotherm could be fitted well with the Langmuir model. In addition, the mechanism of adsorption was presented by analyzing the surface characterization of the composite, which were electrostatic interaction and weak hydrogen bond between the composite and the pollutants. The composite could adsorb both anionic and cationic dyes and had an excellent adsorption capacity for Cr(VI). Therefore, the study of sodium chitosan—lignosulfonate composite has potential value in sewage treatment.

### 4. MATERIALS AND METHODS

#### 4.1. Materials

Sodium lignosulfonate ($C_{20}H_{24}Na_2O_3S_2$, MW 534.51 g/mol, 96%), chitosan ($C_{\text{ch}}H_{11}NO_\text{deac} 95\%$ deacetylated, viscosity 100–200 mPa s), Rhodamine B...
(C₂H₃ClN₃O₆, MW 479.01 g/mol, AR), and Congo red (C₃H₇N₂Na₂O₃S₂, MW 696.66 g/mol, BS) were obtained from Shanghai Macklin Biochemical Co., Ltd. Potassium dichromate (K₂Cr₂O₇, MW 294.18 g/mol, GR) was provided by Sinopharm Chemical Reagent Co., Ltd. Acetic acid (CH₃COOH, MW 60.05 g/mol, AR) was purchased from Beijing Chemical Works. In addition, all other solutions were prepared by distilled water. All chemicals in the experiments were used without further purification.

4.2. Preparation of Chitosan–Lignosulfonate Composite. A certain quantity of sodium lignosulfonate was added to 30 mL of distilled water and stirred well. Chitosan was dissolved in 30 mL of aqueous acetic acid (1% v/v). The sodium lignosulfonate solution was dropped into chitosan solution and stirred for 1 h. Subsequently, the composite was vacuum filtered and then dried at room temperature for 48 h. Finally, the composite was ground into powder. The mass ratios of lignosulfonate to chitosan were 10:1, 10:2, 10:3, 10:4, 10:5, 10:6, 10:7, 10:8, 10:9, and 1:1. To establish the adsorption models of the composite, a further experiment of the composite (10:3) was conducted.

4.3. Characterization. Fourier transform infrared spectroscopy (FT-IR) analysis was taken on a Spectrum 100 (PerkinElmer, England) FT-IR spectrometer in the range of 4000–400 cm⁻¹ using KBr disk method. Thermalgravimetric analysis (TGA) was carried on a TGA2050 analyzer (TA Instruments Ltd.) from 25 to 800 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. The morphologies and structures of the composite, chitosan, and sodium lignosulfonate were characterized by a JSM-6700F (JEOL Ltd., Japan) field-emission scanning electron microscope. An UV–S1000 (Metash Instruments Ltd., China) spectrophotometer was utilized for measuring the adsorption capacity of pollutants. Energy-dispersive X-ray analyses (EDAX) of the composites and pollutant-adsorbed composites were performed by JEOL JSM-7610F field-emission scanning electron microscope.

4.4. Adsorption Experiment. Effect of mass ratio: 20 mL of 100 mg/L Cr(VI) solution was mixed with 0.02 g composites of different mass ratios and then shocked at 25 °C for 24 h at 150 rpm. Rhodamine B solution (100 mg/L) and Congo red solution (1 g/L) were also subjected to same adsorption experiments as described above.

Effect of pH: the initial pH value of the solution was adjusted using 1 mol/L HCl and 1 mol/L NaOH. Twenty milliliters of pollutant solution with different pH values was mixed with 0.02 g of composites and shocked at 25 °C for 24 h at 150 rpm.

Adsorption kinetics: the kinetic studies were conducted through adding 0.02 g of composite (10:3) into 20 mL of pollutant solutions including Cr(VI) solution (100 mg/L), Rhodamine B solution (100 mg/L), and Congo red solution (1 g/L). Afterward, the solution was shaken at 25 °C, 150 rpm, and different time intervals of 5–300 min.

Adsorption isotherms: the isotherm experiments were carried out via putting 0.02 g of composite (10:3) in 20 mL of Cr(VI) solution, Rhodamine B solution, and Congo red solution with different concentrations from 200 to 350, 100–400, and 550–950 mg/L, respectively. Subsequently, the adsorption solution was dispersed at 25 °C for 24 h at 150 rpm.

The pH of Cr(VI) solution was adjusted to 2. Also, the concentration of the pollutant solution was determined by a UV–vis spectrophotometer. Cr(VI) concentration was measured at 540 nm using 1,5-diphenyl carbazide as the complexing agent. The concentrations of Rhodamine B and Congo red were measured in absorbance of the peaks at 554 and 497 nm, respectively. The adsorption capacity (qₑ) was calculated by the following equation

\[ q_e = \frac{(C_0 - C_e) \times V}{W} \]  

where \( C_0 \) (mg/L) and \( C_e \) (mg/L) are the initial concentration and the equilibrium concentration after adsorption, respectively; \( W \) (mg) is the dosage of the composite; and \( V \) (L) is the volume of the solution.

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**Notes**

The authors declare no competing financial interest.

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