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Adsorption of Cr(VI) from aqueous solution by chemically modified natural cellulose

Hongxiang Zhu[a], Qiaoping Kong[a], Xuejuan Cao[a], Hui He[d], Jin Wang[b,*], Yucai He[c]

[a]*College of Light Industry and Food Engineering, Guangxi University, Nanning 530004, China, emails: zhx@gxu.edu.cn (H. Zhu), gxukqp@163.com (Q. Kong), 362594959@qq.com (X. Cao)*
[b]*College of Agriculture and Biology, Shanghai Jiao Tong University, Shanghai 200240, China, Tel./Fax: +86 21 34208042; email: wangjin100@sjtu.edu.cn (J. Wang)*
[c]*College of Pharmaceutical Engineering and Life Sciences, Changzhou University, Changzhou 213164, China, email: heyucai2001@163.com*
[d]*PCFM Lab, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China, email: guizhouhehui@163.com*

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ABSTRACT

The paper researched a novel chelating material made from natural cellulose pretreated with plasma (150 V, 120 s) for the adsorption of heavy metal ions from aqueous solutions. The first section of this paper details our study on the chemical modification of bamboo fibers pretreated with plasma containing epichlorohydrin, diethylenetriamine, and carbon disulfide. Under optimum conditions, the capacity of the bamboo adsorption material prepared with plasma to adsorb Cr(VI) ions was 32.4 mg/g. The treated materials were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), and energy-dispersive X-ray spectroscopy (EDAX). The second section of this paper tests the adsorption capacity of the bamboo material with Cr(VI) ions in an aqueous solution by the classic titration method. The Langmuir adsorption isotherm and Freundlich adsorption isotherm models both provided a good fit to the data. A kinetic study showed that the absorption of Cr(VI) ions onto the modified bamboo fibers could be adequately described by a pseudo-second-order kinetics model ($R^2 = 0.9941$). The model of solid–liquid adsorption in the adsorption process was provided.

Keywords: Bamboo fibers; Plasma; Cr(VI); Adsorption kinetics; Heavy metal remediation

1. Introduction

Chromium is considered one of the most toxic pollutants in nature [1]. A variety of physicochemical treatment technologies have been applied in the removal of Cr(VI), including flotation, adsorption, ion exchange, chemical precipitation, membrane separation, electrochemical, oxidation/reduction, ultrafiltration, and others [2]. Among the various methods available for water treatment, adsorption is believed to be an effective and economical method because of its low impact on the environment and high potential for chemical recovery and water purification. Various materials, including Mg/Fe hydrotalcites-like compounds [3], TiO_2-MCM-41 [4], manganese nodule

*Corresponding author.

leached residue [5], have been reported for adsorption of Cr(VI).

For the past few years, the use of natural cellulose [6] to prepare high value-added functional polymers has attracted much attention. Many agricultural and agroindustrial by-products, such as cotton fiber [7], sugarcane bagasse cellulose [8], sawdust [9], peanut shells [10], and tree bark [11], have been studied for their potential to remove heavy metal ions. Bamboo is a fast-growing and renewable resource and is widely available in Guangxi, China. Lu et al. [12] reported that when bamboo and rice straw biochar were added to naturally contaminated paddy soil, they were able to reduce Cd, Cu, Pb, and Zn concentrations. This study mainly focused on the biochar preparation process, instead of describing the adsorption process. OuYang et al. [13] prepared a new porous succinylated bioadsorbent from bamboo through partial enzymatic hydrolysis. The adsorption of Pb(II) could be accurately fitted to a pseudo-second-order kinetics model. In addition, the adsorption revealed an ion exchange mechanism.

The use of natural cellulose is very wide, especially after chemical modification as adsorbents for the removal of heavy metals from polluted water. Zhong et al. [14] modified wheat straw with epichlorohydrin, ethylenediamide, and triethylamine to form cellulose ether and introduce amine groups. Kinetic data and sorption equilibrium isotherms revealed the complexation and/or electrostatic attraction mechanisms. Functionalized nanocellulose was proved to be a kind of efficient adsorbent for Cr^{6+}. Kiran Singh et al. [15] modified nanocellulose by succination and amination. Except for the good adsorption for Cr(III) and Cr(VI), the sorption capacity of the regenerated biomass was quite satisfied as well. Amine groups played an important role in adsorption process, but the adsorption mechanism was not provided. Extracted cellulose grafted with acrylonitrile monomer was proved to have an acceptable performance for Cr(VI) removal. The adsorption process could be best described by second-order equation. Li et al. [16] prepared a kind of cellulose microsphere (CMS) adsorbent by radiation-induced grafting of dimethylamino ethylmethacrylate (DMAEMA) onto CMS followed by a protonation process. However, this research finished without deeper mechanistic discussion.

Although there have been many studies on cellulose-based heavy metal adsorption, the mechanism of this process has not been fully discussed. We prepared a bamboo cellulose material for Cr(VI) adsorption. The cellulose was prepared by using plasma, epoxidation, amination, and ultrasonic enhancement sulfonation reactions to graft N and S groups. Researchers reported that plasma treatments decomposed the cellulose material by the formation of highly functionalized molecules [17]. The crystal morphology of the bamboo fibers before and after modifications was characterized by XRD and EDAX spectroscopy. The Cr(VI) adsorption properties of the bamboo cellulose material was tested and the adsorption process was described by Langmuir [18] and Freundlich [19] adsorption isotherm models. We conclude with a discussion of the general mechanism of solid–liquid adsorption during the adsorption process.

2. Materials and methods

2.1. Adsorbent material

The bamboo was obtained from Guangxi, China and was cut into 1- to 3 cm-long disks with a knife. Purified bamboo fibers were obtained using the methods of Wang et al. [20], which are briefly described here. The bamboo pieces were ground and sieved (Bertel sieve, 40–60 mesh) and dried in a cabinet oven with air circulation at 60°C for 16 h. Finally, the ground bamboo was mixed with a 2:1 (v/v) acetone/ethanol solution in a Soxhlet apparatus for 6 h to remove fats, waxes, and oils.

Five grams of bamboo fiber was immersed in 2% NaOH for 10 min, and the moisture content was controlled at 60%. The mixture was then pretreated with plasma for 120 s with a plasma voltage of 150 V and vacuum of 160 Pa.

2.2. Synthesis of chelating bamboo fibers

The synthetic chelating reaction was accomplished with the following steps and is described in Fig. 1.

2.3. Epoxidation reaction

A volume of 200 mL of 10% NaOH solution and 5 g of plasma-pretreated bamboo fibers were added to

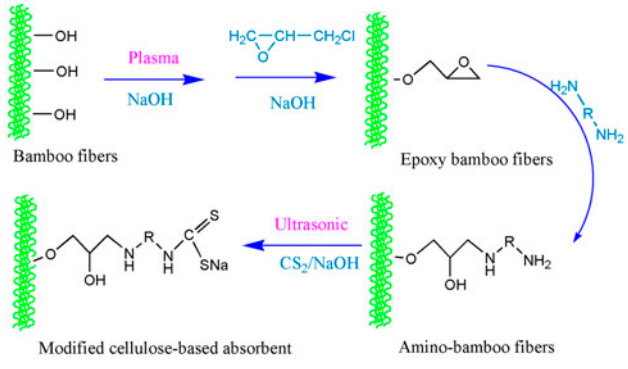

Fig. 1. Preparation procedure of treated bamboo fiber.

a 250 mL three-stoppered flask. Then, the mixture was vigorously shaken for 15 min before an epichlorohydrin (ECH) solution (15 mL) was added. The reaction continued for 150 min at 50℃. The grafted bamboo fibers (epoxy fibers) were then removed from the reaction medium, washed with deionized water, and dried at 60℃ for 4 h. Finally, epoxy bamboo fibers with an epoxy value of 7.3 mmol/g were obtained.

2.4. Amination reaction

First, 5 g of the epoxy bamboo fibers was treated with 200 mL of 3% NaOH solution and the mixture was vigorously shaken for 15 min. Diethylenetriamine (DETA) solution (7 g) was added and shaken for 120 min at 70℃. The modified amino-bamboo fibers were then removed from the mixture and washed with deionized water, ethanol, 1% HCl, and 1% NaOH and dried at 60℃ for 4 h. The zeta potential of the final amino-bamboo fibers was 30.4 mV.

2.5. Ultrasonic enhancement sulfonation reaction

The modified amino-bamboo fibers were then treated with an ultrasonic sulfonation reaction as follows: the fibers were placed in 5 mL of CS_2 and 14% alkali solution for 60 min at 25℃ and exposed to 200 W of ultrasonic energy. Then, the mixture was washed with deionized water, ethanol, 1% HCl, and 1% NaOH and then dried at 60℃ for 4 h. The product was a cellulose-based heavy metal adsorption material and its adsorption capacity of Cr(VI) was 32.4 mg/g adsorbance.

2.6. Adsorption measurement of Cr(VI)

Table 1 shows the comparison of a maximum adsorption capacities of Cr(VI) with various adsorbents. The adsorption of Cr(VI) in grafted bamboo fibers was carried out with a selected amount of adsorbent in 160 mL of Cr(VI) solution at various concentrations. The initial pH of the Cr(VI) solution was adjusted with 0.1 M HCl and NaOH. Then, the adsorption step occurred at 30℃ for 2 h at 150 rpm. Afterwards, the reaction mixture was filtered and the concentration of Cr(VI) in the filtrate was measured by inductively coupled plasma optical emission spectrometry with a Agilent(US)ICP-700 Series OES. The calculation of adsorption of formaldehyde on grafted cellulose was as following Eq. (1):

$$Q = \frac{(C_0 - C_t)V}{m} - Q_0 \quad (1)$$

where Q is the adsorption capacity of treated bamboo fibers, mg/g; Q_0 is the adsorption capacity of native cellulose, mg/g; C_0 is the initial Cr(VI) concentration, mg/L; C_t is the subsequent Cr(VI) concentration, mg/L; V is the volume of Cr(VI) solution, L; m is the weight of treated bamboo fibers, g.

3. Results and discussion

3.1. SEM analysis

The SEM of untreated bamboo fibers (a ×2,000) and treated bamboo fibers was shown in Fig. 2(a) and (b), respectively. It shows that surface morphology of bamboo cellulose was changed at a certain degree after epoxidation, amination, and ultrasonic enhancement sulfonation reaction. The surface of untreated bamboo fibers was relatively smooth. While for the treated bamboo fibers, the surface of fiber adhered some floccule and the surface was very rough. All above changes proved that natural bamboo fibers was successfully modified [25].

3.2. XRD analysis

Changes in the crystalline structure of the bamboo fibers resulting from the chemical treatments were examined with wideangle XRD in a Rioch (Japan) 4153B172 Instrument. The samples were prepared by powdering, laid on an aluminum sample holder (35 mm × 55 mm × 3 mm), then scanned with speed of 2˚/min from 10˚ to 70˚ shown in Fig. 3, the XRD pattern of the untreated bamboo fibers exhibited crystalline peaks at approximately 29.363˚ and 34.941˚, in addition to a sharp intense peak at approximately 16.029˚ and 22.356˚ which is consistent with Zhong's et al. reports [14]. The peaks at 16.029˚ and 22.356˚ indicated that natural cellulose has highly crystalline [26]. In contrast, the crystalline pattern of the treated bamboo fibers presented an intensive peak at approximately 38.7˚ and 52.2˚. Additionally, the treated bamboo fibers did not display any reflections at 15.8˚, the diffraction angle peak at 22.7˚ was widened, and the diffraction intensity decreased upon grafting and modification. In general, the chemical reaction happens in the amorphous regions. In this study, the degrees of crystallinity for modified cellulose-based adsorbent and natural bamboo fibers are 68.02 and 25.32%, respectively [27]. All these findings indicated that both amorphous and crystalline regions were available for various reactions.

Table 1
Adsorption capacities of Cr(VI) with various cellulose-based adsorbents

Adsorbents	Chemical modification for cellulose	Q_e (mg/g)	Initial Cr(VI) concentration (mg/l)	pH
Wheat bran [21]	No	310.6	200	2.0
Cellulose [22]	No	0.37	100	2.0
Mangifera indica sawdust [9]	No	10.7	50	2.6
MCS [23]	Epoxidation & amination	200.0	100	2.3
Cellulose microsphere leaves [16]	Radiation-induced grafting	123.4	100	3.1
Magnetic cellulose composite [24]	Epoxidation & amination	171.5	150	2.0
WSCA [14]	Epoxidation & amination	62.2	150	4.0–4.5
Present work	Epoxidation & amination & Ultrasonic treatment	32.4	400	1.0

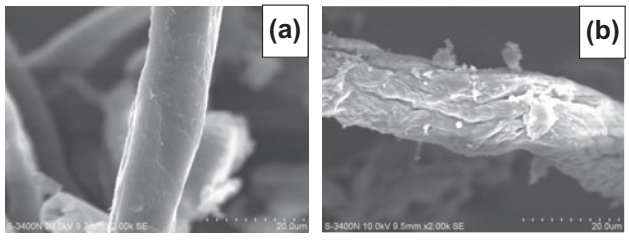

Fig. 2. SEM photographs of untreated bamboo cellulose (a) ×2,000 and treated bamboo fibers (b) ×2,000.

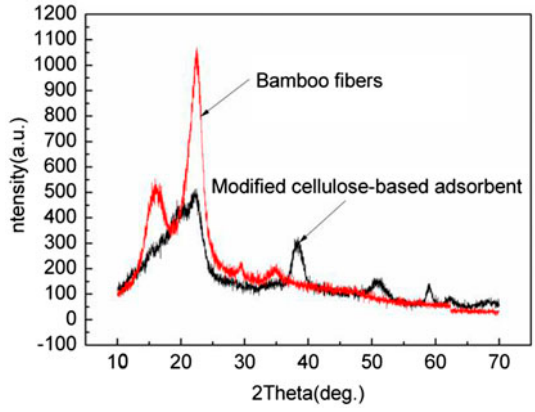

Fig. 3. XRD pattern of untreated and treated bamboo fibers.

3.3. EDAX analysis

The map of the untreated bamboo fibers and treated bamboo fibers was made using SEM/EDAX model Kratos (Britain) AXISULTRANLD equipment. The sample was pressed to make its surface more flat. The analysis was made using potential difference of 20 kv for the tungsten filament. The surface of the untreated bamboo fibers was glossy and the connections between the fibers were tight. As shown in Table 2, the N and S contents greatly increased by 6.43 and 12.07%, respectively. The surface of the treated bamboo fibers was rough and the cellulose linkages were loose. This analysis showed that the treated bamboo fibers had been grafted and their properties were modified. The N and S groups have heavy metal adsorption ability. The increasing of N and S elements content indicates that the improvement of adsorption capacity of heavy metals adsorption material.

4. Effect of absorption conditions

4.1. Effect of pH on adsorption

The removal of pollutants from wastewaters by adsorption is highly dependent on the pH of the solution. This reflects the nature of the physicochemical interaction of the pollutant species in solution and the sites of adsorption. These factors also influence the potential mechanisms of adsorption from the solution onto the surface of the solid adsorbent [28].

The pH tests of Cr(VI) adsorption by the treated bamboo fibers are presented in Fig. 4(a). Based on the pH of the solution, Cr ions may be represented in

Table 2
EDAX element contents of untreated bamboo fibers and treated bamboo fibers

	C	N	O	S
Untreated bamboo fibers				
Wt%	54.24	1.21	44.33	0.21
At%	61.19	1.17	37.55	0.09
Treated bamboo fibers				
Wt%	47.54	7.64	32.54	12.28
At%	56.18	7.74	28.42	7.66

various forms such as $HCrO^-$, CrO_4^{2-}, $HCr_2O_7^-$, and $Cr_2O_7^{2-}$. When the pH values was low, Cr(VI) ions are probably in solution as $HCr_2O_4^-$ and/or $Cr_2O_7^{2-}$ species, where anionic species can be adsorbed to the protonated active sites of the adsorbent [23]. In this study, we found that the pHzpc of treated bamboo fibers was 3.8, suggesting that treated bamboo fibers carry some positive-chargely functional groups. When pH value was less than pHzpc, the surface of the adsorbent was positively charged. In contrast, when pH value was greater than pHzpc, the surface of the adsorbent was negatively charged. In aqueous solution, chromium ions usually existed in the form of anion, including $HCr_2O_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}, so that the positive charge of adsorbent was more conducive to the adsorption of chromium ion. In this study, when the pH was 1, the adsorbent was positive charged which was suitable for attracting for chromium ions. Similar results have been reported in the adsorption of Cr(VI) onto modified corn stalk [23]. Therefore, the optimum pH for adsorption was a highly acidic 1.

4.2. Effect of temperature on adsorption

When other parameters were fixed, the effects of temperature on the adsorption of Cr(VI) ions was studied by testing a range of temperatures from 20 to 90℃, and the results are presented in Fig. 4(b).

There were no measurable impacts to Cr(VI) ion adsorption when the temperature varied. This may indicates that temperature has little effect on chromium ion adsorption. The adsorption capacity of adsorbent increased with temperature increasing from 20˚ to 70℃ and then decreased with further increase in temperature. When the temperature was higher than 70℃, part of the adsorption group might begin to breakdown [27]. From the results, the adsorption capacity of modified cellulose-based adsorbent was decreased. Considering saving the experiment cost, room temperature was chosen as the adsorption temperature used in this study.

5. Research on the adsorption process

5.1. Adsorption isotherms of treated bamboo fiber adsorption to Cr(VI)

As shown in Fig. 5, an increase in adsorption capacity occurred at the initial concentration of Cr(VI) and leveled off when the initial concentration of Cr (VI) was above 400 mg/L. The optimum concentration for adsorption was 400 mg/L and the corresponding adsorption capacity was 25.92 mg/g adsorbent.

The adsorption isotherm of the treated bamboo fibers mixed with Cr(VI) was studied to obtain the law of interaction between this adsorbent and adsorbate and to provide a reference for the adsorption process to determine its parameters.

The Langmuir isotherm mode is provided in Eq. (2):

$$\frac{C}{Q} = \frac{C}{Q_m} + \frac{1}{bQ_m} \tag{2}$$

The Freundlich isotherm model is provided in Eq. (3):

$$\log Q = \log k + 1/n \log C \tag{3}$$

where C (mg/L) and Q_m (mg/g) are the concentration and adsorption capacity at equilibrium, respectively. Q_0 (mg/g) is the adsorption capacity and b, k, and n are coefficients related to the adsorption.

As shown in Fig. 6 and Table 3, the experimental data are a good fit with the Langmuir [18] and Freundlich [19] isothermal adsorption models, as illustrated by the correlation coefficient ($R^2 > 0.99$). This suggests that Cr (VI) adsorption by the treated bamboo fibers was mainly a chemical, monolayer adsorption [21].

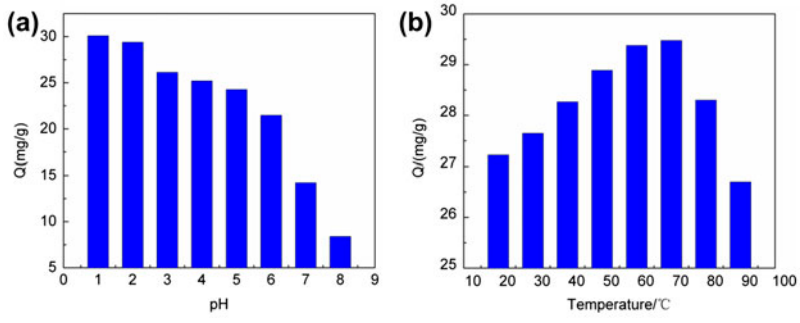

Fig. 4. Effect of (a) pH and (b) temperature on adsorption capacity.

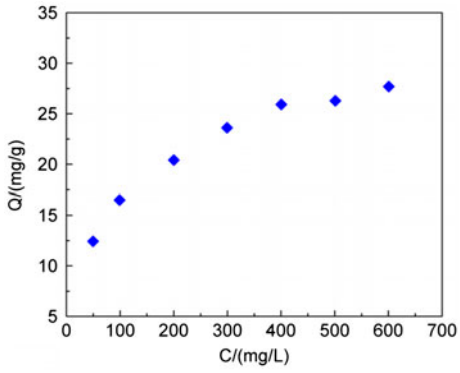

Fig. 5. Effect of Cr(VI) concentration on adsorption capacity.

5.2. Effect of adsorption time on adsorption capacity

As shown in Fig. 7, the adsorption capacity of the treated bamboo fibers for Cr(VI) increased as the reaction time increased. However, the trend ended when the adsorption time exceeded 120 min. The adsorption capacity reached a maximum of 25.5 mg/g when the reaction time was 90 min, and the adsorption became slower after 120 min.

5.3. Pseudo-second-order kinetics

The pesudo-first-order kinetic model can be expressed as Eq. (4):

$$\log(Q_e - Q) = \log Q_e - \frac{k_1}{2.303}t \tag{4}$$

where Q_e and Q are the amounts of adsorbate adsorbed (mg/g) at equilibrium and at any time, t (min), respectively; k is the rate of constant of pesudo-first-order adsorption (min^{-1}).

It can be seen from Fig. 8(a), the value of R^2 was 0.9889 which was lower than the pseudo-second-order model. What is more, the $Q_{e,cal}$ (24.60 mg/g) value calculated from pesudo-first-order model did not agree with the experimental Q_e value. This indicated that the adsorption of Cr^{6+} onto modified bamboo fibers did not follow the pesudo-first-order kinetics.

5.4. Pseudo-second-order kinetics

A pseudo-second-order model [29] could describe the sorption kinetics. The model can be expressed as Eq. (5), and the linear relationship can be expressed as Eq. (6):

$$\frac{dQ}{dt} = k_2(Q_e - Q) \tag{5}$$

$$\frac{t}{Q} = \frac{1}{kQ_e^2} + \frac{t}{Q_e} \tag{6}$$

where t is the adsorption time (min); Q_e (mg/g) is the amount of metal adsorbed at equilibrium; and k_2 is the rate constant of pseudo-second-order kinetics (g/mg min).

The kinetic parameters (Q_e and k_2) were calculated from the slope and intercept of the plot t/Q by a linear regression analysis. Considering these results (Fig. 8(b), the pseudo-second-order kinetic model provides a good correlation for the adsorption of Cr(VI).

6. Solid–liquid-phase adsorption mechanism

Generally, the Dumwald–Wagner formula [30] is used to describe solid–liquid-phase adsorption.

6.1. Surface diffusion

$$\ln(Q_e - Q) = \ln Q_e - B_1 t \tag{7}$$

where B_1 is the coefficient of surface diffusion (min^{-1}).

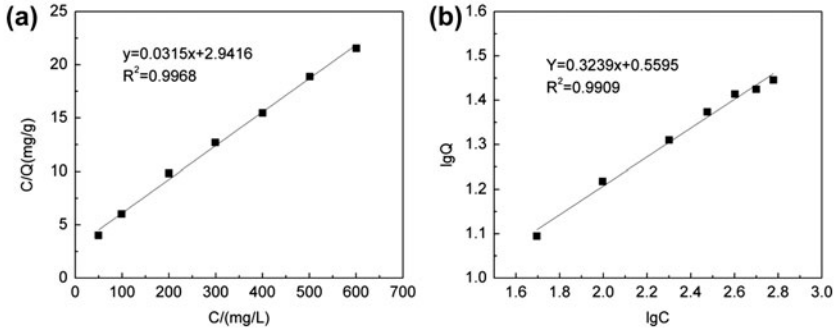

Fig. 6. Langmuir (a) and Freundlich (b) adsorption isotherm curves of treated bamboo fibers acting on Cr(VI).

Table 3
Isotherm parameters

Isotherm models	Fitted equation	R^2	Q_m (mg/g)	b	k	n
Langmuir model	$y = 0.0315x + 2.9416$	0.9968	31.7460	0.0107	–	–
Freundlich model	$y = 0.3239x + 0.5595$	0.9909	–	–	3.6266	3.0874

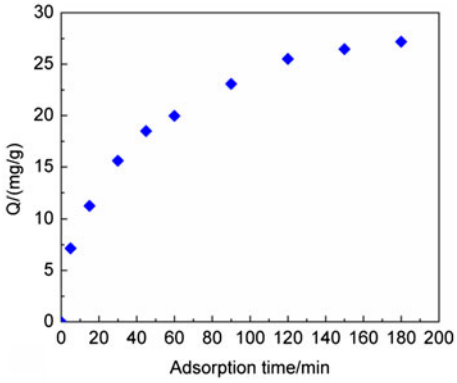

Fig. 7. Effect of adsorption time on adsorption capacity.

The linear plots of $\ln(Q_e - Q)$ vs. t (Fig. 9(a)) show that the R^2 value is greater than 0.98. In addition, B_1 was 0.0110, so the equilibrium adsorption, Q_e, was calculated (21.52 mg/g).

6.2. Intra particle diffusion

$$F = Q/Q_e = (C_0 - C)/(C_0 - C_e) \quad (8)$$

$$F = 1 - (6/\pi^2)\sum_{n=1}^{\infty}[(1/n^2)\exp(-n^2 kt)t] \quad (9)$$

$$k = (\pi^2 R^2)D_i' \quad (10)$$

$$D_i' = D_i/p_s(dQ/dC) \quad (11)$$

$$\log(1 - F^2) = -kt/2.303 \quad (12)$$

where k is the coefficient of internal diffusion (min^{-1}); F is the fraction of balance ($F = Q/Q_e$); R is the average particle radius of adsorption materials; D_i' is the effective diffusion coefficient based on adsorption; and D_i is the effective diffusion coefficient based on the concentration.

As shown in Fig. 9(b), $y = -0.0040x$, $R^2 = 0.9921$, and $k = 0.009212$. Solid–liquid-phase adsorption studies suggest that absorption of Cr(VI) by the treated bamboo fibers was well described by the surface diffusion model ($R^2 > 0.98$) and the particle diffusion model ($R^2 > 0.99$). The results of our solid–liquid-phase adsorption mechanism studies showed that the process of treated bamboo fibers adsorbing Cr(VI) is congruent with a solid–liquid-phase adsorption process. The surface diffusion and particle internal diffusion processes were the prominent factors in deciding the final adsorption rate. The adsorption of Cr(VI) occurred rapidly on the inner surface of the treated bamboo fibers. The proposed process and mechanism for the adsorption of Cr(VI) by treated bamboo fibers from an aqueous solution was shown in Fig. 10.

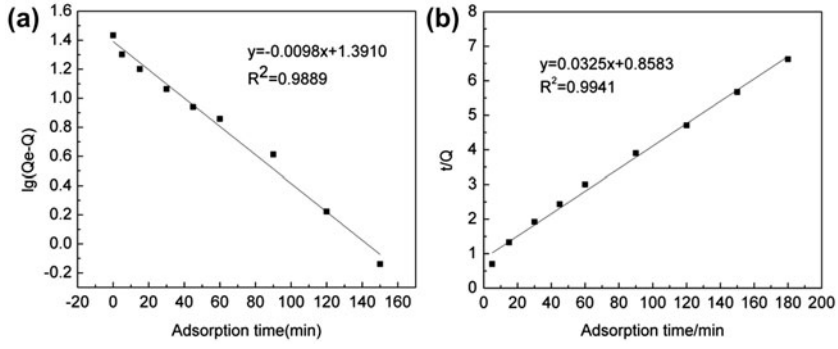

Fig. 8. The Cr(VI) adsorption kinetic curve of pseudo-first-order (a) and pseudo-second-order kinetic model (b).

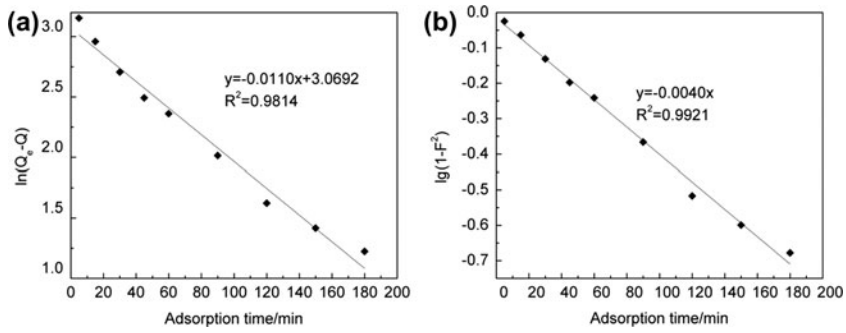

Fig. 9. The Cr(VI) adsorption processes of surface (a) and internal diffusion fitting curves (b).

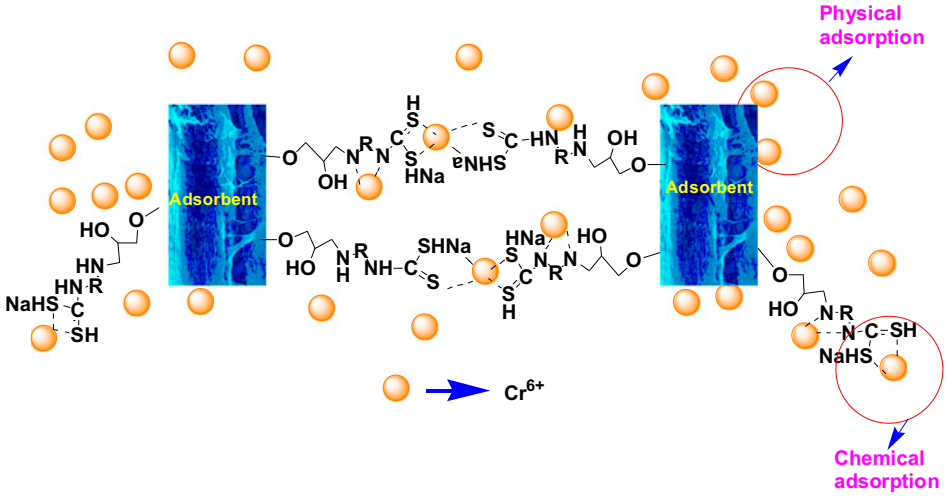

Fig. 10. The proposed process and mechanism for the adsorption of Cr(VI) by treated bamboo fibers from an aqueous solution.

7. Conclusions

(1) A series of treatments including plasma, epoxidation, amination, and ultrasonic enhancement sulfonation reactions were used to prepare a novel, cellulose-based heavy metal adsorbent from bamboo fibers. Its adsorption capacity of Cr(VI) was 32.4 mg/g adsorbance.
(2) The EDAX analysis showed an increase in the N and S contents of bamboo fibers after graft modification. A comprehensive analysis showed that the treated bamboo fibers contained heavy metal adsorption functional groups.
(3) Here provided a good fit to the Langmuir and Freundlich isotherm adsorption models. The adsorption was chemical and monolayer. The solid–liquid-phase adsorption mechanisms and surface and particle internal diffusion processes were the dominant mechanisms of adsorption.

Acknowledgments

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