A Spherical Zwitterionic Cellulose Acetate/ Graphene Oxide Composite Adsorbent for Efficient Removal of Cu²⁺ and Cd²⁺ from Aqueous Solution

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A novel composite adsorbent was prepared by using cellulose acetate modified with zwitterion, for zwitterionic cellulose acetate (ZCA), then blended with graphene oxide (GO). The adsorbent was prepared by sol-gel method and used to remove Cu^{2+} and Cd^{2+} from aqueous solution. The morphologies, surface chemical structures, and crystallinity of the obtained adsorbents were characterized by field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffractometer (XRD), respectively. N_2 adsorption-desorption measurements revealed that the surface area and pore volume were 45.3 m^2g^{-1} and 0.249 cm^3g^{-1}. For adsorption, effect of time, and pH, adsorbate concentration was investigated; different adsorption models were also evaluated. The results showed that the maximum adsorption capacity was 32.0 mg/g for Cu^{2+} and 27.6 mg/g for Cd^{2+}, observed at pH 5.5 and 298 K. Simultaneously, the adsorption isotherms were well-fitted to the Langmuir model, and kinetics study showed that the adsorption process was fitted well by the pseudo-second-order model. Further regeneration experiments revealed that the adsorption of ZCA/GO was about 90% of the initial saturation adsorption capacity after repeated use 5 times, indicating that they are promising absorbents for practical application in industry.

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INTRODUCTION

With the rapid development of modern industry, most industrial wastewater contains toxic metals or other ions that cause environmental pollution and endanger human health. Therefore, the recovery of heavy metals is a worldwide industrialized problem (Liu *et al.* 2010). For example, exposure and intake of Cd^{2+} initiates serious damage to bones and kidneys, causing diseases including "itai-itai disease," anemia, osteoporosis, and hypertension. According to the World Health Organization (WHO), the maximum allowable concentrations of Cu^{2+} and Cd^{2+}, two of the most common heavy metal ions in drinking water, are 1.5 mg/L and 0.005 mg/L, respectively (Wang *et al.* 2017a). Effective removal of toxic heavy metal ions from aqua sources is important for the environment and public health protection (Aziz *et al.* 2014; Hu *et al.* 2017). Numerous technologies have been developed to remove heavy metal ions from aqueous solutions, such as adsorption, ion exchange, precipitation, membrane separation, electrochemical treatment, *etc.* (Abdelwahab *et al.* 2015; Srivastava *et al.* 2016). Water treatment by adsorption has many advantages, such as wide application range, good

treatment effect, easy handling, low cost, and reversibility (Chen *et al*. 2012; El-Naggar *et al*. 2016). Despite the important role of adsorption in water treatment, a low regeneration rate is one of the major restrictive obstacles in adsorption processes. The use of biomaterials makes the adsorption process more environmentally friendly (Hubbe *et al*. 2014; Rull-Barrull *et al*. 2016).

Cellulose, which has many advantages such as biocompatibility, biodegradation, and renewability, is a promising matrix for preparation of adsorbents (Lin *et al*. 2014; Dong *et al.* 2016). However, the native cellulose has lower adsorption for heavy metals due to its limited functional groups (only hydroxyls), so it must be modified before it is used as an adsorbent (Yang *et al.* 2014). Cellulose and some of its derivatives have the ability to combine or chelate with heavy metals and they can be used to recover heavy metals in seawater or to treat heavy metals in sewage. Cellulose acetate (CA) is one of the most economically applicable polymers due to its high hydrophilicity, good toughness, high biocompatibility, good resistance to chlorine and solvents, and cheapness. Cellulose acetate is widely used in photographic film, cigarette filters, plastic materials, and as a fiber in the textile industry (Liu *et al.* 2017; Wang *et al*. 2017b). Among the numerous cellulose derivatives synthesized for the removal of heavy metals, it is uncommon to find absorbent materials with zwitterionic characteristics that have affinity for both cationic and anionic species (Suteu and Malutan 2013; Zhang *et al*. 2015). Little work has been done using zwitterionic hybrid polymers as the adsorbent to remove and recover heavy metal ions from aqueous solution or wastewater (Ma *et al.* 2016).

Graphene oxide was synthesized through the oxidation of graphite powder by a modified Hummers method (Wang *et al*. 2016; Zhang *et al*. 2016). Its surface is rich in oxygen-containing functional groups including hydroxyl, carboxyl, and epoxy groups, which provides various active sites for modification and adsorption of target contaminants (Tang *et al.* 2016; Ma *et al.* 2017).

In a previous work, a new kind of material, zwitterionic cellulose acetate (ZCA), was prepared *via* a three-step procedure consisting of oxidization, Schiff base, and quaternary amination reaction (Liu *et al*. 2017). In the present study, a novel spherical composite material (ZCA/GO) was generated, and its application as an adsorbent was tested for removal of Cu^{2+} and Cd^{2+} from aqueous solution. The objective of this research is to improve reusability and adsorption capacity by incorporating zwitterion and graphene oxide and then preparing a functionalized ZCA/GO composite adsorbent. The synthesized material was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffractometer (XRD), and scanning electron microscopy (SEM). The adsorption performances of ZCA/GO for Cu^{2+} and Cd^{2+} ions, such as the solution pH, adsorbate concentration, and contact time were determined. Furthermore, five adsorption/desorption studies were performed for Cu^{2+} and Cd^{2+} on the ZCA/GO adsorbents. Finally, the adsorption mechanism was studied.

EXPERIMENTAL

Materials

Cellulose acetate (CA, 32 wt% acetyl), sodium periodate ($NaIO_4$), and sodium borohydride ($NaBH_4$) were purchased from Aladdin Reagent (Shanghai, China). Sodium 2-bromoethanesulfonate (SBES) and *N,N*-dimethyl-1,3-propanediamine were purchased

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from Tokyo Chemical Industry (TCI) (Tokyo, Japan). Dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidinone (NMP), ethylene glycol, ethanol, cupric nitrate trihydrate $(Cu(NO_3)_2 \cdot 3H_2O)$, cadmium nitrate tetrahydrate $(CdN_2O_6 \cdot 4H_2O)$, acetic acid, and sodium acetate were purchased from Beijing Chemical Reagent (Beijing, China). Graphene oxide (GO) composite was homemade. Deionized (DI) water was used throughout this study.

Synthesis of zwitterionic cellulose acetate (ZCA)

As shown in Fig. 1, zwitterionic cellulose acetate (ZCA) was synthesized in a three-step procedure. In the first step, cellulose acetate was oxidized by sodium periodate to form dialdehyde-modified cellulose. In the second step, the aldehyde groups were coupled with *N,N*-dimethyl-1,3-propanediamine *via* Schiff base reaction to make amino-modified cellulose. In the third step, the previously obtained amino-modified cellulose was dissolved by DMSO and reacted with sodium 2-bromoethanesulfonate (SBES) through quaternary amination reaction to obtain zwitterionic cellulose acetate (Liu *et al*. 2017).
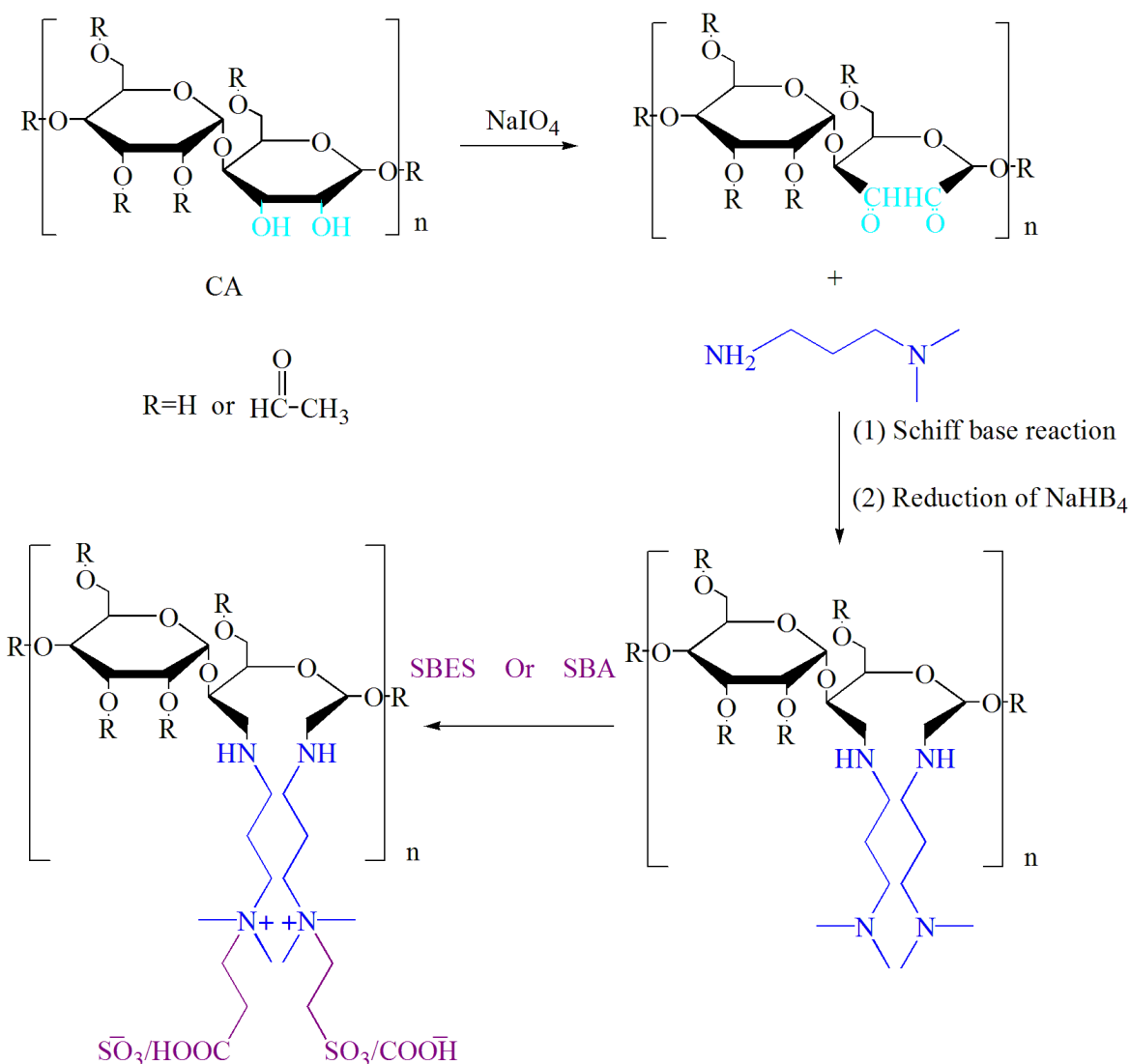

Fig. 1. Synthetic route of zwitterionic cellulose acetate (ZCA)

Preparation of Spherical ZCA/GO Composite Adsorbent

ZCA was synthesized successfully in a previous work (Liu *et al*. 2017). Functionalized ZCA/GO composite adsorbent was prepared in two steps: ZCA (12% w/v) was dissolved in NMP under continuous stirring (24 h) until homogeneous solution was obtained, then GO (1% w/v) was slowly added followed by treatment with ultrasound for 2 h with constant stirring to ensure well-mixed ZCA and GO. The mixture was stirred for another 12 h at room temperature. The obtained viscous gel was precipitated in DI water spherical beads to maintain the shape and size using a nozzle (Xing *et al*. 2017). Precipitated spherical beads were filtered, washed several times with DI water, and dried at room temperature.

Sample Characterization

Fourier transform infrared spectroscopy (Bruker Vertex 80 V, Berlin, Germany) was used to characterize absorbance spectra in the region of 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} for 32 scans by the KBr pellet method.

The X-ray diffraction patterns of the samples used in this study were obtained using an X-ray diffractometer (Ultima IV, Rigaku, Akishima, Japan) at room temperature from 10 ° to 50 ° using Cu/Ka irradiation at 40 kV and 30 mA. The scanning speed was 2°/min, and the data was collected in continuous mode.

The surface and cross-section morphology of spherical ZCA/GO composite adsorbents were observed by field emission scanning electron microscopy (FESEM, JEOL JSM-7500F, Tokyo, Japan). The adsorbent samples were frozen in liquid nitrogen before electron microscopy, then frozen and dehydrated in a vacuum freeze dryer. The samples were cut with a blade to produce cross-sections. The samples were then deposited and subjected to metal coating on the surface and section of the sample to improve the signal strength and enhance the image contrast.

Batch Adsorption Experiment

Batch equilibrium tests were carried out for adsorption of Cu^{2+} and Cd^{2+} on ZCA/GO composite adsorbent. The samples (ZCA/GO) of certain doses were introduced into the 250 mL conical flasks containing 50 mL of Cu^{2+} or Cd^{2+} solution of decided concentration and pH value, respectively (Ma *et al*. 2016). The flasks were then placed on a shaker and shaken with a stirring speed of 150 rpm at the desired temperature until adsorption equilibrium was obtained. During the experiment, the initial pH value of the solutions was adjusted by adding either 0.1 M HCl or 0.1 M NaOH solution before the adsorption experiment (Liu *et al*. 2010).

Under different experimental conditions (adsorbate concentration: 25 mg/L to 200 mg/L; adsorption time: 0.5 h to 12 h; pH: 1 to 7; and ambient temperature: 15 °C to 45 °C), adsorption studies were carried out. After ending adsorption, the solid and liquid fractions were separated by a single filtration, the solid was collected for the reuse study and the concentration of each metal ion in the aqueous solution at a time t was determined by a flame atomic absorption spectrophotometer (FAAS-M6, Thermo) at wavelengths of 324 nm for Cu^{2+} and 228.8 nm for Cd^{2+} (Wang *et al*. 2017b). All the experiments were repeated at least three times, and the results were given as average. The adsorption capacity q_e (mg/g) was calculated by Eq. 1 (Chen *et al*. 2012), and the removal rate W (%) of heavy metals was calculated from the following Eq. 2,

$$q_e = \frac{(c_0 - c_e)V}{M} \qquad (1)$$

$$W = \frac{c_0 - c_e}{c_0} \times 100\% \qquad (2)$$

where V is the volume of aqueous solution (mL), c_0 and c_e are the concentrations of initial and remaining metal ions, respectively (mg/g), and M is the weight (g) of the sample produced.

Adsorption Study

To understand interactions between adsorbate and adsorbents, Langmuir and Freundlich models of equilibrium sorption isotherms were studied. The pseudo-second-order kinetic equation was also analyzed (Li *et al*. 2016).

The desorption and reusability of the adsorbents were studied after adsorption. Desorption of Cu^{2+} and Cd^{2+} ions were performed using 0.1 M HCl as a desorbing agent to estimate the reversibility of spherical ZCA/GO composite adsorbent. This was very important since the regeneration of adsorbent decided the economic success of the adsorption process. After contact with 0.1 M HCl and shaken at 150 rpm for 24 h, the samples were collected by filtration and washed several times with DI water, then dried at 60 °C for use in the next cycle. The adsorption experiments were carried out under a very similar procedure which was shown above.

The desorption and reusability capacity were calculated from Eqs. 3 and 4 (Pan *et al*. 2017),

$$RP = \frac{q_r}{q_e} \times 100\% \qquad (3)$$

$$q_r = \frac{(c_0 - c_r)V}{M} \qquad (4)$$

where q_r is the Cu^{2+} and Cd^{2+} adsorption capacity of the reused ZCA/GO (mg/g), q_e is the adsorption capacity of the fresh adsorbent (mg/g), V is the volume of aqueous solution (mL), and M is the weight (g) of the sample produced.

RESULTS AND DISCUSSION

Characterization of ZCA/GO Adsorbent

FTIR spectra

As shown in Fig. 2, for GO, the peak located at 3409 cm^{-1} is related to the stretching vibration adsorption peak of –OH, the characteristic absorption peak at 1724 cm^{-1} is stretching vibration of carbonyl (-C=O) of the –COOH groups, and the spectra displayed at the absorption bands at 1618 cm^{-1} and 1049 cm^{-1} correspond to the bond stretching of C=C and C–O groups, respectively (Fan *et al*. 2013). These characteristic absorption peaks were almost consistent for both ZCA/GO and CA. Compared with the FTIR spectrum of the reference CA, the absorption peak at 1640 cm^{-1} was observed only for ZCA/GO, which could be attributed to the presence of N–C bonds in the quaternary ammonium groups (Liu *et al*. 2015). In addition, the new peak around 1049 cm^{-1} was

assigned to the stretching of sulfoxide (Tsai *et al*. 2010). These results could indicate that ZCA/GO composite adsorbent was successfully synthesized as expected.
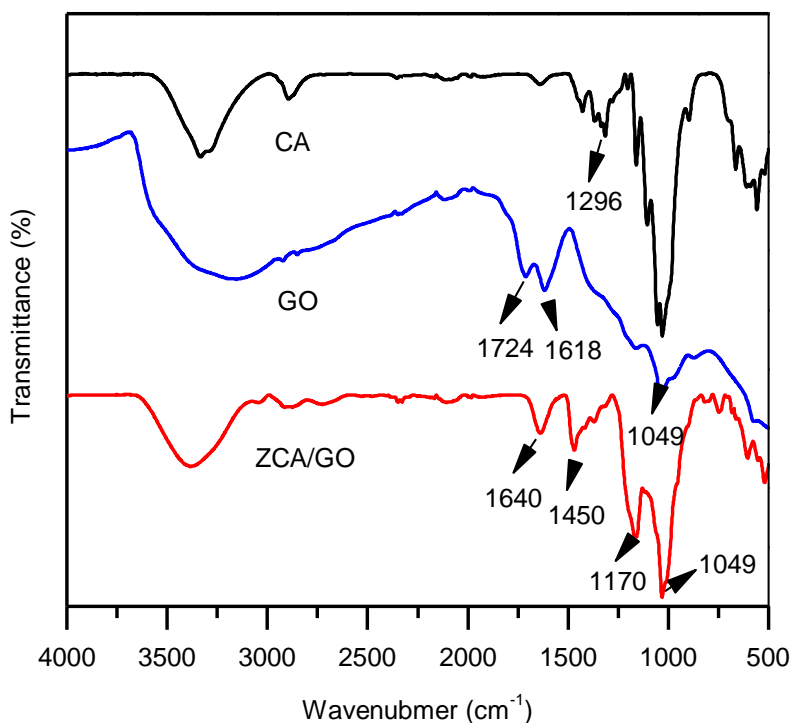

Fig. 2. FTIR spectra of CA, GO, and ZCA/GO

XRD
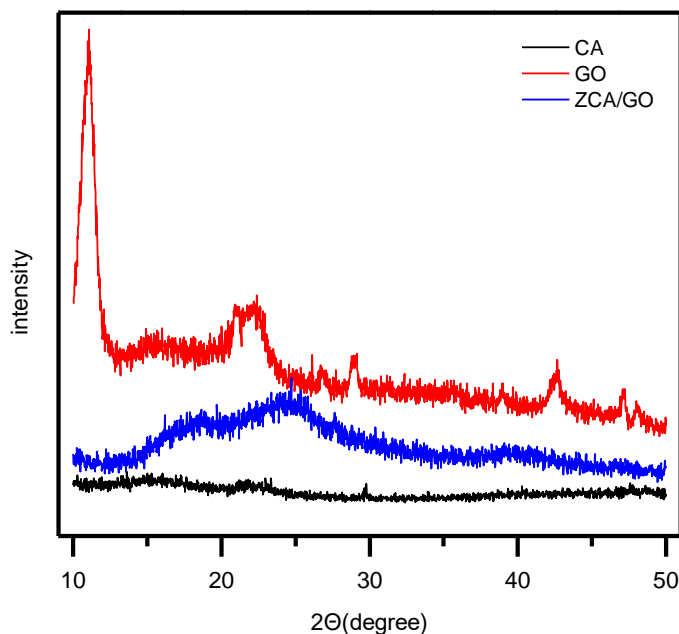
Figure 3 shows the XRD patterns of GO, ZCA, and ZCA/GO.

Fig. 3. XRD patterns of GO, ZCA, and ZCA/GO

The GO showed a sharp diffraction peak at $2\theta = 11.14°$ corresponding to the (0 0 1) plane with an interlayer spacing of 0.74 nm, which can be attributed to the presence of various oxygen-containing groups on the surfaces of graphene oxide nanosheets (Kong and Wilson 2017; Dong *et al*. 2018). ZCA showed no obvious crystalline behavior due to the destruction of inter- and intra-molecular hydrogen bonding. After blending with GO, the crystalline structures of ZCA/GO turned amorphous, and this may be attributed to hydrogen bonding between ZCA and GO chains, which was also good evidence for high removal efficiency achieved by ZCA/GO composite adsorbent (Soylak *et al*. 2017).

SEM images

The FESEM method was employed to study the surface and cross-section morphology of the adsorbent. As shown in Fig. 4, the shape was regular, and the surface was rough with a large number of small holes. The inner structure was a porous cross-linked network, which indicated that the ZCA/GO composite adsorbent was more suitable for adsorption.
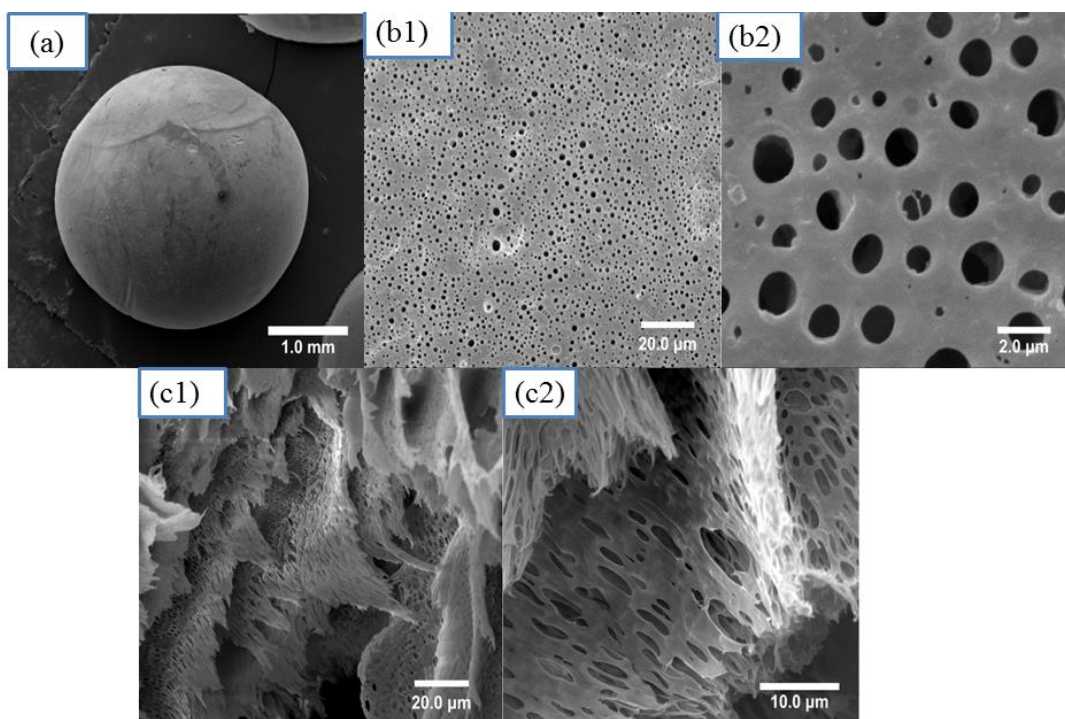

Fig. 4. SEM images of the surface (b1, b2) and cross-section (c1, c2) morphology of the adsorbent

BET analysis

N$_2$ adsorption-desorption isotherms of the ZCA/GO composite adsorbent are shown in Fig. 5 by BET analysis, which could demonstrate the existence of pore structure. The pore-size distribution of the ZCA/GO composite adsorbent in Fig. 5 showed that the average diameter of micropore was in the range of 30 to 90 nm, which could provide a large number of adsorption sites. The BET surface area and pore volume were 45.3 m^{2}g^{-1} and 0.249 cm^{3}g^{-1}, which was desirable for efficient and rapid removal of heavy metals. However, there is a lot of space for the improvement of the surface area and pore volume.
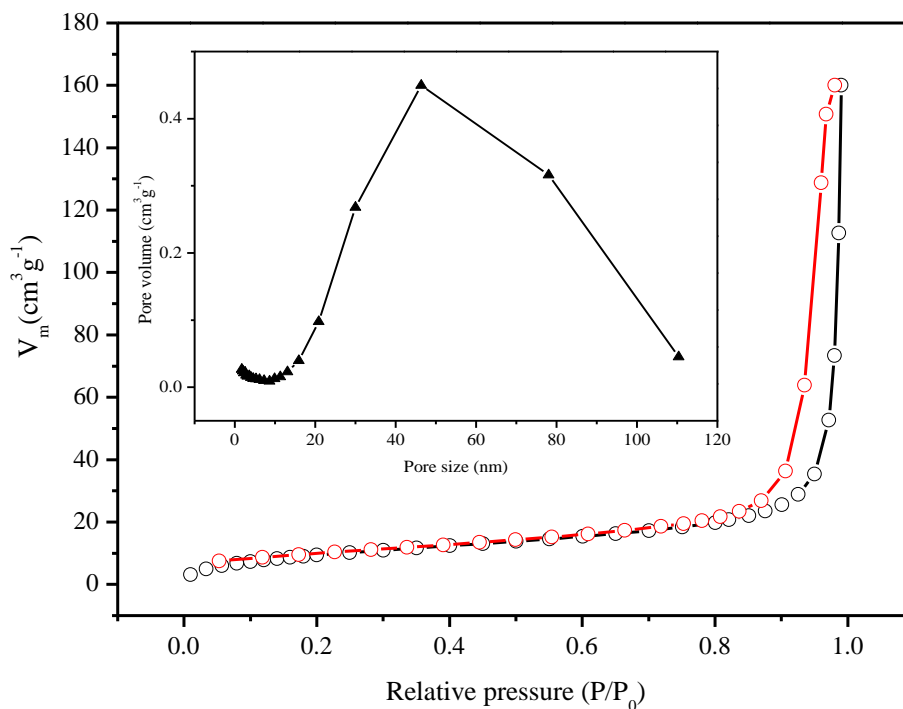
Fig. 5. N_2 adsorption-desorption isotherms and pore size distributions of the ZCA/GO composite adsorbent

Adsorption of Cu^{2+} and Cd^{2+} on ZCA/GO

To examine the adsorption behaviors of the above samples, adsorption experiments for Cu^{2+} and Cd^{2+} ions were conducted. In Fig. 6, adsorption capacity among CA, ZCA, and ZCA/GO is shown with a bar diagram.
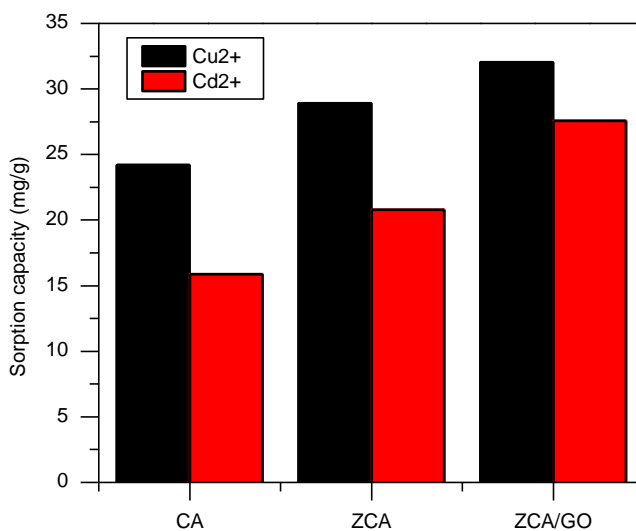

Fig. 6. The adsorption capacity of Cu^{2+} and Cd^{2+} on the prepared samples CA, ZCA, ZCA/GO

It is interesting to find that ZCA/GO samples showed the largest adsorption capacity among these samples for both Cu^{2+} and Cd^{2+}. Since sample ZCA/GO indicated

larger adsorption capacity for Cu^{2+} and Cd^{2+} in this case, the adsorption behaviors of sample ZCA/GO for Cu^{2+} and Cd^{2+} was examined for the study of adsorption kinetics and isotherms herein, respectively.

Effect of Adsorption Time

The effect of adsorption time on Cu^{2+} and Cd^{2+} adsorption is described in Fig. 7(a). As can be seen, the adsorption capacity rose very quickly during the first 10 min, and the adsorption equilibrium was gradually achieved within 120 min. Initially, the adsorption process was at a fast stage up to 120 min, and the maximum removal of Cu^{2+} and Cd^{2+} was 32.0 mg/g and 27.6 mg/g, respectively. After 120 min, the two curves in Fig. 6(a) were essentially unchanged. This indicated the adsorption saturability was reached. As a result, the adsorption experiments in the other parts were carried out for 120 min.

Effect of Cu^{2+} and Cd^{2+} Concentration

The 50 mL Cu^{2+} and Cd^{2+} solutions, with the concentration range from 25 mg/L to 200 mg/L, were placed in the flasks and added with 0.10 g of ZCA/GO, respectively. Then the adsorption experiment was taken under the condition of 25 °C and pH 5.5 for 120 min. Figure 7(b) shows the effect of initial ion concentration on the adsorption of ZCA/GO composite adsorbent. The better Cu^{2+} and Cd^{2+} adsorption capacity was achieved at the higher initial ion concentration. Before the ion concentration reached 100 mg/L, it had a linear relationship between initial concentration and adsorption capacity, which was because the ions gradually integrated with the active sites of ZCA/GO composite adsorbent easily with the rising ion concentration. The adsorption saturability was attained at a concentration of about 100 mg/L for Cu^{2+} and 75 mg/L for Cd^{2+}, at which the maximum adsorption capacities for Cu^{2+} and Cd^{2+} were 33 mg/g and 28 mg/g, respectively.

Effect of Initial pH

The optimum pH value of adsorption was different for the different kinds of heavy metal ions and adsorbent. The initial pH values of 100 mg/L Cu^{2+} and 75 mg/L Cd^{2+} were adjusted from 1.0 to 7.0 by HCl. The adsorption experiment was also taken under the condition of 25 °C for 120 min. The results are shown in Fig. 7(c).

As shown in Fig. 7(c), in the beginning, the adsorption capacity followed an approximate linear relationship with the initial pH. The maximum adsorption capacity was obtained at about pH 5.5 for both Cu^{2+} and Cd^{2+} adsorption. During the experiment, as the initial pH increased to over 5.6, the precipitation began to occur. On the other hand, the initial pH value cannot be too low, or the excessive H^+ would compete with the Cu^{2+} and Cd^{2+} to be adsorbed on the active sites of ZCA/GO composite adsorbent. Therefore, pH 4.5 to 5.5 was a suitable initial range for the batch experiments.

Effect of Temperature

The effect of ambient temperature on the adsorption of Cu^{2+} and Cd^{2+} was investigated between 15 °C and 45 °C, and the results are presented in Fig. 7(d). The uptakes of Cu^{2+} and Cd^{2+} were increased from 17.3 mg/g and 20.6 mg/g to 28.2 mg/g and 33.4 mg/g, respectively, as the temperature increased from 15 °C to 45 °C. It is suggested that the increase of ambient temperature facilitated the adsorption of Cu^{2+} and Cd^{2+} onto ZCA/GO and that this process was dominated by endothermic character.
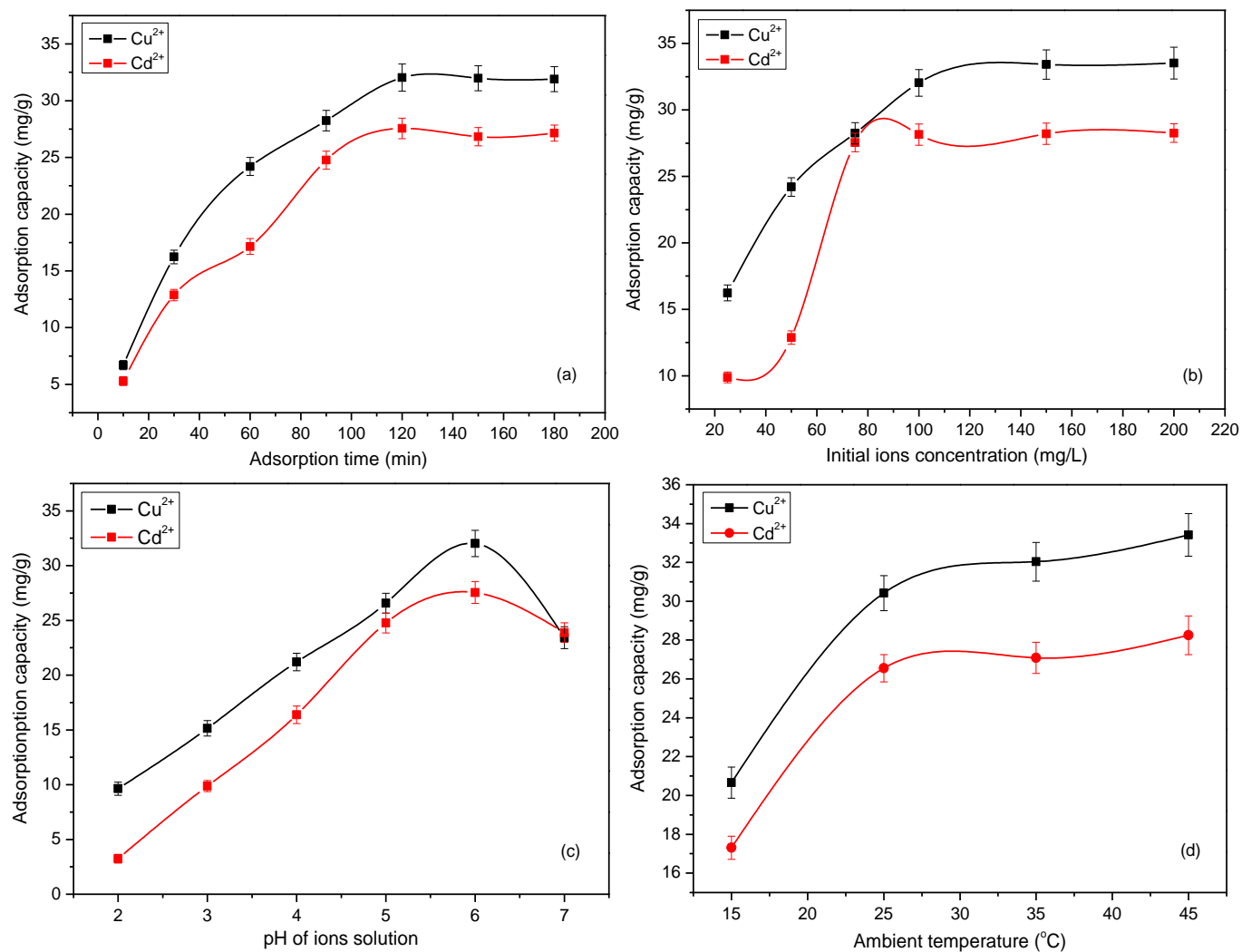
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Fig. 7. The effects of sorption time (a); initial ions concentration (b); pH (c); ambient temperature (d) for Cu^{2+} and Cd^{2+} on the prepared sample ZCA/GO

It is well known that ambient temperature has an important influence on the random motion of adsorbate and the fracture or combination of chemical bonds between the adsorption and binding sites. However, the sorption capacity did not improve obviously after 25 °C. Therefore, the ambient temperature was chosen at 25 °C for further study.

Adsorption Mechanism of Cu^{2+} and Cd^{2+} on ZCA/GO

The adsorption mechanism was studied by using the Langmuir isotherm model and the Freundlich isotherm model. The Langmuir isotherm equation is based on an assumption of monolayer adsorption on the active sites of the adsorbent. The Langmuir model can be expressed as Eq. 5 (Hu *et al*. 2016; Zhou *et al*. 2016),

$$\frac{c_e}{q_e} = \frac{1}{bQ_{max}} + \frac{c_e}{Q_{max}} \tag{5}$$

where c_e (mg/L) and q_e (mg/g) are the equilibrium concentrations of metal ion and the adsorption capacity, respectively. Q_{max} (mg/g) and b (L/mg) are the Langmuir constants, which represent the saturation adsorption capacity and adsorption energy.

However, the Freundlich isotherm model is considered as the adsorption occurred on a heterogeneous surface with uniform energy; which can be expressed as Eq. 6 (Deng *et al*. 2017),

$$\ln q_e = \ln K_f + \frac{1}{n} \ln c_e \tag{6}$$

where c_e (mg/L) and q_e (mg/g) are the equilibrium concentrations of metal ion and the adsorption capacity, respectively. K_f and n are the Freundlich constants, which can be calculated from the slope and intercept of the linear plot.
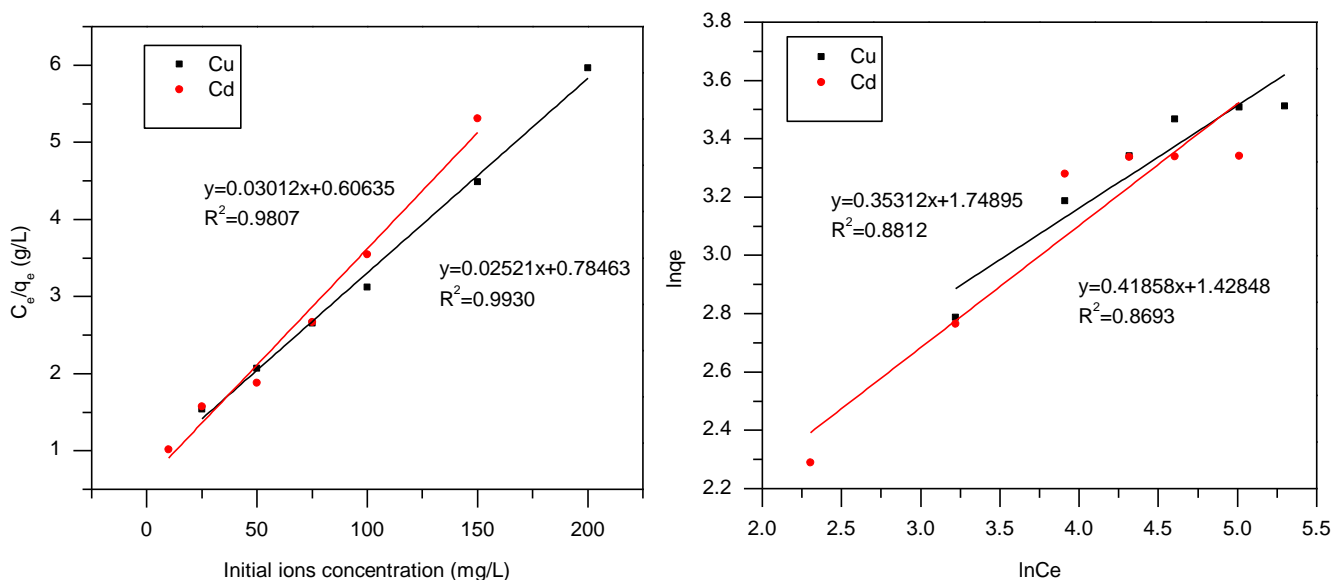

**Fig. 8.** Adsorption isotherm of Cu^{2+} and Cd^{2+} ions on sample ZCA/GO: (a) Langmuir model; (b) Freundlich model

Table 1. Langmuir and Freundlich Isotherm Parameters for Cu^{2+} and Cd^{2+} Adsorption

		ZCA/GO-Cu	ZCA/GO-Cd
Langmuir	Q_m (mg/g)	32.03	27.55
	K_l (L/mg)	0.032	0.049
	R^2	0.9930	0.9807
Freundlich	K_f ($mg^{(1-n)}L^n/g$)	5.748	4.172
	n	2.83	2.39
	R^2	0.8812	0.8693

The isotherm fitting results are shown in Fig. 8 and Table 1. The values of the coefficient of determination (R^2) for the adsorption of Cu^{2+} and Cd^{2+} onto ZCA/GO obtained from the Langmuir model were 0.9930 and 0.9807, respectively, which were higher than that from the Freundlich model. It can be seen that the experimental data fitted well with the Langmuir isotherm model. Based on these results, it can be deduced that the adsorption process is Langmuir monolayer adsorption rather than heterogeneous surface adsorption.

Table 2. Pseudo-Second-Order Kinetics Model Parameter

	ZCA/GO		
Anion	R^2	K_2	Q_e (mg/g)
Cu^{2+}	0.988	0.031	41.65
Cd^{2+}	0.968	0.027	37.45
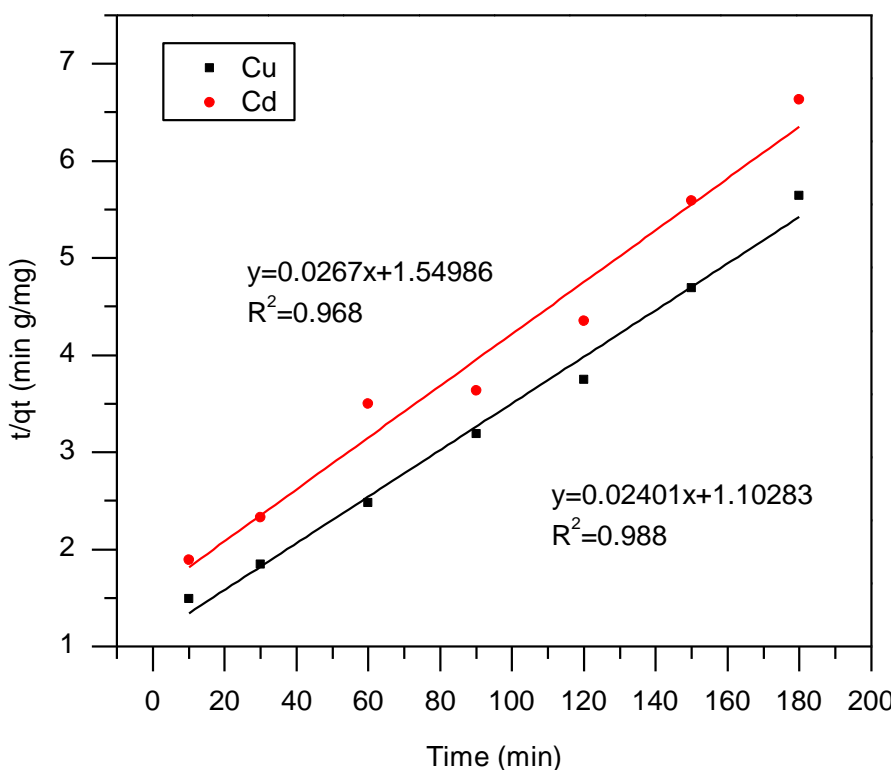
Fig. 9. The pseudo-second-order kinetics

To quantify the changes in adsorption with times, pseudo-first-order and pseudo-second-order were investigated and compared to get an appropriate kinetic model. The pseudo-second-order model is expressed by Eq. 7 (Jia *et al.* 2015),

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{7}$$

where q_e and q_t represent the amount of heavy metal ions adsorbed at equilibrium and at time t, respectively (mg/g), t is the contact time (min), and k_2 is the equilibrium rate constant of pseudo-second-order adsorption (min mg/g).

The fitting results corresponding to the pseudo-second-order are given in Fig. 9 and Table 2. The pseudo-second-order model describes the adsorption data with higher R^2 approaching 1 (0.968, 0.988), which was obviously higher than the pseudo-first-order ($R^2 = 0.36, 0.34$).

Regeneration and Reusability

Reusability and regeneration properties are very important for the practical use of adsorbents (Gu *et al.* 2015). After the attainment of equilibrium, the ZCA/GO composite adsorbent was washed several times with distilled water to remove any unabsorbed heavy metal ions. Thereafter, the adsorbents were immersed into 0.1 M HCl solution (50 mL) for 2 h to remove the adsorbed ions and then regenerated with 0.1 M NaOH for 2 h. Finally, before the adsorption experiment, the adsorbents were thoroughly washed with DI water to reach a neutral pH. Figure 10 shows the experimental results in five consecutive adsorption-desorption cycles.
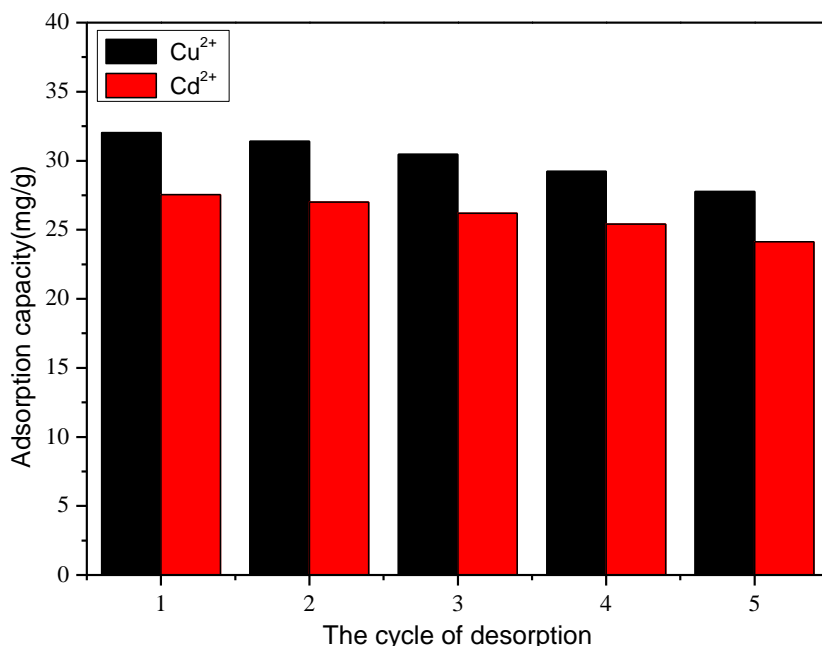

Fig. 10. Influence of the reuse cycles on the adsorption capacity and reuse percentage of ZCA/GO saturated with Cu^{2+} and Cd^{2+} (conditions: t=120 min, C_0=100 mg/L for Cu^{2+}, C_0=75 mg/L for Cd^{2+}, Dose=2 g/L, pH=5.5, T=25 °C)

Furthermore, it can be seen that, in 5 cycles, the fouling resistant ability adsorbent could still maintain 85% of Cu^{2+} and Cd^{2+} removal performance compared with that of the new adsorbents. This was because the introduction of zwitterion can improve the fouling resistant ability effectively (Jain *et al*. 2016). These observations suggest that ZCA/GO composite adsorbent could be reported as promising material for the separation and recovery of heavy metal ions from wastewater.

CONCLUSIONS

In this work, the ZCA was prepared by employing three types of chemical reaction including oxidization, Schiff base, and quaternary amination reaction. A ZCA/GO composite adsorbent was prepared by sol-gel method and then freeze-dried to obtain spheres with a porous structure. The BET surface area and pore volume were 45.3 m^2g^{-1} and 0.249 cm^3g^{-1}, which was desirable for efficient and rapid removal of heavy metals. The adsorption behaviors for Cu^{2+} and Cd^{2+} ions confirmed that the adsorption followed pseudo-second-order kinetic model and Langmuir monolayer adsorption, which might be related to the electrostatic attraction between the ionic groups and the metal ions. What is more, the desorption and reusability analysis displayed that the adsorption of ZCA/GO was about 90% of the initial saturation adsorption capacity after repeated use 5 times, indicating that they are promising absorbents for practical application in industry.

ACKNOWLEDGMENTS

REFERENCES CITED

Abdelwahab, N. A., Ammar, N. S., and Ibrahim, H. S. (2015). "Graft copolymerization of cellulose acetate for removal and recovery of lead ions from wastewater," *Int. J. Biol. Macromol.* 79, 913-922. DOI: 10.1016/j.ijbiomac.2015.05.022

Aziz, A. S. A., Manaf, L. A., Man, H. C., and Kumar, N. S. (2014). "Kinetic modeling and isotherm studies for copper (II) adsorption onto palm oil boiler mill fly ash (POFA) as a natural low-cost adsorbent," *BioResources* 9(1), 336-356. DOI: 10.15376/biores.9.1.336-356

Chen, J. H., Ni, J. C., Liu, Q. L., and Li, S. X. (2012). "Adsorption behavior of Cd(II) ions on humic acid-immobilized sodium alginate and hydroxyl ethyl cellulose blending porous composite membrane adsorbent," *Desalination* 285(3), 54-61. DOI: 10.1016/j.desal.2011.09.033

Deng, J., Liu, Y., Liu, S., Zeng, G., Tan, X., Huang, B., Tang, X., Wang, S., Hua, Q., and Yan, Z. (2017). "Competitive adsorption of Pb(II), Cd(II) and Cu(II) onto chitosan-pyromellitic dianhydride modified biochar," *J. Colloid Interface Sci.* 506 355-364. DOI: 10.1016/j.jcis.2017.07.069

Dong, Z., Zhao, J., Du, J., Li, C., and Zhao, L. (2016). "Radiation synthesis of spherical

cellulose-based adsorbent for efficient adsorption and detoxification of Cr(VI),"
Radiat. Phys. Chem. 126, 68-74. DOI: 10.1016/j.radphyschem.2016.05.013

Dong, C. C., Lu, J., Qiu, B. C., Xing, M. Y., and Zhang, J. L. (2018). "Developing
stretchable and graphene-oxide-based hydrogel for the removal of organic pollutants
and metal ions," *Applied Catalysis B: Environmental* 222, 146-156. DOI:
10.1016/j.apcatb.2017.10.011

El-Naggar, A. H., Alzhrani, A. K. R., Ahmad, M., Usman, A. R. A., Mohan, D., Ok, Y.
S., and Al-Wabel, M. I. (2016). "Preparation of activated and non-activated carbon
from conocarpus pruning waste as low-cost adsorbent for removal of heavy metal
ions from aqueous solution," *BioResources* 11(1), 1092-1107. DOI:
10.15376/biores.11.1.1092-1107

Fan, G., Wang, M., Liao, C., Fang, T., Li, J., and Zhou, R. (2013). "Isolation of cellulose
from rice straw and its conversion into cellulose acetate catalyzed by phosphotungstic
acid," *Carbohydr. Polym.* 94(1), 71-76. DOI: 10.1016/j.carbpol.2013.01.073

Gu, Z., Gao, M., Lu, L., Liu, Y., and Yang, S. (2015). "Montmorillonite functionalized
with zwitterionic surfactant as a highly efficient adsorbent for herbicides," *Ind. Eng.
Chem. Res.* 54(18), 4947-4955. DOI: 10.1021/acs.iecr.5b00438

Hu, C., Hu, H., Zhu, J., Deng, Y., and Li, C. (2016). "Adsorption of Cu^{2+}, on
montmorillonite and chitosan-montmorillonite composite toward acetate ligand and
the pH dependence," *Water, Air, Soil Pollut.* 227(10), 1-10. DOI: 10.1007/s11270-
016-3067-9

Hu, L. Q., Dai, L., Liu, R., and Si, C. L. (2017). "Lignin-graft-poly(acrylic acid) for
enhancement of heavy metal ion biosorption," *J. Mater. Sci.* 52(24), 13689-13699.
DOI: 10.1007/s10853-017-1463-1

Hubbe, M. A., Park, J., and Park, S. (2014). "Cellulosic substrates for removal of
pollutants from aqueous systems: A review. Part 4. Dissolved petrochemical
compounds," *BioResources* 9(4) 7782-7925. DOI: 10.15376/biores.9.4.7782-7925.

Jain, M., Garg, V. K., Kadirvelu, K., and Sillanpää, M. (2016). "Adsorption of heavy
metals from multi-metal aqueous solution by sunflower plant biomass-based carbons,"
Int. J. Environ. Sci. Technol. 13(2), 493-500. DOI: 10.1007/s13762-015-0855-5

Jia, Q., Li, D., Gao, X., Yan, J., Ma, Q., and Meng, F. (2015). "Hydrazinolyzed cellulose-
g-polymethyl acrylate as adsorbent for efficient removal of Cu(II) and Ni(II) ions
from aqueous solution," *J. Chem. Technol. Biotechnol.* 91(5), 1378-1386. DOI:
10.1002/jctb.4734

Kong, D., and Wilson, L. D. (2017). "Synthesis and characterization of cellulose-goethite
composites and their adsorption properties with roxarsone," *Carbohydr. Polym.* 169,
282-294. DOI: 10.1016/j.carbpol.2017.04.019

Lin, C., Qiao, S., Luo, W., Liu, Y., Liu, D., Li, X., and Liu, M. (2014).
"Thermodynamics, kinetics, and regeneration studies for adsorption of Cr(VI) from
aqueous solutions using modified cellulose as adsorbent," *BioResources* 9(4), 6998-
7017. DOI: 10.15376/biores.9.4.6998-7017.

Liu, J., Ma, Y., Xu, T., and Shao, G. (2010). "Preparation of zwitterionic hybrid polymer
and its application for the removal of heavy metal ions from water," *J. Hazard. Mater.*
178(1-3), 1021-1029. DOI: 10.1016/j.jhazmat.2010.02.041

Liu, G., Zhang, L., Mao, S., Rohani, S., Ching, C., and Lu, J. (2015). "Zwitterionic
chitosan–silica–PVA hybrid ultrafiltration membranes for protein separation," *Sep.
Purif. Technol.* 152, 55-63. DOI: 10.1016/j.seppur.2015.08.006

Liu, Y., Huang, H., Huo, P., and Gu, J. (2017). "Exploration of zwitterionic cellulose

acetate antifouling ultrafiltration membrane for bovine serum albumin (BSA) separation," *Carbohydr. Polym.* 165, 266-275. DOI: 10.1016/j.carbpol.2017.02.052

Ma, L., Chen, Q., Zhu, J., Xi, Y., He, H., Zhu, R., Tao, Q., and Ayoko, G. A. (2016). "Adsorption of phenol and Cu(II) onto cationic and zwitterionic surfactant modified montmorillonite in single and binary systems," *Chem. Eng. J.* 283, 880-888. DOI: 10.1016/j.cej.2015.08.009

Ma, X., Liu, C., Anderson, D. P., and Chang, P. R. (2016). "Porous cellulose spheres: Preparation, modification and adsorption properties," *Chemosphere* 165, 399-408. DOI: 10.1016/j.chemosphere.2016.09.033

Ma, Y. X., Xing, D., Shao, W. J., Du, X. Y., and La, P. Q. (2017). "Preparation of polyamidoamine dendrimers functionalized magnetic graphene oxide for the adsorption of Hg(II) in aqueous solution," *J. Colloid Interface Sci.* 505, 352-363. DOI: 10.1016/j.jcis.2017.05.104

Pan, N., Li, L., Ding, J., Wang, R., Jin, Y., and Xia, C. (2017). "A Schiff base/quaternary ammonium salt bifunctional graphene oxide as an efficient adsorbent for removal of Th(IV)/U(VI)," *J. Colloid Interface Sci.* 508(2), 303-312. DOI: 10.1016/j.jcis.2017.08.068

Rull-Barrull, J., d'Halluin, M., Le Grognec, E., and Felpin, F. X. (2016). "Harnessing the dual properties of thiol-grafted cellulose paper for click reactions: A powerful reducing agent and adsorbent for Cu," *Angew. Chem.* 55(43), 13549-13552. DOI: 10.1002/anie.201606760

Soylak, M., Acar, D., Yilmaz, E., El-Khodary, S. A., Morsy, M., and Ibrahim, M. (2017). "Magnetic graphene oxide as an efficient adsorbent for the separation and preconcentration of Cu(II), Pb(II), and Cd(II) from environmental samples," *J. AOAC Int.* 100(5), 1544-1550. DOI: 10.5740/jaoacint.16-0230

Srivastava, N., Thakur, A. K., and Shahi, V. K. (2016). "Phosphorylated cellulose triacetate-silica composite adsorbent for recovery of heavy metal ion," *Carbohydr. Polym.* 136, 1315-1322. DOI: 10.1016/j.carbpol.2015.10.047

Suteu, D., and Malutan, T. (2013). "Industrial cellolignin wastes as adsorbent for removal of methylene blue dye from aqueous solutions," *BioResources* 8(1), 427-446. DOI: 10.15376/biores.8.1.427-446

Tang, J., Huang, Y., Gong, Y., Lyu, H., Wang, Q., and Ma, J. (2016). "Preparation of a novel graphene oxide/Fe-Mn composite and its application for aqueous Hg(II) removal," *J. Hazard. Mater.* 316, 151-158. DOI: 10.1016/j.jhazmat.2016.05.028

Tsai, H. S., Wang, Y. Z., Lin, J. J., and Lien, W. F. (2010). "Preparation and properties of sulfopropyl chitosan derivatives with various sulfonation degree," *J. Appl. Polym. Sci* 116(3), 1686-1693. DOI: 10.1002/app.31689

Wang, Y., Li, L., Luo, C., Wang, X., and Duan, H. (2016). "Removal of Pb^{2+} from water environment using a novel magnetic chitosan/graphene oxide imprinted Pb^{2+}," *Int. J. Biol. Macromol.* 86, 505-511. DOI: 10.1016/j.ijbiomac.2016.01.035

Wang, F. T, Pan, Y. F, Cai, P. X, Guo, T. X, and Xiao, H. N. (2017a). "Single and binary adsorption of heavy metal ions from aqueous solutions using sugarcane cellulose-based adsorbent," *Bioresource Technol.* 241, 482-490. DOI: 10.1016/j.biortech.2017.05.162

Wang, Z., Shen, D., Shen, F., Wu, C., and Gu, S. (2017b). "*Ginkgo biloba*, L. shells-based adsorbent for the removal of Cu^{2+} and Cd^{2+} from aqueous solution: Kinetics, isotherm, thermodynamics and mechanisms," *J. Mol. Liq.* 241, 603-611. DOI: 10.1016/j.molliq.2017.05.102

Xing, M. Y, Qiu, B. C, Du, M. M, Zhu, Q. H, Wang, L. Z, and Zhang, J. L. (2017). "Spatially separated CdS shells exposed with reduction surfaces for enhancing photocatalytic hydrogen evolution," *Advanced Functional Materials* 27(35). DOI: 10.1002/adfm.201702624

Yang, J., Kubota, F., Baba, Y., Kamiya, N., and Goto, M. (2014). "Application of cellulose acetate to the selective adsorption and recovery of Au(III)," *Carbohydr. Polym.* 111, 768-774. DOI: 10.1016/j.carbpol.2014.05.003

Zhang, M., Ding, C., Chen, L., and Huang, L. (2015). "Preparation of tannin-immobilized collagen/cellulose bead for Pb(II) adsorption in aqueous solutions," *BioResources* 10(1), 1773-1789. DOI: 10.15376/biores.10.1.1773-1789.

Zhang, L., Luo, H., Liu, P., Fang, W., and Geng, J. (2016). "A novel modified graphene oxide/chitosan composite used as an adsorbent for Cr(VI) in aqueous solutions," *Int. J. Biol. Macromol.* 87, 586-596. DOI: 10.1016/j.ijbiomac.2016.03.027

Zhou, G., Luo, J., Liu, C., Chu, L., Ma, J., Tang, Y., Zeng, Z., and Luo, S. (2016). "A highly efficient polyampholyte hydrogel sorbent based fixed-bed process for heavy metal removal in actual industrial effluent," *Water Res.* 89, 151-160. DOI: 10.1016/j.watres.2015.11.053