Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1060904

57 (2016) 14060–14066
June

Taylor & Francis
Taylor & Francis Group

Adsorption removal of Congo red by epichlorohydrin-modified cross-linked chitosan adsorbent

Chunguang Li*, Jiehu Cui, Fan Wang, Weigong Peng, Yanhong He

Key Laboratory of Environment Functional Materials, Zhengzhou Institute of Aeronautical Industry Management, Zhengzhou 450015, China, emails: hycgli@126.com (C. Li), cuijiehu@163.com (J. Cui), faye91@163.com (F. Wang), zziapwg@163.com (W. Peng), hyh@zzia.edu.cn (Y. He)

Received 12 December 2014; Accepted 6 June 2015

ABSTRACT

A new cross-linked chitosan-based adsorbent was prepared by the cross-linked reaction between chitosan and epichlorohydrin under alkaline conditions. The chemical structure of this new adsorbent was characterized by infrared spectra analysis. The static adsorption using Congo red solution as simulated dye wastewater was investigated. The results suggested that there was an increased surface roughness and granular material on the cross-linked chitosan adsorbent surface and that the adsorption capacity of the modified chitosan adsorbents was higher than the parent chitosan. It was found out that adsorption behavior match well with Freundlich isotherm and pseudo-second-order kinetic models. The optimal conditions about the adsorption of Congo red are as follow: The dosage of modified chitosan was 30 mg/25 mL, the pH was 4, the time was 120 min, and the temperature was 40℃.

Keywords: Chitosan; Congo red; Modify; Adsorption; Epichlorohydrin

Nowadays, removal of various pollutants such as heavy metals and dyes from industrial effluents has become a critical issue due to strict environmental regulations. In particular, the dyes wastewater such as Congo red has adverse effects on human health and environment because of big quantity, complicated composition, deep chroma, high pH changes, high concentration of organics and inorganic salt, and difficult to biodegrade [1].

The adsorption method has received increasing attention due to its merits, for example easy to operate, low investment cost, and good removal effect. In recent years, many materials of biological origin such as chitosan and modified chitosan have been used as adsorbents to remove pollutants from industrial effluents. Chitosan is a natural biopolymer and has the adsorption ability, so it has a good application because of its abundant resources, good adsorbability and biocompatibility, easily biodegradable etc. [2]. However, the amino of chitosan molecule easily combined with H^+ in acid solution, which may result in the loss of adsorbent and limit the application of the chitosan.

Therefore, various physical and chemical modifications have been adopted to improve the chemical stability and adsorption ability [3–5]. Some researchers suggested that chemical modification of chitosan can enhance its stability in acid medium and improve the adsorption properties. Chitosan can be cross-linked in intramolecular or intermolecular with the difunctional aldehyde, acid anhydrides, and epoxides. Then, the insoluble cross-linked products were obtained. Although the adsorption ability of epichlorohydrin

---

*Corresponding author.

cross-linked chitosan has reported the removal of the heavy metal ion [6–14], the research of removal of Congo red wastewater was less. In this study, chemical modification was applied on chitosan by cross-linking the chitosan with epichlorohydrin. The chemical structure of this new adsorbent was characterized by infrared spectra analysis and scanning electron microscopy. Removal of Congo red from aqueous solutions was studied under static conditions using cross-linked chitosan.

1. Experiment

1.1. Materials

All reagents used in this work were of analytic grade. Chitosan, Congo red, and epichlorohydrin were purchased from Sinopharm Chemical Reagent Co. Ltd. Other chemicals were purchased from Xi'an Chemical Reagent Factory.

The surface morphology of the absorbent was visualized by field-emission scanning electron microscope (SEM) (S-8400, Japan). Fourier transform infrared spectroscopy (FTIR) of the samples was taken using an Avatar-360 IR spectrometer from Nicolet in the wave number range of 400–4,000 cm^{-1}. The pH value of tested solution was adjusted by adding 0.1 M HCl or NaOH solutions. The aqueous samples were analyzed for the Congo red concentration with a UV-250 spectrophotometer (Shimadzu, Japan) at 496 nm.

1.2. Preparation of modified chitosan adsorbent

Chitosan powder (12 g) was dissolved in 400 mL 2% aqueous acetic acid solution under constant stirring, and then, 12 mL epichlorohydrin was added in chitosan solution and the pH of this mixture was adjusted to 8–9 with appropriate amount of NaOH. After this reaction mixture was maintained for 15 h, the pH of this reaction mixture was adjusted to 7 with dilute HCl, and then, the solid was filtered and was washed with water and acetone. After drying, the grinded adsorbent was obtained using 200-mesh sieve, and then, the epichlorohydrin-modified cross-linked chitosan adsorbent was produced.

1.3. Infrared spectrum analysis

IR spectra (KBr disk, 400−4,000 cm^{-1}) were recorded on a Perkin–Elmer Model 1320 spectrometer. IR spectra were collected as follows: a small amount of chitosan and cross-linked chitosan adsorbents samples were taken and grinded into powder in agate mortar, respectively. Then, KBr was added and grinded for 15 min and pressed into a transparent sheet using bead machine. The sheets were analyzed by the infrared spectrometer.

1.4. Scanning electron microscopy observations

The surface morphology of the absorbent was visualized by field-emission SEM. Chitosan and cross-linked chitosan adsorbents samples were coated with gold before analysis. Under the 2 kV accelerating voltage, the overall shape of particles were observed by SEM.

1.5. Adsorption equilibrium experiments

A 25 mL solution containing 40 mg/L Congo red was put in the conical flasks and the pH of the solution was adjusted to 2–9; then, 10–200 mg adsorbents were added into the solution. The conical flasks were oscillated at a certain rate for 5–150 min under the temperature (15–60℃). Last, it was centrifugal separated for 5 min at a speed of 3,000 r/min. The absorbance of supernatant fluid was measured at 496 nm using UV-250 spectrophotometer. The amount of Congo red adsorbed per unit mass of was calculated using the mass balance equation given in Eq. (1).

$$q_\text{e} = \frac{(C_0 - C_\text{e})V}{m} \tag{1}$$

where q_e is adsorption capacity in mg/g at equilibrium time, C_0 is initial concentration of Congo red in mg/L, C_e is equilibrium concentration in mg/L, V is total volume of solution in L, and m is adsorbent dosage in g.

1.6. Adsorption removal detection

The adsorption rate was calculated by absorption intensity at 496 nm as the Eq. (2).

$$D = \frac{A_0 - A_\text{e}}{A_0} \times 100\% \tag{2}$$

where D is the percentage removal of the adsorbate, A_0 is the absorbance value of initial concentration of Congo red, and A_e is the absorbance value of equilibrium concentration of Congo red.

1.7. Adsorption isotherms

The sorption isotherm experiments were performed in flasks containing 25 mL of 30 mg cross-linked chitosan adsorbent and Congo red with initial concentrations varying from 50 to 100 mg/L at pH 6.0 for 120 min at 30℃. Langmuir and Freundlich sorption isotherm models were used to determine the proper isotherm for Congo red adsorption by cross-linked chitosan adsorbent. The Langmuir isotherm is based on the assumption of monolayer on the adsorbent surface. The linear form of the Langmuir equation is as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of the solute in the bulk solution (mg/L), q_m is the maximum adsorption capacity (mg/g), and K_L is the Langmuir constant related to affinity of binding sites (L/mg).

The Freundlich isotherm describes a heterogeneous system and reversible adsorption, is not restricted to monolayer formation, and is expressed as follows:

$$\ln\ q_e = \ln\ k + \frac{1}{n}\ \ln\ C_e \tag{4}$$

where k and n are constant values related to adsorption capacity and adsorption intensity, respectively.

1.8. Adsorption kinetics

The effect of contact time on the adsorption of Congo red by cross-linked chitosan adsorbent was performed in flasks containing 25 mL of 40 mg/L at initial concentrations Congo red and 30 mg cross-linked chitosan adsorbent at pH 6.0. The samples were taken from different flasks at predetermined time intervals (from 10 to 60 min). To examine adsorption kinetics mechanisms, two kinetics models including the pseudo-first-order model and the pseudo-second-order model were used to fit the experimental data.

The pseudo-first-order kinetic model is expressed as follows:

$$\ln(q_e - q_t) = \ln\ q_e - k_1 t \tag{5}$$

The pseudo-second-order kinetic model is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where q_t is the adsorption capacity (at time t) and k_1 and k_2 are the rate constants of first- and second-order kinetics models, in min^{-1} and $\text{g/mg}^{-1}\ \text{min}^{-1}$, respectively.

2. Results and discussion

2.1. FTIR analysis of modified chitosan adsorbent

The IR spectra of the chitosan (a) and the modified chitosan (b) adsorbents show absorption bands in the 4,000–400 cm^{-1} region (Fig. 1(a) and (b)). As shown in Fig. 1, there is difference between the spectrum of modified chitosan adsorbent (b) and the characteristic adsorption peaks of chitosan (a). It is obvious that a wide and strong adsorption peak at 3,410 cm^{-1} assigned to the –OH stretching vibration absorption peak appeared, while it was shifted to lower wavenumber which indicated that the hydroxyl groups of chitosan molecules were involved in the cross-linking reaction. It can be seen that the adsorption peak of secondary hydroxyl group (C_3–OH) on chitosan molecules at 1,080 cm^{-1} has also shifted which showed that the secondary hydroxyl group (C_3–OH) of chitosan molecules had reacted with epichlorohydrin. The adsorption peak at 1,640 cm^{-1} is assigned to $–NH_2$ and shifted to lower wavenumber which indicated that $–NH_2$ of chitosan has participated in the reaction. From the analysis of IR spectrum, it can be confirmed that cross-linked chitosan-based adsorbent was prepared by the cross-linked reaction between chitosan and epichlorohydrin under alkaline conditions.

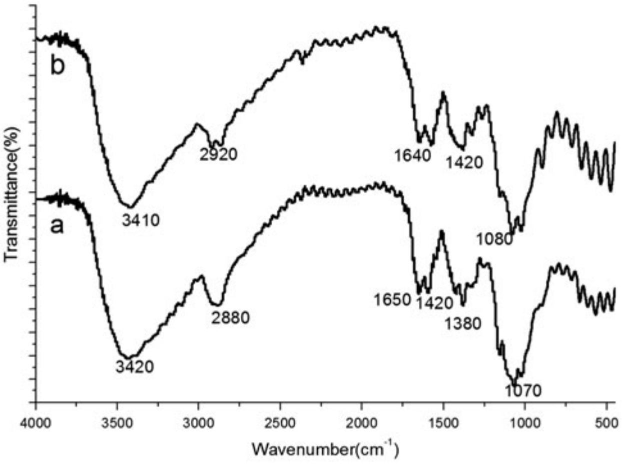

Fig. 1. The FTIR spectra of chitosan (a) and modified chitosan adsorbents (b).

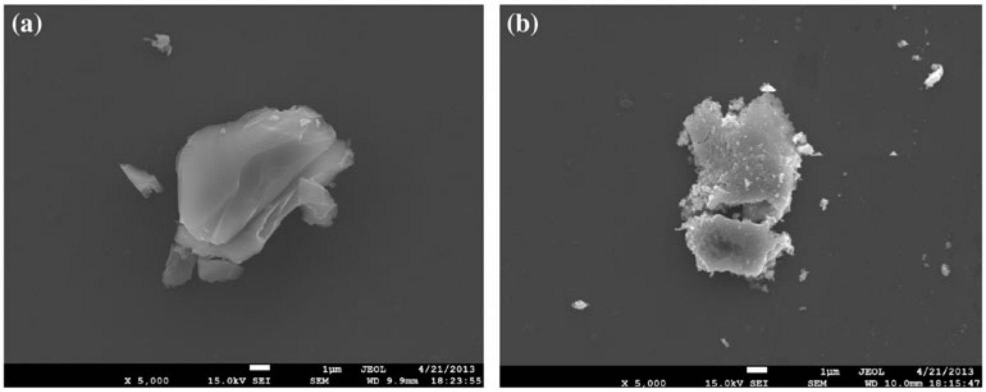

Fig. 2. SEM image of chitosan (a) and modified chitosan adsorbents (b).

2.2. SEM analysis of modified chitosan adsorbents

The overall morphology and surface structure of chitosan and cross-linked chitosan adsorbents was observed, respectively, by SEM. As can be shown in Fig. 2, the surface of chitosan was smooth, while the surface of cross-linked chitosan adsorbent was very rough. There were many particles in the surface of cross-linked chitosan adsorbent which demonstrated that cross-linked chitosan adsorbent is a suitable new sorbent of dyes.

2.3. Adsorption capacity of modified chitosan adsorbent

The adsorption capacity of chitosan and modified chitosan adsorbent was investigated at pH 6.0, with temperature at 30℃, the contact time of 120 min, and 30 mg of adsorbents. As shown in Fig. 3, it was obvious that the adsorption capacity increased with the increase of Congo red concentration. At the same concentration of Congo red, the adsorption capacity of modified chitosan adsorbent was better than that of chitosan, which is in agreement with the results of SEM analysis. Based on the reported Ref. [15] and above results, modified chitosan adsorbent is a good candidate adsorbent for Congo red among AC, bentonit, activated clay, and spirulina powder.

2.4. Adsorption technology of modified chitosan adsorbent

2.4.1. Effect of modified chitosan adsorbent dosage

The optimum dosage of modified chitosan adsorbent to achieve the highest adsorption capacity was determined at pH 6.0, with temperature at 30℃, the contact time of 120 min, and at an initial Congo red concentration of 40 mg/L. From Fig. 4, it was shown that adsorption rate of congo red enhanced with the increase of dosage, but then, it decreased. The decrease in adsorption capacity with increase in the sorbent dosage is because the aggregation of sorbent under high concentration reduced the specific surface area for adsorption of Congo red, which resulted in above phenomenon. When the dosage of modified chitosan adsorbent was 30 mg, the adsorption effect was best and it attained equilibrium.

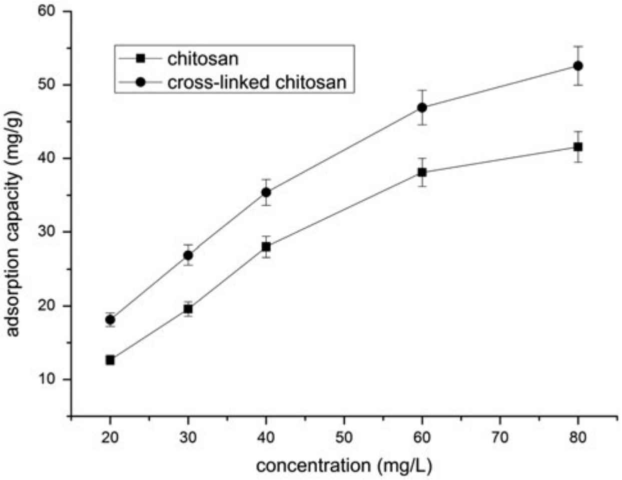

Fig. 3. Adsorption properties of modified chitosan adsorbents. Dose of adsorbent = 30 mg/25 mL; temperature of CR soln. = 30℃; volume of solution = 25 mL; pH of solution of CR = 6; shaking time = 120 min; RPM of shaker = 120.

2.4.2. Effect of time

After fixing the pH at 6.0, temperature at 30℃, and sorbent dosage at 30 mg, the effect of contact time on adsorption capacity of modified chitosan adsorbent was investigated and the result is shown in Fig. 5.

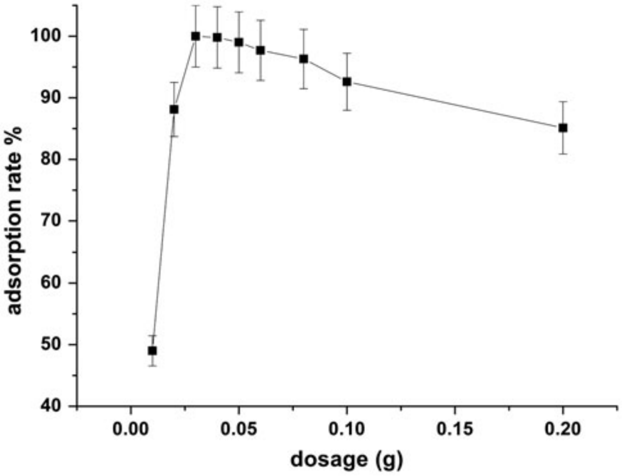

Fig. 4. Effect of modified chitosan dosage on adsorption of CR. Amount of CR = 40 mg/L; temperature of CR soln. = 30℃; volume of solution = 25 mL; pH of solution of CR = 6; shaking time = 120 min; RPM of shaker = 120.

It could be found that the adsorption rate gradually increased with the increase of the adsorption time which induces a fast diffusion of Congo red from bulk to the adsorbent. When the time is 120 min, the adsorption rate reached the maximum, but then, it decreased.

2.4.3. *Effect of temperature*

Under different temperature, the effect of temperature on adsorption capacity was studied for 120 min at pH 6.0 and 30 mg of adsorbents using an initial concentration of Congo red as 40 mg/L, and the results are shown in Fig. 6. The adsorption rate increased along with the rise of temperature. The dye adsorption rate range was observed among 30–50℃, and there was a maximum peak at 40℃.

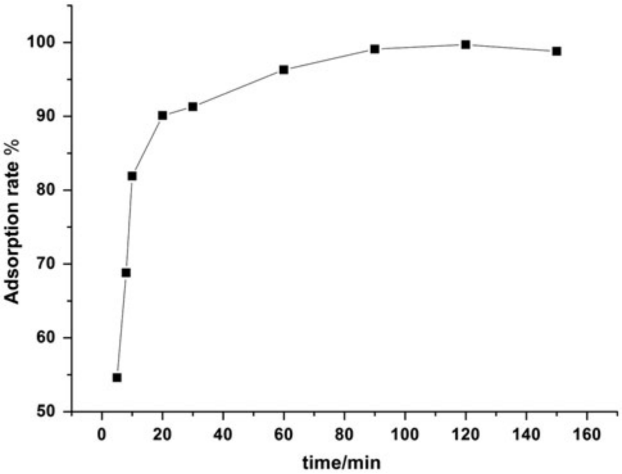

Fig. 5. Effect of time on adsorption of CR. Amount of CR = 40 mg/L; temperature of CR soln. = 30℃; dose of adsorbent = 30 mg/25 mL; volume of solution = 25 mL; pH of solution of CR = 6; RPM of shaker = 120.

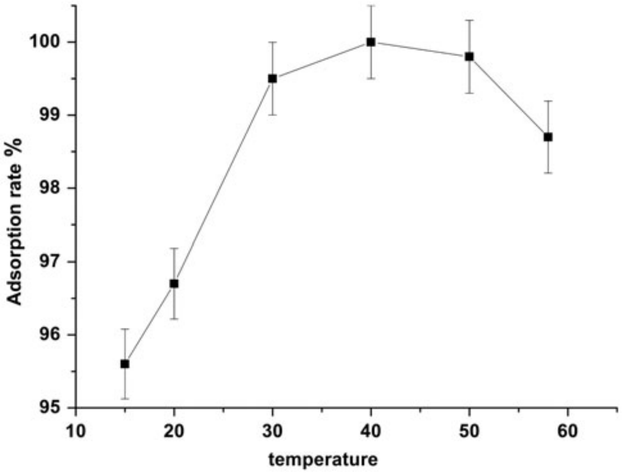

Fig. 6. Effect of temperature on adsorption of CR. Amount of CR = 40 mg/L; dose of adsorbent = 30 mg/25 mL; volume of solution = 25 mL; shaking time = 120 min; pH of solution of CR = 6; RPM of shaker = 120.

2.4.4. *Effect of pH*

Effect of initial pH was studied by varying solution pH from 2 to 9 for 120 min at 30℃ and 30 mg adsorbent using an initial concentration of Congo red as 40 mg/L. As shown in Fig. 7, when pH was 2, the adsorption rate was relatively low. The adsorption rate sharply increased when the value range of pH is between 2 and 3. While the dye adsorption rate was little change in the acidic range of 3–7, the adsorption rate achieves maximum when pH was 4. Decolorization rate decreased obviously when the pH value increased over 7, which may be due to the electrostatic repulsion between Congo red and the negatively charged surface of the adsorbent. In addition, the reason is the attraction between the protonated amine and the negatively charged surface of the adsorbent because of the zwitterionic molecule at low pH [16].

2.4.5. *Adsorption Isotherm*

The experimental data fitted to Langmuir and Freundlich isotherm equations are shown in Fig. 8. The values of Langmuir and the Freundlich parameters were obtained from the slope and the intercept of

Fig. 8. As can be understood from the correlation factor, the Langmuir isotherm model ($R^2 = 0.9907$) fits the equilibrium data better than the Freundlich model ($R^2 = 0.9528$), which indicates that the Langmuir isotherm model can represent the adsorption process than Freundlich isotherm model and explain monolayer adsorption nature of the adsorption surface on the modified chitosan adsorbent.

2.4.6. Adsorption kinetics

To examine the controlling mechanism of the adsorption process, adsorption kinetic studies were performed for modified chitosan. The adsorption rate constants (k_1 and k_2) and the amount of adsorption in equilibrium were calculated using the slope and the intercept of plots of $\log(q_e - q_t)$ vs. t (Fig. 9(a)) and t/q_t vs. t (Fig. 9(b)) for the pseudo-first-order and the pseudo-second-order reactions, respectively. The

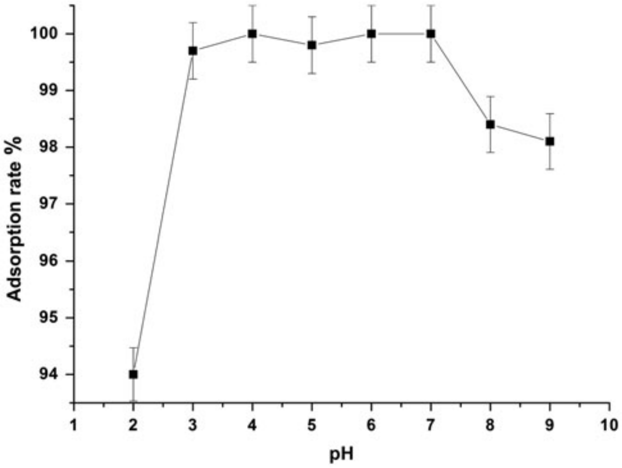

Fig. 7. Effect of pH on adsorption of CR. Amount of CR = 40 mg/L; dose of adsorbent = 30 mg/25 mL; volume of solution = 25 mL; temperature of CR soln. = 30℃; shaking time = 120 min; RPM of shaker = 120.

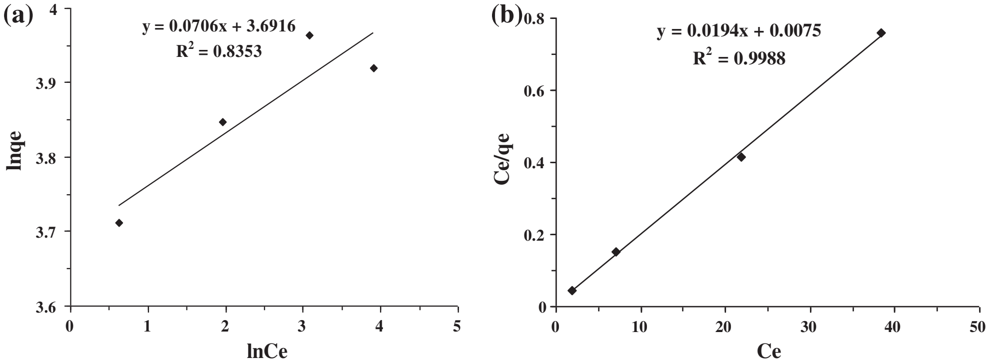

Fig. 8. Isotherm plots for Congo red adsorption: (a) Freundlich plot, and (b) Langmuir plot. Adsorption conditions: adsorbent dosage: 30 mg/25 mL; initial Congo red concentration 50–100 mg/L; temperature: 30 ℃; contact time: 120 min; RPM of shaker = 120.

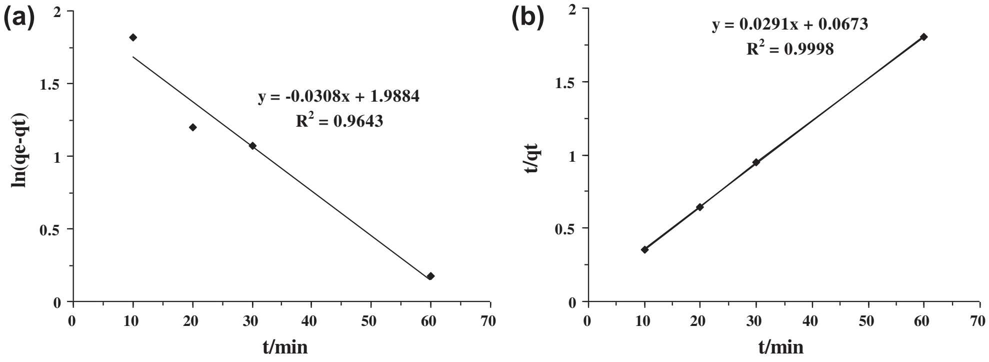

Fig. 9. Kinetic plots for Congo red adsorption：(a) the pseudo-first-order kinetics plot, and (b) the pseudo-second-order kinetics plot. Adsorption conditions: adsorbent dosage: 30 mg/25 mL; initial Congo red concentration: 40 mg/L; temperature: 30℃; contact time: 10–60 min; RPM of shaker = 120.

constants and correlation coefficient are presented in Fig. 9(a) and (b). From Fig. 9(a) and (b), it is observed that the pseudo-second-order kinetics model ($R^2 = 0.9998$) fits the experimental data better than the pseudo-first-order kinetics model ($R^2 = 0.9643$), which supports that adsorption is due to chemisorption involving valence forces through sharing or exchanging of electrons [17].

3. Conclusions

In this study, a new cross-linked chitosan-based adsorbent was prepared. The FTIR analysis results showed that chitosan molecules had cross-linked with epichlorohydrin. The surface of modified chitosan was very rough which can increase its specific surface area by SEM observation. The Freundlich model fits the equilibrium data better than the Langmuir model. Adsorption mechanism was analyzed using two kinetic models to fit the experimental data. The pseudo-second-order kinetics model fits the experimental data better than the pseudo-first-order kinetic model. The best condition of the adsorption rate of Congo red by modified chitosan adsorbent is as follows: the dosage of modified chitosan adsorbent was 30 mg/25 mL, the pH was 4, the time was 120 min, and the temperature was 40℃.

Acknowledgment

This work was financially supported by the Henan province basis and advancing technology research project (102300410130).

References

[1] P. Miretzky, A.F. Cirelli, Hg(II) removal from water by chitosan and chitosan derivatives: A review, J. Hazard. Mater. 167 (2009) 10–23.
[2] M. Chander, D.S. Arora, Evaluation of some white-rot fungi for their potential to decolourise industrial dyes, Dyes Pigm. 72 (2007) 192–198.
[3] Y. Xing, Modification of Chitosan and Investigation of its Adsorption Behavior for Heavy Metal Ions and Dyes, PhD Thesis, Wuhan University, China, 2009.
[4] G.H. Wang, J. Luo, X.G. Wang, R. Yu, N.S. Deng, Study on adsorption of azo dye acid red B onto cross-linked chitosan, Speciality Petrochem. (In Chinese) 2 (2010) 46–48.
[5] H. Xu, Y.Q. Wu, Y. Liu, Research on adsorption characteristic of novel chitosan material to Pb(II) in groundwater, Equip. Environ. Eng. (In Chinese) 5 (2010) 42–45.
[6] B. Kannamba, K.L. Reddy, B.V. AppaRao, Removal of Cu(II) from aqueous solutions using chemically modified chitosan, J. Hazard Mater. 175 (2010) 939–948.
[7] Z.J. Wu, S.Y. Li, J.F. Wan, Y. Wang, Cr(VI) adsorption on an improved synthesised cross-linked chitosan resin, J. Mol. Liq. 170 (2012) 25–29.
[8] M. Vakili, M. Rafatullah, B. Salamatinia, A.Z. Abdullah, M.H. Ibrahim, K.B. Tan, Z. Gholami, P. Amouzgar, Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: A review, Carbohydr. Polym. 113 (2014) 115–130.
[9] R. Laus, T.G. Costa, B. Szpoganicz, V.T. Fávere, Adsorption and desorption of Cu(II), Cd(II) and Pb(II) ions using chitosan crosslinked with epichlorohydrin-triphosphate as the adsorbent, J. Hazard. Mater. 183 (2010) 233–241.
[10] V. Nair, A. Panigrahy, R. Vinu, Development of novel chitosan–lignin composites for adsorption of dyes and metal ions from wastewater, Chem. Eng. J. 254 (2014) 491–502.
[11] S. Zarghami, T. Mohammadi, M. Kazemimoghadam, Adsorption behavior of Cu(II) ions on crosslinked chitosan/polyvinyl alcohol ion imprinted membrane, J. Dispersion Sci. Technol. 36 (2015) 190–195.
[12] R.H. Huang, B.C. Yang, Q. Liu, Y.P. Liu, Simultaneous adsorption of aniline and Cr(VI) ion by activated carbon/chitosan composite, J. Appl. Polym. Sci. 131 (2014) 39903.
[13] L. Zhang, J.Q. Xue, X.W. Zhou, X. Fei, Y. Wang, Y.Z. Zhou, L.L. Zhong, X.L. Han, Adsorption of molybdate on molybdate-imprinted chitosan/triethanolamine gel beads, Carbohydr. Polym. 114 (2014) 514–520.
[14] A.H. Chen, S.C. Liu, C.Y. Chen, C.Y. Chen, Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin, J. Hazard. Mater. 154 (2008) 184–191.
[15] Z. Cheng, L. Zhang, X. Guo, X. Jiang, T. Li, Adsorption behavior of direct red 80 and congo red onto activated carbon/surfactant: Process optimization, kinetics and equilibrium, Spectrochim. Acta A Mol. Biomol. Spectrosc. 137 (2015) 1126–1143.
[16] V. Vimonses, S.M. Lei, B. Jin, C.W.K. Chow, C. Saint, Adsorption of congo red by three Australian kaolins, Appl. Clay Sci. 43 (2009) 465–472.
[17] V. Nair, A. Panigrahy, R. Vinu, Development of novel chitosan–lignin composites for adsorption of dyes and metal ions from wastewater, Chem. Eng. J. 254 (2014) 491–502.