A Spherical Zwitterionic Cellulose Acetate/Graphene Oxide Composite Adsorbent for Efficient Removal of Cu$^{2+}$ and Cd$^{2+}$ 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$^2$/g and 0.249 cm$^3$/g. 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.

Keywords: Zwitterionic cellulose acetate; Graphene oxide; Adsorption; Heavy metal

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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.
from Tokyo Chemical Industry (TCI) (Tokyo, Japan). Dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidinone (NMP), ethylene glycol, ethanol, cupric nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O), cadmium nitrate tetrahydrate (CdN$_2$O$_6$·4H$_2$O), 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)](image-url)
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,
\[ q_e = \frac{(c_0 - c_e)W}{M} \]  

\[ W = \frac{c_0 - c_e}{c_0} \times 100\% \]

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),

\[ RP = \frac{q_r}{q_e} \times 100\% \]  

\[ q_r = \frac{(c_0 - c_e)W}{M} \]

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 $2\theta = 11.14^\circ$ 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.

![SEM images](image_url)

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

**Effect of Adsorption Time**

The effect of adsorption time on Cu\textsuperscript{2+} and Cd\textsuperscript{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\textsuperscript{2+} and Cd\textsuperscript{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\textsuperscript{2+} and Cd\textsuperscript{2+} Concentration**

The 50 mL Cu\textsuperscript{2+} and Cd\textsuperscript{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\textsuperscript{2+} and Cd\textsuperscript{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\textsuperscript{2+} and 75 mg/L for Cd\textsuperscript{2+}, at which the maximum adsorption capacities for Cu\textsuperscript{2+} and Cd\textsuperscript{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\textsuperscript{2+} and 75 mg/L Cd\textsuperscript{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\textsuperscript{2+} and Cd\textsuperscript{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\textsuperscript{+} would compete with the Cu\textsuperscript{2+} and Cd\textsuperscript{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\textsuperscript{2+} and Cd\textsuperscript{2+} was investigated between 15 °C and 45 °C, and the results are presented in Fig. 7(d). The uptakes of Cu\textsuperscript{2+} and Cd\textsuperscript{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\textsuperscript{2+} and Cd\textsuperscript{2+} onto ZCA/GO and that this process was dominated by endothermic character.
Fig. 7. The effects of sorption time (a); initial ions concentration (b); pH (c); ambient temperature (d) for Cu²⁺ and Cd²⁺ 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),

\[
\frac{c_e}{q_e} = \frac{1}{bQ_{\text{max}}} + \frac{c_e}{Q_{\text{max}}}
\]

where \(c_e\) (mg/L) and \(q_e\) (mg/g) are the equilibrium concentrations of metal ion and the adsorption capacity, respectively. \(Q_{\text{max}}\) (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),

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln c_e
\]

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.

![Graph](https://example.com/graph.png)

**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

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

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

<table>
<thead>
<tr>
<th>Anion</th>
<th>ZCA/GO</th>
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<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$K_2$</td>
<td>$Q_e$ (mg/g)</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>0.988</td>
<td>0.031</td>
<td>41.65</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>0.968</td>
<td>0.027</td>
<td>37.45</td>
</tr>
</tbody>
</table>

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),

\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2q_e^2}
\]

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 \( \text{Cu}^{2+} \) and \( \text{Cd}^{2+} \) (conditions: \( t=120 \) min, \( C_0=100 \) mg/L for \( \text{Cu}^{2+} \), \( C_0=75 \) mg/L for \( \text{Cd}^{2+} \), 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\(^2\)g\(^{-1}\) and 0.249 cm\(^3\)g\(^{-1}\), 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.

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