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Shellac-coated iron oxide nanoparticles for removal of cadmium(II) ions from aqueous solution

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Abstract

This study describes a new effective adsorbent for cadmium removal from aqueous solution synthesized by coating a shellac layer, a natural biodegradable and renewable resin with abundant hydroxyl and carboxylic groups, on the surface of iron oxide magnetic nanoparticles. Transmission Electron Microscopy (TEM) imaging showed shellac-coated magnetic nanoparticle (SCMN) adsorbents had a core-shell structure with a core of 20 nm and shell of 5 nm. Fourier Transform Infrared Spectroscopic analysis suggested the occurrence of reaction between carboxyl groups on the SCMN adsorbent surface and cadmium ions in aqueous solution. Kinetic data were well described by pseudo second-order model and adsorption isotherms were fitted with both Langmuir and Freundlich models with maximum adsorption capacity of 18.80 mg/g. SCMN adsorbents provided a favorable adsorption capacity under high salinity conditions, and cadmium could easily be desorbed using mild organic acid solutions at low concentration.

Key words: cadmium ions; shellac; iron oxide nanoparticles; natural material; magnetic separation

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Introduction

Cadmium as a minor component of zinc ores is a toxic heavy metal of environmental concern and is classified as a B1 carcinogen by the U.S. Environmental Protection Agency (Wang et al., 2010; Waalkes, 2003). Exposure to cadmium released in food and drinking water will lead to cardiovascular and cerebrovascular diseases, as well as calcareous bone and kidney dysfunction (Järup and Alfvén, 2004). Attempts have been made at developing techniques for cadmium removal from water involving adsorption, chemical precipitation, ion exchange, reverse osmosis, electrochemical treatments, hyperfiltration, evaporation and membrane separation (Chen et al., 2009; Liu et al., 2006; Jang et al., 2008; Chang et al., 2006). The adsorption technique is an attractive approach for water treatment, especially if the adsorbent is low-cost, convenient to separate and easily regenerated before its application (Mohammed et al., 2011).

Considering their low cost, abundant supply and readily availability, adsorbents coated with organic polymers including industrial byproducts, agricultural wastes, biomass and polymeric materials have been widely applied to separate heavy metal ions (Abdel-Halim and Al-Deyab, 2011; Bailey et al., 1999). Various studies on cheap polymer-coated adsorbents have focused on polysaccharides such as chitosan, alginic acid, starch and cyclodextrin, particularly chitosan due to its amino group and hydroxyl group, which can easily be functionalized to form various chitosan-based derivatives with enhanced sorption capacities and selectivity for heavy metal ions (Bratskaya et al., 2011; Wang et al., 2011; Babel and Kurniawan, 2003). However, there are no prior reports regarding shellac polymers used as adsorption materials for removing heavy metal ions, to our knowledge. Shellac is widely used in pharmaceutical, confectionery and food coatings (Xue and Zhang, 2009), and is a natural biodegradable and renewable resin with abundant hydroxyl and carboxylic groups (Limmatvapirat et al., 2007), thus providing the possibility of chelating heavy metal ions.

In recent years, low-cost polymer-coated magnetic nanoparticle adsorbents have attracted growing interest in water treatment and environmental remediation (Yantasee et al., 2007). They combine the separation convenience of magnetic species with the adsorption properties of natural polymers, which contain abundant functional groups. It has been well documented that various polymer-modified magnetic adsorbents, such as ethylenediamine-modified magnetic chitosan complex, gum arabic-modified magnetic nano-adsorbent, magnetic alginate beads, and humic

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acid-coated Fe_3O_4 nano-adsorbent, are effective for the removal of metal ions from water (Wang et al., 2011; Banerjee and Chen, 2007; Rocher et al., 2008; Liu et al., 2008).

In the present article, we examined the capacity of shellac-coated magnetic nanoparticles (SCMN) as an adsorbent for cadmium(II) ion removal from water by coating a shellac layer on the surface of iron oxide nanoparticles. The SCMN were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), TEM, Field Emission Scanning Electron Microscopy (SEM) and Energy dispersive X-ray (EDX) spectroscopy. In addition, the kinetics, sorption isotherm, desorption behavior and effects of pH, dosage and salt on the adsorption process were investigated.

1 Materials and methods

1.1 Materials

Shellac was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Cadmium nitrate standard samples were obtained from the Institute for Environmental Protection in China. All metal solutions were prepared from their nitrate salts (AR). The standard sample was diluted using ultrapure water. All other chemicals (analytical grade) were dissolved in distilled water.

1.2 Synthesis of shellac-coated magnetic nanoparticles adsorbent

A mixed ferric and ferrous salt solution ($FeCl_3 \cdot 6H_2O$ 0.0227 mol, $FeCl_2 \cdot 4H_2O$ 0.0151 mol, 100 mL of oxygen-free water) was stirred and heated to 90°C under N_2 atmosphere followed by addition of 10 mL of 13.38 mol/L ammonium hydroxide solution in a stepwise manner. It was noted that an iron oxide black precipitate appeared rapidly. Then, shellac solution prepared by dissolving 1.5 g shellac into 20 mL of 3.34 mol/L ammonium hydroxide solution was added dropwise to the black slurry. The mixture was stirred for 30 min at 90°C under N_2 atmosphere, and then cooled to room temperature. Finally, the black precipitate was collected with a permanent magnet and washed with copious distilled water. The obtained black precipitate was SCMN, and was dispersed in distilled water to form a suspension with final concentration ranging from 41.6 to 67.8 mg/mL (the specific concentration for the adsorption process is given for each experimental step). An aliquot of 0.5 mL SCMN suspension dispersed in a beaker was dried in an oven at 80°C for 2 hr and then cooled down to room temperature followed by weighing the mass of the beaker. The mass of dried SCMN was equal to the weight difference between the beaker alone and the beaker after drying SCMN. The final concentration of the SCMN suspension was calculated from the dried SCMN mass divided by the corresponding volume (0.5 mL). Bare magnetic nanoparticles (BMN) were synthesized by a similar method without the addition of shellac solution.

1.3 Characterization

The FT-IR spectra of shellac, BMN and SCMN were collected by Fourier Transform Infrared Spectroscopy (WQF-410, Beijing Second Optical Instrument Factory, China). Transmission Electron Microscopy (JEOL 1230, JEOL Ltd., Japan) was utilized to identify the morphology and microscopic structure of the SCMN. A Field Emission Scanning Electron Microscope (JSM-6700F, JEOL Ltd., Japan) was used to characterize the sizes and surface morphologies of the prepared SCMN and BMN. The elemental content of the adsorbent was detected by EDX spectroscopy performed *in situ* in an Environmental SEM (FEI Quanta-200, FEI Company, Holland). The specific surface area was measured by a nitrogen adsorption BET surface area and pore size distribution tester at 77.35 K (ASAP 2010, Micromeritics Instrument Corp., USA). The Zeta potentials of the adsorbents were obtained by a Zeta Sizer and Nano series instrument equipped with a microprocessor unit (ZEN3690, Malvern, UK). The magnetic properties were characterized by magnetization curves using a vibrating sample magnetometer (VSM, HH-50, China) with sensitivity of 20 mV. All the metal concentrations were measured with a Perkin-Elmer Analyst 700 atomic absorption spectrophotometer (AAS, Perkin-Elmer, USA). The surface compositions of the SCMN adsorbent before and after Cd uptake were analyzed by X-ray Photoelectron Spectroscopy (XPS) (K-Alpha 1063, Thermo Fisher Scientific, Britain). Total organic carbon (TOC) measurements were performed by a TOC analyzer (TOC-V CPH/CPN, Shimadzu, Japan).

1.4 Adsorption experiments

Batch adsorption experiments were carried out in a thermostated oscillator with a speed of 120 r/min at 25°C. The adsorbents were separated from aqueous solution by magnetic separation using a permanent magnet. All samples were prepared in duplicate.

The kinetics of Cd(II) sorption on SCMN adsorbents was studied in flasks containing 150 mL of 50 mg/L Cd(II) solution and 1.5 mL of SCMN (67.8 mg/mL) adsorbent at pH 8.0. Experimental samples were transferred by pipet into different flasks at preselected time intervals (from 10 min to 48 hr). After magnetic separation the remaining Cd(II) concentrations in the supernatant were measured.

To assess the effect of initial pH on the adsorption capacity, flasks containing 50 mL of 50 mg/L Cd(II) solution and 0.5 mL of SCMN (49.0 mg/mL) adsorbent were shaken for 24 hr at different pH values from 2.5 to 8.0. Then, the magnetic adsorbent was separated and the residual metal concentrations in the supernatant were determined.

The effects of salt on adsorption were investigated in flasks containing 50 mL of 50 mg/L Cd(II) solution, 0.5 mL SCMN (67.0 mg/mL) adsorbent and different concentrations of sodium chloride (0–3.5%) at pH 8.0. After 24 hr, the magnetic adsorbent was separated and the residual metal concentration was analyzed.

Various amounts of SCMN (61.0 mg/mL) adsorbents

(0.1, 0.2, 0.3, 0.5, 0.75 and 1 mL) were added to 50 mL of 50 mg/L Cd(II) ions solution at pH 8.0 to determine the optimal adsorbent dosage. After 24 hr, the magnetic adsorbent was separated and the residual cadmium ion concentration was analyzed.

The sorption isotherm experiments were conducted in a batch process by mixing 0.5 mL of SCMN (41.6 mg/mL) adsorbent with 50 mL of Cd(II) solution over a range of concentrations (0.469–82.8 mg/L) at pH 8.0 for 24 hr. Subsequently, the magnetic adsorbents were separated using a permanent magnet followed by analysis of the residual metal concentration in the supernatant.

1.5 Desorption experiments

To investigate the desorption properties of SCMN adsorbent, various eluants and methods were applied including EDTA, citric acid, acetic acid buffer, $Ca(OH)_2$, NaOH, HNO_3 and ultrasonic bath method. SCMN adsorbents were immersed into different eluants for 24 hr at 25°C, with subsequent magnetic separation and the analysis of cadmium ion concentrations desorbed from the surface of the SCMN adsorbents.

1.6 Leaching tests

To evaluate the stability of the SCMN material under acidic conditions, leaching tests were conducted by mixing SCMN adsorbent with various concentrations of HNO_3 solutions for 24 hr at 25°C, and analyzing the TOC and iron content of the SCMN before and after the leaching experiment.

2 Result and discussion

2.1 Characterization of adsorbent

The sizes and morphologies of BMN and SCMN are shown in Fig. 1a, b. SCMN adsorbents had a core-shell structure and easily aggregated (Fig. 1c). The diameter of the SCMN and thickness of the shellac shell were about 20 nm and 5 nm, respectively. The results shown in the TEM image were consistent with that in the SEM image. The BET surface areas of BMN and SCMN were 96.91 and 56.95 m^2/g, respectively. Compared to BMN nanoparticles, the stability of SCMN nanoparticles was enhanced with the decreased specific surface area, which may be caused by the formation of dense shellac membranes on the surface of the BMN and the increased particle size.

Many additional peaks appeared in the infrared spectrum of SCMN compared with BMN (Fig. 2a), attesting to the successful coating of the shellac layer on the BMN surface. Additionally, the C=O peaks of SCMN appearing at 1587 and 1415 cm^{-1} (Fig. 2a) were similar to the previous report (Yantasee et al., 2007), where a direct Fe-carboxylate linkage between polymer and iron oxide was shown to occur since the C=O peak in free carboxylic acid would be above 1700 cm^{-1} (Yantasee et al., 2007). On the other hand, the C=O peak in free carboxylic acid (at 1716 cm^{-1}) existing in both shellac alone and in SCMN nanoparticles (Fig. 2a), provides an opportunity for chelating cadmium ions. The bands at 2856 and 2929 cm^{-1} appearing only in shellac were due to the CH_2 symmetric stretching vibration, and the bands at 2854 and 2927 cm^{-1} only in SCMN were caused by the asymmetric stretching vibration. Moreover, comparing the IR spectrum of shellac with that of SCMN, most of the peaks had a slight deviation, and there was no Fe–O bond vibration in shellac (Fig. 2a). An obvious shift of spectrum peaks appeared after Cd(II) adsorption by SCMN (Fig. 2b). The stretching vibration peak of –OH at 3394 cm^{-1} shifted to 3371 cm^{-1}, 1716 cm^{-1} shifted to 1712 cm^{-1} and 1415 cm^{-1} shifted to 1408 cm^{-1}, suggesting the occurrence of interaction between carboxyl groups on the SCMN adsorbent surface and cadmium ions in aqueous solution. To further demonstrate the chemical adsorption mechanism, we conducted XPS experiments to characterize the surface compositions of SCMN adsorbent before and after Cd uptake. Results show that no Cd species can be found in the SCMN adsorbent before Cd uptake (Fig. 2c), while the peaks of Cd $3d_{3/2}$ (412.27 eV) and Cd $3d_{5/2}$ (405.36 eV) appeared for the SCMN adsorbent after Cd uptake (Fig. 2d). Thus, XPS data provided the evidence that Cd(II) was chemically adsorbed by SCMN, confirming the chemical reaction between cadmium ions and the carboxyl groups on the SCMN surface (Xu and Liu, 2008; Xiao et al., 2008).

The EDX patterns of SCMN (Fig. 3) revealed changes in the weights and atoms of every element in SCMN before and after cadmium adsorption, suggesting that the contents of Fe and C decreased, while the content of O increased after cadmium ion uptake. Cadmium species have been reported previously (Wang et al., 2010) to exist in the forms of Cd^{2+}, $Cd(OH)^+$, $Cd(OH)_2^0$, and $Cd(OH)_2(s)$ in

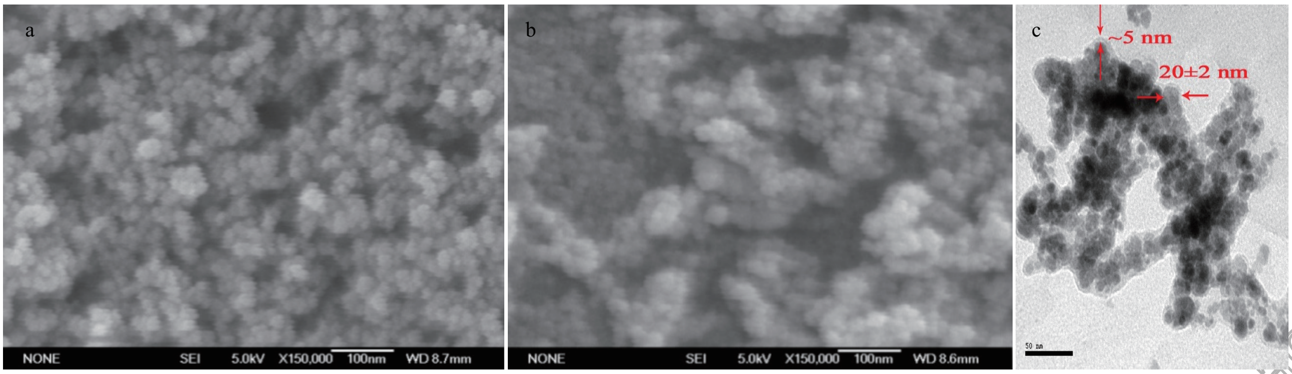


Fig. 1 SEM images of magnetic nanoparticles (BMN) (a) and shellac-coated magnetic nanoparticles (SCMN) (b) and TEM image of SCMN (c).

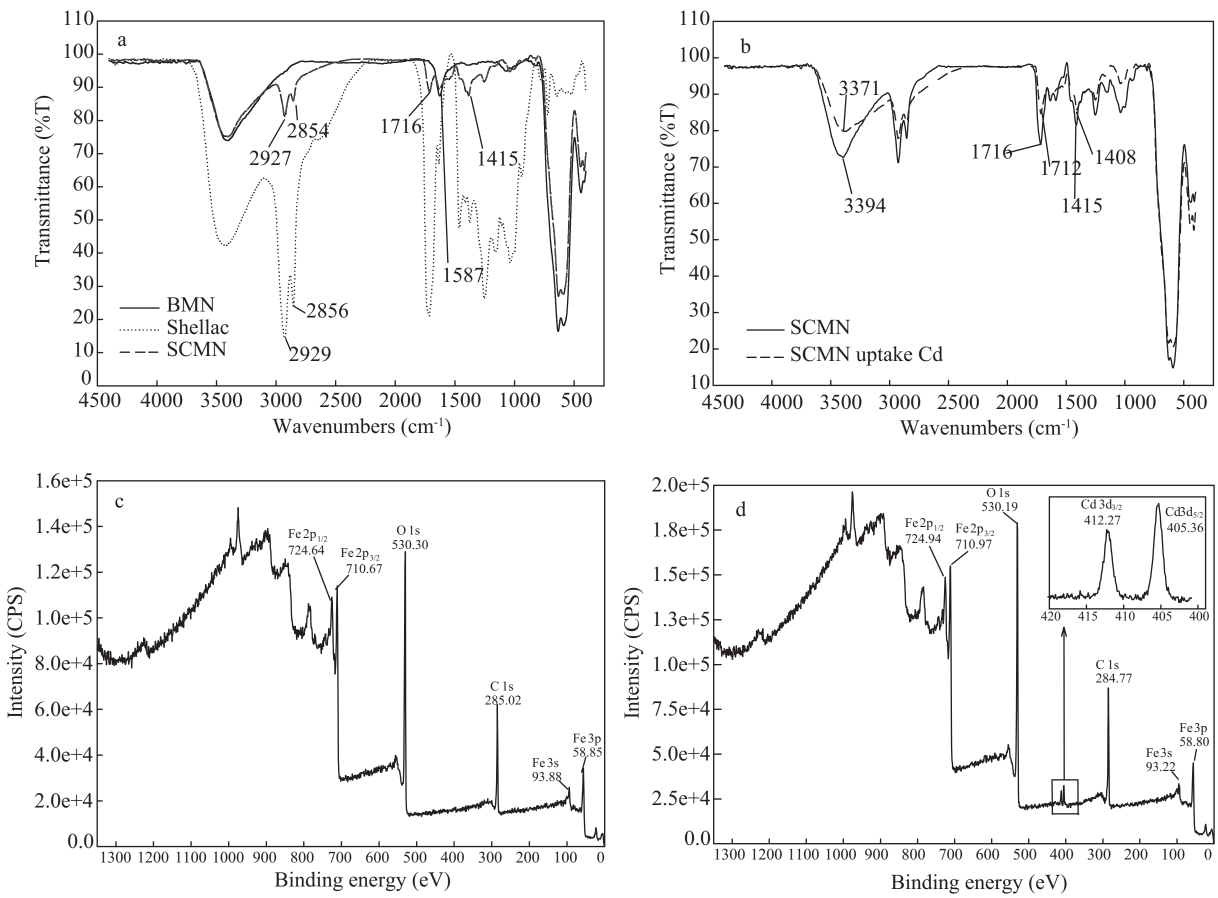
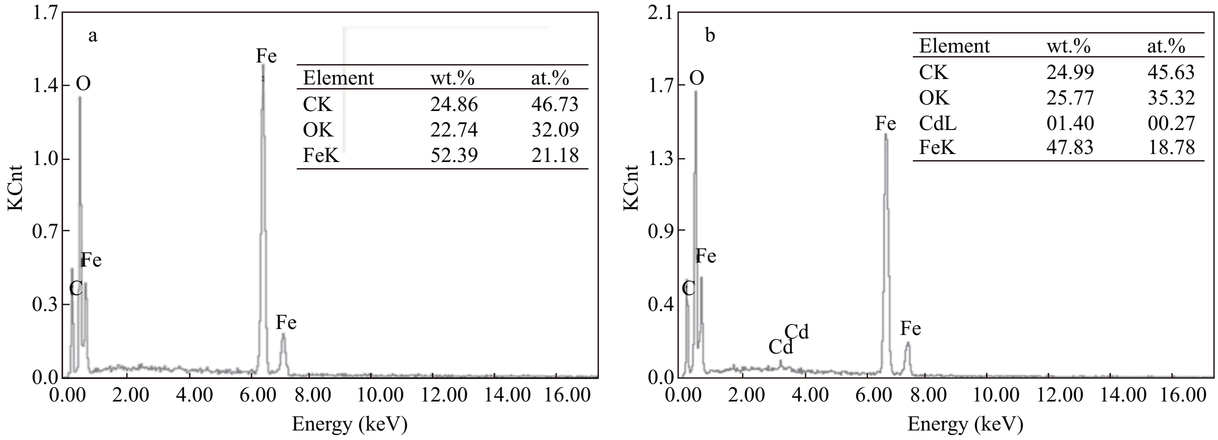


Fig. 2 FT-IR spectra of shellac, BMN and SCMN (a), before and after Cd(II) adsorption (b), and XPS spectra of SCMN before (c) and after (d) Cd(II) adsorption.



Element	wt.%	at.%
CK	24.86	46.73
OK	22.74	32.09
FeK	52.39	21.18

Element	wt.%	at.%
CK	24.99	45.63
OK	25.77	35.32
CdL	01.40	00.27
FeK	47.83	18.78

Fig. 3 EDX spectra of SCMN before (a) and after (b) Cd(II) adsorption.

deionized water, and Cd^{2+} was the only ionic species present in aqueous solution at pH < 6.0. Furthermore, the dominant Cd(II) species was Cd^{2+} and $Cd(OH)^{+}$ at pH < 8.0, and $Cd(OH)_2$ at pH > 8.0. Thus, the increase of O content after cadmium ion uptake may be caused by cadmium hydroxide adsorption on the surface of SCMN.

Saturation magnetization, a measure of maximum magnetic strength, is critical for successful magnetic separation. The magnetic hysteresis curves of BMN and SCMN (Fig. 4a) revealed that the saturation magnetizations of BMN and SCMN were 52.4 and 39.1 emu/g, respectively. The saturation magnetization of BMN decreased after modification with shellac. It was reported that a saturation value of 16.3 emu/g is sufficient for magnetic separation with a conventional magnet (Ma et al., 2005). Therefore, the saturation magnetization of SCMN (39.1 emu/g) was strong enough to separate the adsorbent from aqueous solution in a few minutes. SCMN adsorbent suspensions in aqueous solution can be conveniently separated from the solutions by an external magnet (Fig. 4b).

2.2 Sorption kinetics

To investigate the equilibrium time, pseudo first-order, pseudo second-order and intra-particle diffusion models were used to disclose the detailed dynamic process. Adsorption equilibrium was reached in 1 hr (Fig. 5a), which

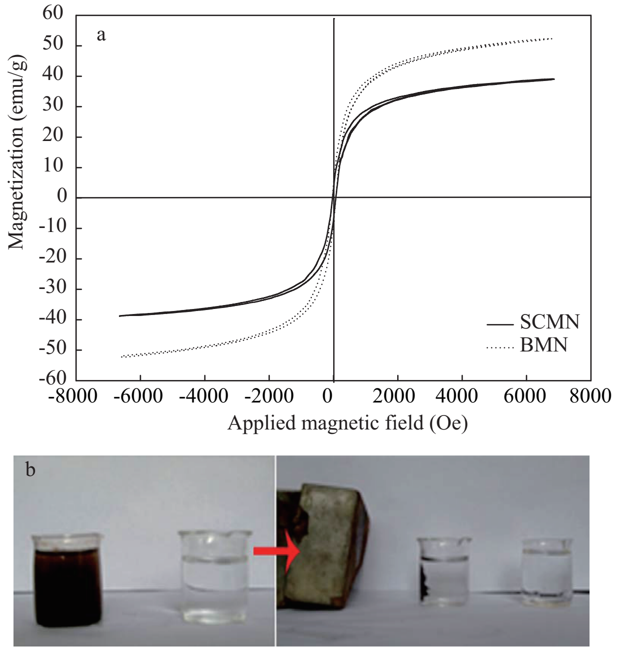


Fig. 4 Magnetization curves of SCMN and BMN (a), and the images of the SCMN magnetic separation (b).

was relatively longer than those previously reported, such as for humic acid-coated magnetic nanoparticles (15 min) (Liu et al., 2008) and dimercaptosuccinic acid-modified nanoparticles (1 min) (Yantasee et al., 2007). The slower equilibrium process may have resulted from saturation of the outer binding sites. It was difficult for metal ions to migrate into the inner surface of the nanoparticles because of the heterogeneity and compact structure of the shellac layer. However, the adsorption equilibrium time in this work was much shorter than that for immobilized chitosan biosorbent (8 hr) (Copello et al., 2008).

The equilibrium experimental results were not well fitted with the pseudo first-order model (Table 1). The linear form of the pseudo second-order kinetic model can be described as shown in Eq. (1):

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

where, k_2 (g /(mg·hr)) is the pseudo second-order rate constant. The values of q_e and k_2 can be calculated from the slope and intercept of the plot of t/q_t versus t (Fig. 5b). The results listed in Table 1 show that the correlation coefficient (R^2) was higher than 0.999. Furthermore, the calculated equilibrium adsorption capacity was consistent with the experimental result. This result suggested that the kinetic data was better described with a pseudo second-order kinetic model, which supported the assumption that the rate-limiting step may be chemical sorption (Wu et al., 2001).

To identify the diffusion mechanism of the sorption process, the intra-particle diffusion model was also applied to assess the experimental data. The equation can be described as Eq. (2):

$$q_t = k_p t^{0.5} + C \tag{2}$$

where, k_p (mg/(g·hr$^{1/2}$)) is the intra-particle diffusion rate constant and C is the intercept. The values of k_p and R^2 of the intra-particle diffusion model are listed in Table 1. The plot of q_t versus $t^{0.5}$ depicted in Fig. 5c reveals that the sorption rate is distinct in the initial and final stages, with different slopes for the experimental straight lines. The initial uptake was rapid on the external surface, and the resulting fitting line did not pass through the origin, which may be due to the existence of a boundary layer. After the external surface loading sites were saturated, the intra-particle diffusion to the internal surface took place. The sluggish cadmium uptake process in the final stage and the fact that the fitting line did not pass through the origin indicated that intra-particle diffusion was not the rate-controlling step (Smičklas et al., 2006).

2.3 Sorption isotherms

Both the Langmuir model and Freundlich model are widely used to describe the adsorption equilibrium between adsorbed metal ions on adsorbent surfaces and metal ions in solution at room temperature. The Langmuir model fits for monolayer adsorption onto a surface containing a restricted number of binding sites, while the Freundlich model is considered to be appropriate for describing sorption on heterogeneous surfaces (Coles and Yong, 2006).

The experimental data were plotted as q_e versus C_e

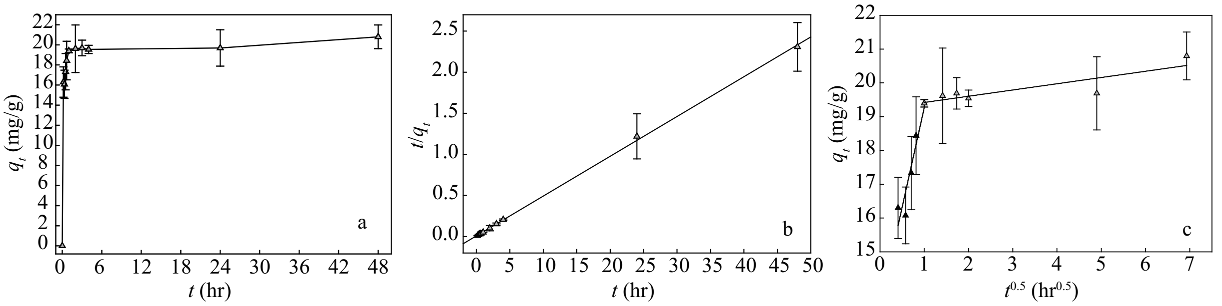


Fig. 5 Influence of contact time on the Cd(II) adsorption by SCMN (a); pseudo second-order kinetic model (b); intra-particle diffusion model (c).

Table 1 Kinetic parameters for Cd(II) adsorption on SCMN

Pseudo first-order			Pseudo second-order				Intra-particle diffusion	
$q_{e,cal}$ (mg/g)	k^1 (hr^{-1})	R^2	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_2 (g/(mg·hr))	R^2	k_p (mg /(g·hr$^{1/2}$))	R^2
0.2768	0.6057	0.8326	20.7965	20.6612	0.2822	0.9994	0.1847	0.7510

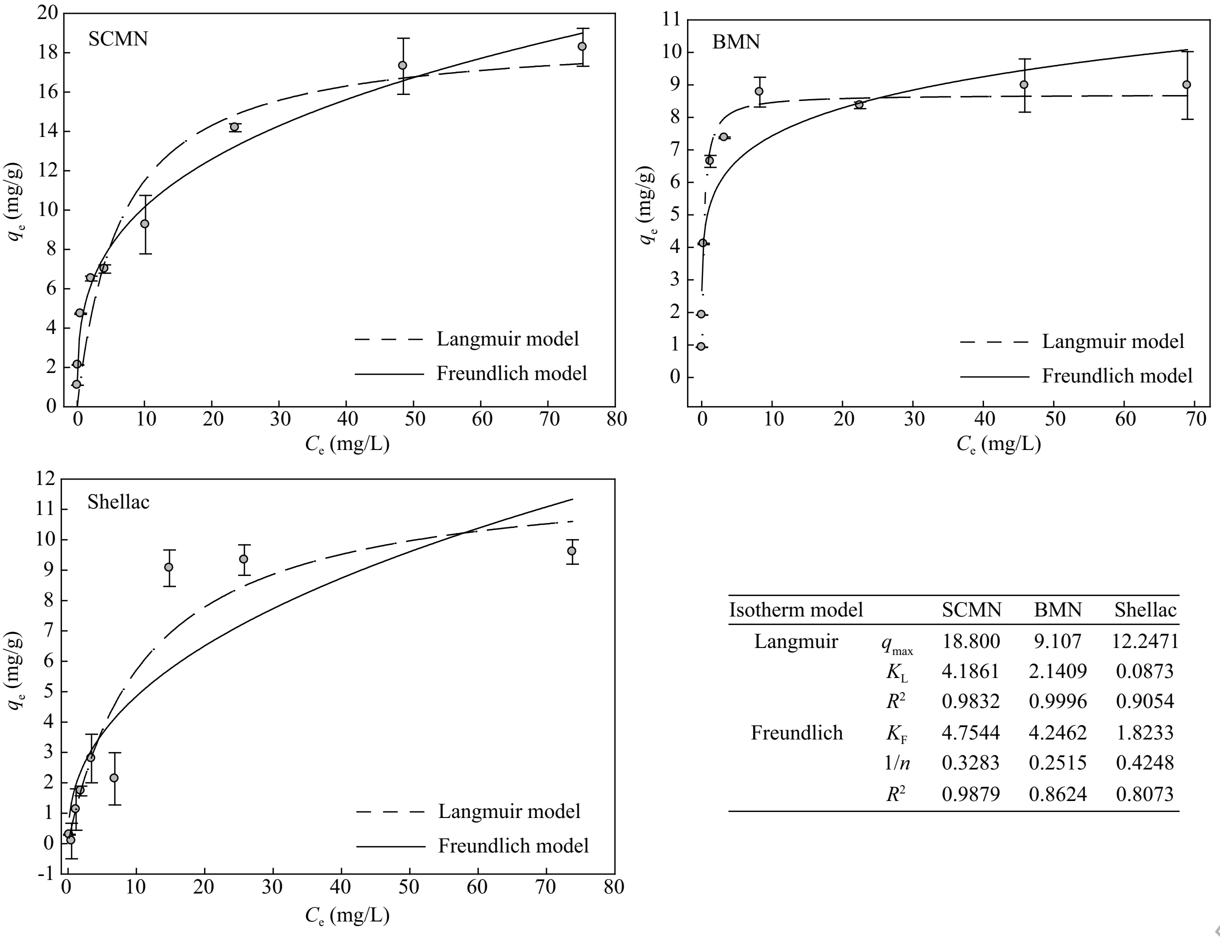
curves and shown in Fig. 6. The values of the Langmuir and Freundlich constants were obtained by a non-linear regression method. The adsorption isotherm of SCMN was well fitted with both the Freundlich and Langmuir model, while the equilibrium data of BMN and shellac were better described by the Langmuir model. The maximum adsorption capacity $q_{\max}$ of SCMN was higher than that of BMN and shellac. The comparison shown in Table 2 indicates that SCMN is an effective adsorbent for the removal of Cd(II) ions from aqueous solution, with $q_{\max}$ value 18.80 mg/g.

2.4 Effect of initial pH

The relationship between the initial pH values and the amount of Cd(II) adsorbed on SCMN is displayed in Fig. 7a. The amount of Cd(II) adsorbed on both SCMN and BMN increased slowly with increasing pH value at pH < 7.0 with the increase for SCMN much greater than for BMN, while adsorbed cadmium on SCMN increased rapidly at pH = 8.0 followed by a slow increase in BMN. Thus, the much higher adsorption capacity of SCMN compared to BMN at pH = 8.0 was not derived from the precipitation formation between cadmium ions and hydroxyl ions. To further disclose the adsorption mechanism between SCMN and Cd(II), Zeta potential experiments on SCMN and BMN were conducted at different pH values. The charge on the surface of SCMN and BMN changed from positive to negative with increasing pH (Fig. 7b). Noticeably, the experimental results showed that adsorption capacity of SCMN and BMN for metal ions was much less at lower pH compared with higher pH. Therefore, the adsorption mechanism was partly attributed to electrostatic force between the negatively charged SCMN adsorbent and positive cadmium ions. Furthermore, the charge on the SCMN surface was higher than that of BMN (Fig. 7b), providing the evidence that the adsorption capacity of SCMN was higher than that of BMN. On the other hand, the remarkably higher adsorption of cadmium ions on SCMN compared with BMN when the pH value changed from 7 to 8, revealed that some other sorption mechanism should exist during the adsorption process besides electrostatic force. The IR results described above and the sorption kinetics analysis result that the rate-limiting step was

Table 2 Comparison of adsorption capacities of some low-cost adsorbents for Cd(II)

Adsorbent	$q_{\max}$ (mg/g)	Reference
SCMNs	18.80	This work
Nano NH_2-MCM-41	18.25	Heidari et al., 2009
Bamboo charcoal	12.08	Wang et al., 2010
Carbon nanotubes	11.00	Li et al., 2003
Coconut copra meal	1.84	Ofomaja and Ho, 2007
Hazelnut shell	5.42	Bulut and Tez, 2007
Almond shell	3.18	Bulut and Tez, 2007
Carbon F-400	8.00	Mohan et al., 2007
Oak bark char	5.40	Mohan et al., 2007
Magnetic malto-dextrin	22.0	Paulino et al., 2011



Isotherm model		SCMN	BMN	Shellac
Langmuir	$q_{\max}$	18.800	9.107	12.2471
	K_L	4.1861	2.1409	0.0873
	R^2	0.9832	0.9996	0.9054
Freundlich	K_F	4.7544	4.2462	1.8233
	$1/n$	0.3283	0.2515	0.4248
	R^2	0.9879	0.8624	0.8073

Fig. 6 Adsorption isotherm for Cd(II) by SCMN, BMN, Shellac.

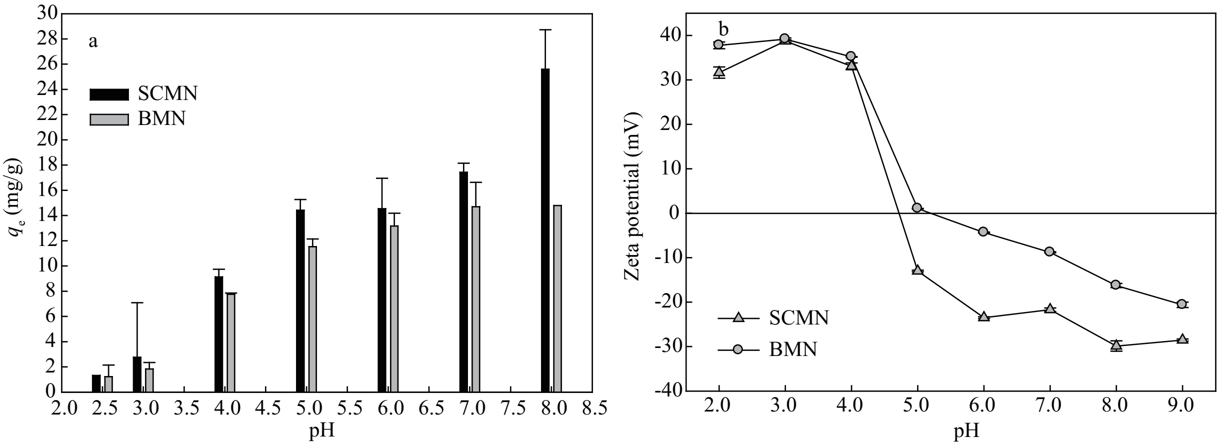


Fig. 7 Effect of initial pH on the adsorption of Cd(II) onto SCMN and BMN (a) and Zeta potential of SCMN and BMN (b).

chemical sorption suggest the occurrence of reaction between carboxyl groups on the surface of SCMN adsorbent and cadmium ions in solution. Furthermore, XPS data also provided the evidence that Cd(II) was chemically adsorbed by SCMN. Thus, the adsorption mechanism between the SCMN adsorbent and cadmium(II) was electrostatic attraction as well as chemisorption.

2.5 Effect of sodium chloride concentration

The change in salinity from 0 to 3.5% sodium chloride (the average salinity of seawater) had significant effects on the removal of Cd(II) by SCMN and BMN (Fig. 8). The amount of adsorbed cadmium ions decreased with increasing salinity, whereas SCMN had a favorable adsorption capacity for cadmium ions when the salinity was up to 3.0%.

2.6 Effect of adsorbent dosage

The amount of cadmium adsorbed increased with increasing SCMN dosage and reached a maximum at 0.24 g/L, then decreased. The reason was that increasing SCMN dosage provided more sorption sites for a fixed initial concentration. A large amount of SCMN effectively reduced the unsaturation state of these sites per unit adsorbent before the maximum (conditions of saturation). Thus, the adsorption quantity increased with increasing adsorbent dosage (Bhattacharyya and Gupta, 2007). However, equal amounts of cadmium ions were distributed on larger surfaces and caused excessive adsorption sites when SCMN adsorbents were further added, thus leading to the decrease of adsorption quantity on the unit adsorbent.

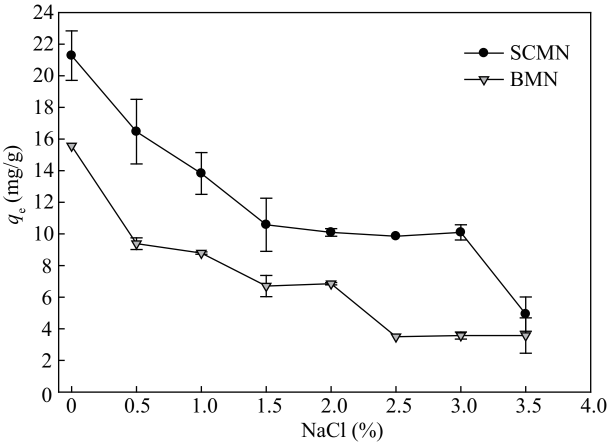


Fig. 8 Influence of salinity on the removal of cadmium (II) ions by SCMN and BMN.

2.7 Desorption

Results listed in Table 3 show that the desorption efficiencies in organic mild acids were better than in basic solution or the ultrasonic method. The reason may be derived from the formation of complex compounds between organic mild acid and Cd(II) (Yuan et al., 2007).

Eluants such as EDTA, citric acid and HAcqNaAc buffer exhibited favorable desorption efficiency for the SCMN adsorbent. Noticeably, the lower the solution pH was, the higher the organic mild acid desorption efficiency was. Therefore, It seemed that the mechanism of cadmium desorption from SCMN was not attributable to the complexation between the cadmium and organic mild acid, but rather the effect of solution pH. To understand this phenomenon, further desorption experiments were carried out where SCMN adsorbents saturated with cadmium ions were immersed in HNO_3 solutions at different pH values. The results are listed in Table 3. It can be found that both solution pH and organic acids affected the desorption efficiency, with much better desorption efficiency for EDTA compared to citric acid and acetic sodium buffer. Therefore, the use of low concentration EDTA solution as eluant would be an effective and economical way to desorb Cd from SCMN adsorbent.

Table 3 Desorption of Cd(II) from saturated SCMN

Eluants	Initial pH	Final pH	Desorbed Cd(II) (%)
EDTA (5 mmol/L)	2.5	2.62	86.75
Citric acid (10 mmol/L)	2.62	2.71	76.81
HAc·NaAc buffer (20 mmol/L)	4.65	4.68	63.29
NaOH (10 mmol/L)	11.69	11.22	0.45
$Ca(OH)_2$ (5 mmol/L)	11.67	11.02	0.00
Ultrasonic elution (30 min)	6.53	6.54	6.15
HNO_3	3.16	3.35	39.34
HNO_3	3.64	4.67	54.48
HNO_3	4.67	6.61	4.88
HNO_3	5.17	6.78	11.51

Table 4 Leaching of Fe and shellac from SCMN adsorbent in acidic solutions

Water matrix	TOC leached per total TOC (%)	Fe leached per total Fe (%)
Ultrapure water, pH 6.62	0.810	0.376
HNO_3, pH 4	0.837	0.611
HNO_3, pH 3	3.50	2.12
HNO_3, pH 2.5	3.52	4.00
HNO_3, pH 2	3.59	4.80
HNO_3, 5 mol/L	100	100

In addition, stability is an important factor for adsorbents in their application in wastewater treatment. In this study, the results of leaching tests (Table 4) revealed that the SCMN adsorbent was stable in acidic solutions, which may be due to the shellac polymer on the iron oxide nanoparticle surface acting as a protective layer.

2.8 Cost evaluation

The main advantage of the SCMN adsorbent was its low cost. Considering the price of chemicals, electrical energy and labor expense in China, the final cost of SCMN is approximately US $670 per ton. It was reported that the export price of activated carbon in China was US $1077.89 per ton in 2009 and showed an increasing trend (Dai, 2010).

3 Conclusions

Iron oxide nanoparticles coated with a shellac layer were synthesized and used as an effective magnetic nanoparticle adsorbent for cadmium removal from aqueous solution. Although the maximum adsorption capacity was not very high, there is much room for improvement such as optimizing the synthesis conditions to coat a much thicker shellac layer on the magnetic particles. Furthermore, SCMN can easily be regenerated by organic acids. Thus, this work provides an alternative adsorbent for cadmium removal from aqueous solution. The following conclusions can be obtained in this study. (1) The stability of magnetic nanoparticles coated with shellac was greatly enhanced in contrast with the bare ones. (2) Adsorption kinetic data were well described by a pseudo second-order model with a high correlation coefficient (R^2 = 0.9994). Adsorption isotherm data of SCMN were well fit with both the Langmuir model (R^2 = 0.9832) and Freundlich model (R^2 = 0.9879). (3) The adsorption capacity increased with increasing pH and the maximum adsorption capacity of SCMN was 18.80 mg/g (pH = 8.0). The optimum adsorbent dose for this experiment was found to be 0.24 g/L. (4) The adsorbent possessed favorable adsorption capacity at high salinity (q_e equals 10.10 mg/g at 3.0% sodium chloride). Therefore, the adsorbent prepared can be used to treat high-salinity wastewater containing heavy metals. The adsorbent also can be easily desorbed by a low concentration organic mild acid solution. (5) It was suggested that carboxyl groups on the surface of SCMN participated in the reaction with cadmium ions. The adsorption mechanism included both electronic attraction and chemical adsorption.

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