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Removal of Cd(II) from aqueous solution by a composite hydrogel based on attapulgite

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Chitosan-*g*-poly(acrylic acid)/attapulgite composite with 30 wt% attapulgite content was used to remove Cd(II) from aqueous solutions. The parameters influencing the adsorption were investigated. When Cd(CH₃COO)₂ was used as the solute of the solution, the equilibrium adsorption capacity was evidently larger than that of the other three cadmium salts (Cd(NO₃)₂, CdCl₂, CdSO₄). Results from kinetic experiments showed that the rate of Cd(II) adsorption on the composite was quite fast, more than 90% of Cd(II) adsorption occurred within the initial 3 min, and the adsorption equilibrium may be reached within 10 min. The adsorption process can be well described by the pseudo-second-order kinetic model. The equilibrium adsorption isotherm was fitted for not only the Langmuir model but also the Freundlich model. Fourier transform infrared spectra before and after adsorption of Cd(II) on the composite showed that complexation was considered as the main mechanism. To evaluate the reuse value of the composite, a consecutive adsorption–desorption process was performed five times, and the results implied that the composite has the potential for regeneration and reuse.

Keywords: composite hydrogel; attapulgite; cadmium; adsorption mechanism; thermodynamic parameters

Introduction

It is now recognized that adsorption using low-cost adsorbents is an effective and economic method for water decontamination. With the selection of a proper adsorbent, the adsorption process can be a promising technique for the removal of Cd(II) from wastewater [1–3]. Hydrogels are slightly cross-linked hydrophilic polymers with excellent three-dimensional cross-linked polymeric networks consisting of flexible chains. Recently, the preparation of organic–inorganic composite hydrogels has attracted a great deal of attention because of their low production cost, higher mechanical resistance and extensive applications. Composite hydrogels based on clay may be used as alternative adsorbents for the removal of metal ions or dyes from aqueous solution [4,5].

Attapulgite (APT) is a natural clay mineral that is found in many places of the world. It is a crystalline hydrated magnesium silicate with a fibrous morphology, large specific surface area and moderate cation exchange capacity, and has been widely studied as an adsorbent for the removal of heavy metals from solutions [6–8]. However, the adsorption capability of natural APT is very poor [6,9]; some special treatments or modifications, such as heat treatment, acid treatment [7] or graft reaction [8], are needed to enhance its adsorption performance and selectivity.

In our previous study, we prepared a series of chitosan-*g*-poly(acrylic acid)/attapulgite (CTS-*g*-PAA/APT) composite hydrogels [10] and found that such composite hydrogels are excellent adsorbents for copper ions, with a high adsorption capacity and fast adsorption rate [11]. To discover whether the composite hydrogels are also excellent adsorbents for Cd(II), in the present study a composite with 30 wt% attapulgite (CTS-*g*-PAA/30%APT) was selected and used to remove Cd(II) from aqueous solutions. The parameters influencing the adsorption capacity of the composite, such as the species of cadmium salts (Cd(NO₃)₂, CdCl₂, CdSO₄ and Cd(CH₃COO)₂), the initial pH value (pH₀) of the Cd(II) solution, contact time (*t*) and the initial Cd(II) concentration (*C*₀) were investigated. The adsorption kinetics and isotherms of the composite for Cd(II) were studied, and the desorption study of the composite was also investigated. To understand the adsorption mechanism, Fourier transform infrared (FTIR) spectroscopy was used to characterize the adsorption samples.

Experimental

Materials

Acrylic acid (AA, distilled under reduced pressure before use), ammonium persulphate (APS, recrystallized

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from distilled water before use) and *N,N'*-methylenebisacrylamide (MBA, used as received) were supplied by Shanghai Reagent Corp. (Shanghai, China). Chitosan (degree of deacetylation: 0.85, average molecular weight: 3×10^5) was supplied by Zhejiang Yuhuan Ocean Biology Co. (Zhejiang, China). Attapulgit (supplied by Jiangsu Autobang International Co., Ltd, Jiangsu, China) was milled and sieved through a 320-mesh screen. The cation exchange capacity of the APT sample was 30.0 meq per 100 g.

Cadmium acetate solution, prepared by dissolving a certain amount of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (analytical reagent, 266.53, supplied by Shanghai Chemical Reagent Factory, Shanghai, China) in distilled water, was taken as the adsorptive solution. Other cadmium salts such as $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (guaranteed reagent, 228.34), $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (analytical reagent, 769.58) and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (analytical reagent, 308.49) were also supplied by Shanghai Chemical Reagent Factory (Shanghai, China). Other reagents used were all of analytical grade, and all aqueous solutions were prepared with distilled water.

Preparation of the composite

The CTS-g-PAA/30%APT composite was prepared according to our previous reports [10]. Half a gram of CTS was dissolved in 30 mL acetic acid solution (1%) in a 250 mL four-neck flask, equipped with a mechanical stirrer, a reflux condenser, a funnel and a nitrogen line. After being purged with nitrogen for 30 min to remove the oxygen dissolved from the system, the solution was heated to 333 K, and then 0.10 g APS was introduced to initiate the CTS to generate radicals. Ten minutes later, the mixed solution of 3.60 g AA, 0.15 g MBA and 1.86 g APT was added. The water bath was kept at 333 K for 3 h. The resulting granular product was transferred into sodium hydroxide aqueous solution (1 mol L^{-1}) to be neutralized to pH 7.0, and then dehydrated with ethanol as a dewatering agent. After wiping off excessive ethanol on the surface using filter paper, the sample was spread on a dish to dry overnight at room temperature. The product was milled and sieved through an 80-mesh screen. The preparation procedure of CTS-g-PAA was similar to that of CTS-g-PAA/30%APT composite except without APT.

Adsorption experiments

All batch adsorption experiments were carried out by mixing 0.1 g of adsorbent with 25 mL of Cd(II) solution with the desired concentration and pH_0 , and then the mixture was shaken in a thermostatic shaker bath (THZ-98A) at 120 rpm at 303 K (except for the temperature

influence) for a given time. The pH values of the initial cadmium acetate solutions were adjusted with dilute acetic acid or sodium hydroxide solution using a Mettler Toledo 320 pH meter. Considering the high adsorption capacity of the composite for Cd(II), very high initial Cd(II) concentrations were selected in the study. For the kinetic study, a concentration of 2248 mg L^{-1} was selected as the initial Cd(II) concentration of the cadmium acetate solution. For equilibrium adsorption experiments at different temperatures, cadmium acetate solutions with initial Cd(II) concentrations ranging from 1211 mg L^{-1} to 2975 mg L^{-1} were used. In order to observe the effect of different cadmium salts on the Cd(II) adsorption by the composite, different cadmium salts such as $\text{Cd}(\text{NO}_3)_2$, CdCl_2 , CdSO_4 and $\text{Cd}(\text{CH}_3\text{COO})_2$ were used, and all of the solutions had the same C_0 (2248 mg L^{-1}) and pH_0 (6.5). The pH value of each cadmium salt solution was adjusted with the corresponding aqueous acid solution.

The suspensions after adsorption were centrifuged at 5000 rpm for 10 min, and the pH of each suspension was measured with a pH meter. Both the initial and the final concentrations of Cd(II) in solutions were determined by the EDTA titrimetric method using 0.005 mol L^{-1} EDTA solution as the standard solution and 0.5% xylene orange solution as the indicator. The amount of Cd(II) adsorbed at time t or at equilibrium by the material can be calculated by using Equation (1):

$$q = [V(C_0 - C)]/m \quad (1)$$

where q is the amount of Cd(II) adsorbed at time t or at equilibrium (mg g^{-1}), C_0 is the initial concentration of Cd(II) solution (mg L^{-1}). C is the liquid-phase Cd(II) concentration at time t or at equilibrium (mg L^{-1}), m is the mass of adsorbent used (g) and V is the volume of Cd(II) solution used (L).

Desorption and regeneration experiments

The cadmium-loaded sample was prepared by mixing 0.5 g of the composite and 125 mL of cadmium acetate solution (C_0 2248 mg L^{-1} , pH_0 6.5) and shaking the mixture at 303 K for 60 min. For the desorption study, the cadmium-loaded sample was agitated with 0.05 mol L^{-1} of an appropriate volume of hydrochloric acid solution (dose: 0.1 g per 20 mL) on a magnetic agitator at 220 rpm for 30 min at room temperature. In order to estimate the recycling property of the composite, the adsorption-desorption process was performed five times. Accompanying each adsorption or desorption process, the sample was washed with distilled water three times to remove Cd(II) ions or hydrochloric acid before being dried at 358 K.

Characterization

Fourier transform infrared spectra measurements were done on a Nicolet Nexus TM spectrophotometer (Thermo, Madison, USA) using KBr pellets. The spectrum was collected 32 times and corrected for background noise. A JSM-6701F field-emission scanning electron microscope (FE-SEM) (JEOL, Tokyo, Japan) was used to investigate the surface morphology of the sample after Cd(II) adsorption. The specific surface area of the composite measured by using an Accelerated Surface Area and Porosimetry System (ASAP 2020, Micromeritics, Atlanta, USA) by the BET method at 76 K.

Results and discussion

Effect of the species of cadmium salt on adsorption

To investigate the effect of the species of cadmium salt on the Cd(II) adsorption by the composite, four cadmium salts, $\text{Cd}(\text{NO}_3)_2$, CdCl_2 , CdSO_4 and $\text{Cd}(\text{CH}_3\text{COO})_2$, were selected. The result of the effect of the species of cadmium salts on the adsorption capacity of the composite for Cd(II) are shown in Table 1. It can be seen that the adsorption capacities were different when different cadmium salts were used as the solute of the solution. A similar phenomenon for Cu(II) has been observed by Chen and Wang [12]. When $\text{Cd}(\text{CH}_3\text{COO})_2$ was used as the solute of the solution, the equilibrium adsorption capacity is evidently larger than that of the other three cadmium salts. Also, different adsorption phenomena were observed for the different cadmium salts. The sample was dispersive in the solution when $\text{Cd}(\text{CH}_3\text{COO})_2$ was used as the solute; however, when $\text{Cd}(\text{NO}_3)_2$, CdCl_2 and CdSO_4 were used as the solutes, the samples were all found to be conglomerated. In order to investigate the surface morphology of the sample after Cd(II) adsorption when using different cadmium salts as the solute of the solution, SEM was used in this section (shown in Figure 1). It can be seen from Figure 1d that, when using $\text{Cd}(\text{CH}_3\text{COO})_2$ as the solute of the solution, the sample showed a much looser and more alveolate structure. The difference in adsorption phenomenon and the surface morphology of the sample after Cd(II) adsorption when using different cadmium salts as the solute of the solution may indicate that the

Table 1. Effect of the species of cadmium salts on the Cd(II) adsorption capacity of the composite. Adsorption experiments: C_0 : 2248 mg L⁻¹; sample dose: 0.1 g per 25 mL; pH_0 : 6.50; T : 303 K; t : 60 min.

Sample	Equilibrium adsorption capacity (mg g ⁻¹)			
	$\text{Cd}(\text{NO}_3)_2$	CdCl_2	CdSO_4	$\text{Cd}(\text{CH}_3\text{COO})_2$
CTS-g-PAA/ 30%APT	133.7	126.8	130.2	323.2

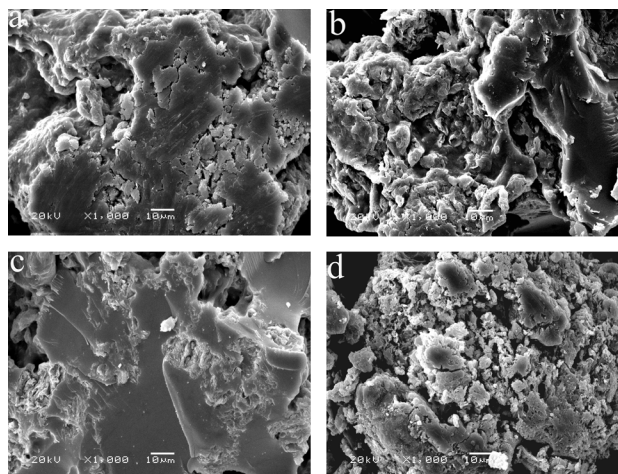


Figure 1. Scanning electron micrograph of the composite after Cd(II) adsorption when using different cadmium salts as the solute of the solution. (a) CdSO_4 , (b) $\text{Cd}(\text{NO}_3)_2$, (c) CdCl_2 , (d) $\text{Cd}(\text{CH}_3\text{COO})_2$.

Cd(II) adsorption by the composite may only occur on the surface of the particles when $\text{Cd}(\text{NO}_3)_2$, CdCl_2 and CdSO_4 are used as the solutes, whereas, when $\text{Cd}(\text{CH}_3\text{COO})_2$ is used as the solute, the adsorption may involve the internal functional groups in the composite.

To explain the differences in the Cd(II) adsorption process of the composite when using different cadmium salts as the solute of the solution, FTIR spectra were used to characterize the adsorption samples. When using $\text{Cd}(\text{CH}_3\text{COO})_2$ as the solute, it can be seen from Figure 2e that the stretching vibration absorption band of $-\text{COOH}$ groups near 1716 cm^{-1} almost disappeared and the stretching vibration absorption band of $-\text{COO}^-$ groups near 1561 cm^{-1} were obviously enhanced and shifted to the lower wavenumbers (1554 cm^{-1}). Moreover, the deformation vibration absorption bands of $-\text{OH}$ groups were obviously enhanced and shifted to the higher wavenumbers (1325 cm^{-1}). However, when using CdSO_4 , $\text{Cd}(\text{NO}_3)_2$ and CdCl_2 as the solute (Figure 2b, 2c and 2d, respectively), the strong stretching vibration absorption band of $-\text{COOH}$ groups and $-\text{COO}^-$ groups changed very little. Such a result indicated that the property of the anions existing in the solution may affect the Cd(II) adsorption on the composite, and the existence of CH_3COO^- anions in the solution may be more propitious to the Cd(II) complexation reaction of the composite than that of SO_4^{2-} , NO_3^- and Cl^- anions. However, it is still not clear how the anions in the solution may affect the Cd(II) adsorption by the composite, and further study is needed.

Effect of pH_0 on adsorption

Because the composite was prepared from CTS, AA and APT, there are $-\text{NH}_2$, $-\text{COOH}$ and $-\text{OH}$ groups

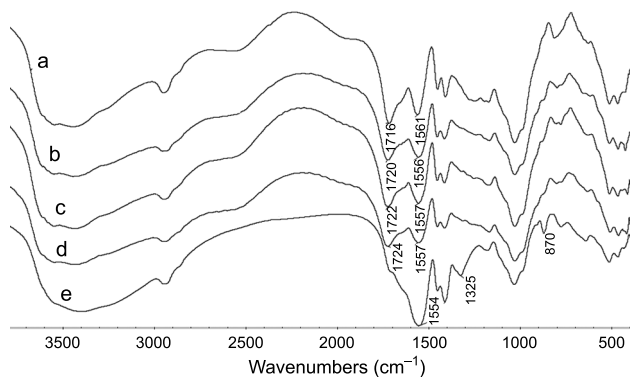
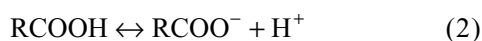


Figure 2. Comparison of IR spectra of the composite before and after Cd(II) adsorption when using different cadmium salts as the solute of the solution. (a) the composite before Cd(II) adsorption, (b) CdSO₄, (c) Cd(NO₃)₂, (d) CdCl₂, (e) Cd(CH₃COO)₂.

in the composite. At lower pH: (i) it can be expected that -NH₂ in the composite would be protonated and would be present in the form of NH₃⁺ ions; thus, the electrostatic repulsion may hold back the adsorption of Cd(II) ions on to the composite; (ii) meanwhile, -COOH groups in the composite cannot dissociate into -COO⁻ ions, which also does not favour the adsorption of Cd(II) ions on to the composite. Increasing the pH may result in more functional groups being available for binding of Cd(II) ions, and hence the adsorption capacity is enhanced. Results from the effect of pH₀ of the cadmium acetate solution on the Cd(II) adsorption substantiated such an expectation. In strong acid medium (pH < 4.50), the final pH of the solution is higher than the initial pH, which indicated that the H⁺ ions also competed with Cd(II) ions for binding with the surface groups of the composite. The reverse phenomenon was observed in weak acid medium (pH > 4.50), and the decrease in the final pH of the solution may be explained by the following equations:



It can be seen from Figure 3 (C_0 : 2248 mg L⁻¹; sample dose: 0.1 g per 25 mL; pH₀: 3.0–7.0; T : 303 K; t : 240 min) that a minimum adsorption capacity was found at pH₀ 3.0, and the adsorption capacity increased sharply with the increase in pH₀ from 3.0 to 5.0. At pH₀ greater than 6.0, the adsorption capacity of the composite for Cd(II) changed very little. Therefore, to ensure that Cd²⁺ ions would not be precipitated as hydroxide and for experimental convenience, a pH value of 6.5, close to neutral, was selected.

Effect of contact time and adsorption kinetics

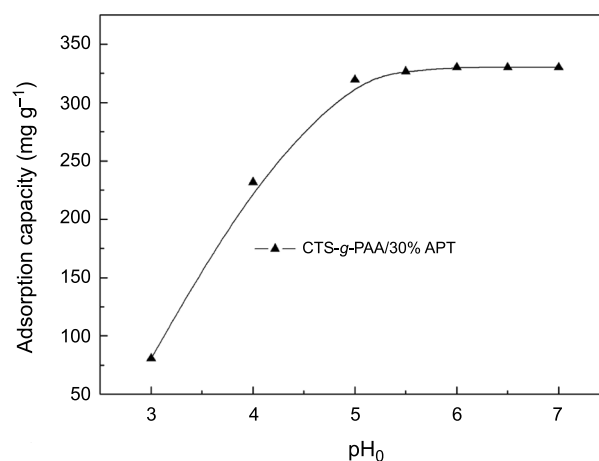


Figure 3. Effect of pH₀ on the Cd(II) adsorption capacity of the composite. Adsorption experiments – C_0 : 2248 mg L⁻¹; sample dose: 0.1 g per 25 mL; pH₀: 3.0–7.0; T : 303 K; t : 240 min.

Contact time is another important variable in adsorption processes [13]. Figure 4 shows the effect of contact time on the adsorption capacity of the composite for Cd(II) (C_0 : 2248 mg L⁻¹; sample dose: 0.1 g per 25 mL; pH₀: 6.5; T : 303 K). Obviously, the adsorption process is a quite rapid process, and more than 90% of Cd(II) adsorption occurred within the initial 3 min. After about 10 min, the adsorption equilibrium was reached. Because the adsorption equilibrium may be influenced by the temperature, 60 min was selected as the contact time for the following thermodynamic experiments, to ensure all adsorption processes reached equilibrium adequately.

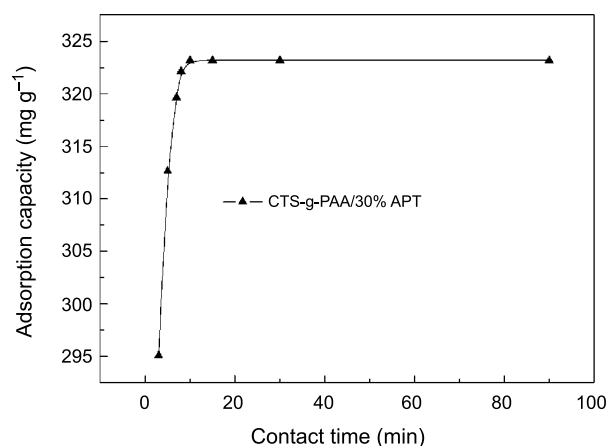


Figure 4. Effect of contact time on the Cd(II) adsorption capacity of the composite. Adsorption experiments – C_0 : 2248 mg L⁻¹; sample dose: 0.1 g per 25 mL; pH₀: 6.5; T : 303 K.

The experimental equilibrium adsorption capacity of the composite was 323.18 mg g^{-1} , which is a quite attractive number because of the high APT content (30 wt%) in the composite. Such a high equilibrium adsorption capacity may be attributed to the following reasons. The specific surface area of the composite is $24.66 \text{ m}^2 \text{ g}^{-1}$. Compared with that of CTS-g-PAA polymer ($1.83 \text{ m}^2 \text{ g}^{-1}$), the specific surface area of the composite was obviously enhanced because the introduction of APT into the polymer formed a much looser and more porous structure [10]. The composite possesses amino groups, acetamide groups and hydroxyl groups from CTS, and carboxyl groups from poly(acrylic acid), which is beneficial for trapping metal ions through chelation and is the reason why such a composite can be selected as the adsorbent for the removal of Cd(II) from aqueous solutions.

The pseudo-first-order and the pseudo-second-order kinetic models were used to evaluate the experimental data obtained from the Cd(II) removal experiments. The pseudo-first-order kinetic model was suggested by Lagergren [14] for the adsorption of solid-liquid systems, and its linear form can be formulated as:

$$\log(q_e - q_t) = \log(q_e) - (k_1 t)/2.303. \quad (4)$$

The pseudo-second-order equation is based on the sorption capacity on the solid phase. It predicts the behaviour over the whole range of studies supporting a pseudo-second-order equation, and is in agreement with chemisorption being the rate-controlling step. Ho and McKay's pseudo-second-order kinetics model [15] can be expressed as:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (5)$$

where q_e and q_t are the amount of Cd(II) adsorbed at equilibrium and time t (mg g^{-1}), respectively; k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) are the equilibrium rate constant of the pseudo-first-order and the pseudo-second-order adsorption, respectively. All the corresponding parameters obtained from the linear plots of $\log(q_e - q_t)$ versus t , and t/q_t versus t (plots not shown), are listed in Table 2.

From Table 2, it can be seen that the linear correlation coefficient (R^2) of the pseudo-first-order kinetic model is very high; however, the calculated value of q_e ($q_{e,cal}$) from the first-order kinetic model is lower than the experimental one ($q_{e,exp}$), which indicates that the sorption system of Cd(II) on to the composite does not

follow the first-order reaction. It can also be found from Table 2 that the R^2 of the pseudo-second-order kinetic model is equal to one; moreover, the $q_{e,cal}$ value of the pseudo-second-order kinetic model agreed perfectly with the $q_{e,exp}$ value, which suggests that the adsorption process of the composite for Cd(II) can be well described by the pseudo-second-order kinetic model, i.e. chemisorption being the rate-controlling step.

Adsorption isotherms

There are important correlations between metal ion concentration and the metal-bonding capacity of the adsorbent. Generally speaking, at a fixed adsorbent dose, the amount adsorbed increases with increasing concentration of solution, but the percentage of removal decreases. The influence of C_0 on the adsorption capacity of the composite for Cd(II) at different temperatures is shown in Figure 5 (C_0 : 1211–2975 mg L^{-1} ; sample dose: 0.1 g per 25 mL; pH_0 : 6.5; T : 293–333 K; t : 60 min). It is clear that C_0 plays an important role in the adsorption process. The adsorption capacity of the composite increased sharply with the increase in C_0 , because the increase in the driving force of the concentration gradient at the solid-liquid interface may cause the increase in the amount of metal ions adsorbed on to the adsorbent. Meanwhile, it can also be seen from Figure 5 that temperature has a positive influence on the Cd(II) adsorption by the composite, which suggests that the adsorption process is an endothermic process. Thus, the influence of temperature on the adsorption capacity is not very prominent, i.e. the adsorption capacity increased very little with the increase in the temperature.

The equilibrium adsorption isotherms are one of the most important data for understanding the mechanism of the adsorption system. Hence, the Langmuir and the Freundlich isotherm models were selected to interpret the adsorption data of the composite for Cd(II). The Langmuir model is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent. The linear form of the Langmuir equation is formulated as [16]:

$$C_e/q_e = 1/K_L + (a_L/K_L)C_e. \quad (6)$$

The Freundlich model is applied to describe heterogeneous systems characterized by a heterogeneity factor of $1/n$. This model describes reversible adsorption and

Table 2. Constants and correlation coefficients of the two kinetic models for Cd(II) adsorption on to the composite.

$q_{e,exp}$ (mg g^{-1})	Pseudo-first-order model			Pseudo-second-order model		
	$q_{e,cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$)	R^2
323.2	287.6	0.6764	0.9862	322.6	0.0320	1

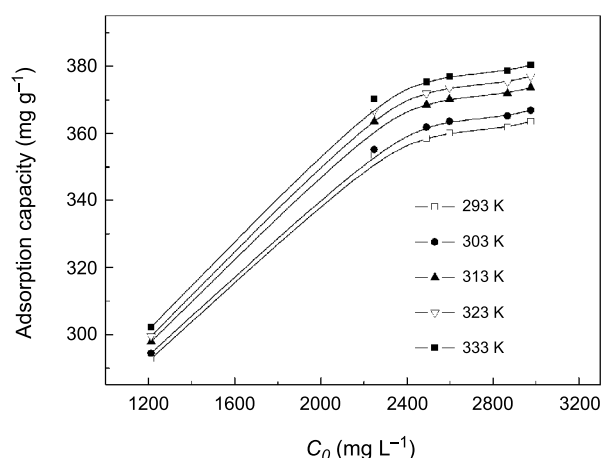


Figure 5. Effect of the initial concentration (C_0) of Cd(II) on the adsorption capacity of the composite at different temperatures. Adsorption experiments – C_0 : 1211–2975 mg L⁻¹; sample dose: 0.1 g per 25 mL; pH₀: 6.5; T : 293–333 K; t : 60 min.

is not restricted to the formation of the monolayer. The Freundlich model is expressed as follows [17]:

$$\log(q_e) = 1/n[\log(C_e)] + \log K \quad (7)$$

where C_e (mg L⁻¹) and q_e (mg g⁻¹) are the liquid-phase concentration and solid-phase concentration of adsorbate at equilibrium, respectively; K_L (L g⁻¹) and a_L (L mg⁻¹) are the Langmuir isotherm constants. By plotting C_e/q_e against C_e , it is possible to obtain the value of K_L from the intercept, which is $1/K_L$, and the value of a_L from the slope, which is a_L/K_L . The maximum adsorption capacity of the adsorbent, $q_{m,cal}$, (equilibrium monolayer capacity or saturation capacity) is numerically equal to K_L/a_L . K is the Freundlich isotherm constant (L g⁻¹) and $1/n$ (dimensionless) is the heterogeneity factor. The Langmuir and Freundlich parameters obtained from the plots of C_e/q_e versus C_e , and $\log(q_e)$ versus $\log(C_e)$, (plots not shown) are listed in Table 3.

From Table 3, it can be seen that value of R^2 for both the linear form of the Langmuir model and the linear

form of the Freundlich model is very high. This indicates that the adsorption of Cd(II) on to the composite fitted not only the Langmuir model but also the Freundlich model. Meanwhile, in the range of C_0 from 1211 mg L⁻¹ to 2975 mg L⁻¹, it can be seen that the Langmuir maximum adsorption capacities ($q_{m,cal}$) at all temperatures agreed perfectly with the experimental values ($q_{m,exp}$). Such a result further suggests that the Langmuir model can be used to describe the adsorption of Cd(II) on to the composite.

Thermodynamic parameters

To substantiate our prediction about the endothermic nature of the adsorption process of the composite for Cd(II), thermodynamic parameters such as Gibbs free energy change (ΔG , J mol⁻¹), enthalpy change (ΔH , J mol⁻¹) and entropy change (ΔS , J mol⁻¹ K⁻¹) were calculated using the Gibbs equation and the Van't Hoff equation, listed as follows:

$$\Delta G = -RT \ln K_L \quad (8)$$

$$\ln K_L = -\Delta H/(RT) + \Delta S/R \quad (9)$$

where K_L is the Langmuir isotherm constant (L g⁻¹), which can be evaluated through the linear form of the Langmuir equation (shown in Equation (4)); T (K) is the temperature; R (J mol⁻¹ K⁻¹) is the gas constant. The values of ΔH and ΔS can be determined from the slope and intercept of the plot of $\ln K_L$ versus $1/T$, respectively (plot not shown).

Thermodynamic parameters associated with the Cd(II) adsorption by the composite are listed in Table 3. It can be seen that the values of ΔG are all negative, and the value of ΔG decreases with the increase in temperature, which indicates that the Cd(II) adsorption process of the composite is spontaneous and that this spontaneous nature may be enhanced at higher temperature. The positive value of ΔH confirmed the endothermic nature of the adsorption process of the composite for Cd(II), which is consistent with the result for the influence of

Table 3. Isotherm constants, correlation coefficients and thermodynamic parameters associated with the adsorption of Cd(II) onto the composite at different temperatures in cadmium acetate solution (T : K; $q_{m,exp}$: mg g⁻¹; K_L : L g⁻¹; a_L : L mg⁻¹; $q_{m,cal}$: mg g⁻¹; ΔG : kJ mol⁻¹; ΔH : kJ mol⁻¹; ΔS : kJ mol⁻¹ K⁻¹; K : L g⁻¹).

T	$q_{m,exp}$	Langmuir equation				ΔG	ΔH	ΔS	Freundlich equation		
		K_L	a_L	$q_{m,cal}$	R^2				K	$1/n$	R^2
293	363.5	21.5657	0.0591	365.0	0.9999	-7.4812			234.37	0.0605	0.9989
303	366.9	22.1976	0.0602	369.0	0.9999	-7.8093			239.87	0.0585	0.9992
313	373.6	30.2663	0.0808	374.5	0.9999	-8.8739	15.787	0.0787	253.91	0.0534	0.9993
323	376.9	34.9528	0.0926	377.4	0.9999	-9.544			263.53	0.0495	0.9996
333	380.3	45.7457	0.1203	380.2	0.9999	-10.585			291.47	0.0365	0.9998

temperature. In general, the randomness at the solid–liquid interface always increases during spontaneous processes, i.e. the value of ΔS should be positive. In our present study, the positive value of ΔS confirmed the spontaneous nature of the Cd(II) adsorption process of the composite once again.

Adsorption mechanism

The metal ion binding could be attributed to several mechanisms such as ion-exchange, complexation, electrostatic attraction and precipitation [18]. The typical dependence of Cd(II) uptake on pH suggests that the weak acidic carboxylic groups R–COO[−] (apparent pK_a in the range 3.5–5.0) of the composite are the probable sorption sites. The –OH and –NH₂ groups are also present in the composite but are less abundant. These may also contribute to Cd(II) adsorption. So, the complexation may be considered as one of the main mechanisms for the Cd(II) adsorption by the composite, and such an expectation can be confirmed by the spectra of the composite before and after Cd(II) adsorption in cadmium acetate solution (shown in Figure 2a and 2e).

After Cd(II) adsorption, the disappearance of the strong stretching vibration absorption band of C=O of the –COOH groups near 1716 cm^{−1} and the enhancement and transfer of the stretching vibration absorption band of –COO[−] groups indicated that lots of –COOH groups dissociated into –COO[−] groups during the Cd(II) adsorption process of the composite. The ionized carboxyl groups (–COO[−]) can bond with Cd(II) ions to form a neutral species and establish equilibrium [19]. Meanwhile, it can be seen from Figure 2a and 2e that the deformation vibration adsorption band of –OH groups shifted to the higher wavenumbers (1325 cm^{−1}) and the stretching vibration absorption band of –NH₂ groups and –OH groups near 3400 cm^{−1} became widened, which indicated that –NH₂ and –OH groups also reacted with Cd(II) during the adsorption process. Based on the above analysis, it can be considered that –COOH, –NH₂ and –OH groups are all involved in the adsorption process of the composite for Cd(II) in cadmium acetate solution, and –COOH groups may be the main groups responsible for Cd(II) adsorption.

Another mechanism responsible for the Cd(II) adsorption by the composite may be ion-exchange, because there is 30 wt% APT in such an organic–inorganic composite hydrogel. Natural APT particles adsorb many exchangeable cations, such as K⁺, Na⁺, Ca²⁺ and Mg²⁺, as a result of isomorphic substitution during its formation process. These exchangeable cations can be exchanged by Cd(II) ions during the adsorption process.

Comparison with other adsorbents

Under the same experimental conditions (C_0 : 2248.2 mg L^{−1}; sample dose: 0.1 g per 25 mL; pH₀: 6.50; T : 303 K; t : 60 min), the equilibrium adsorption capacities of APT, CTS and CTS-g-PAA were also measured and found to be 30.85, 85.05 and 435.25 mg g^{−1}, respectively. The equilibrium adsorption capacity of CTS-g-PAA/30%APT composite was 323.18 mg g^{−1}. Compared with CTS-g-PAA, the equilibrium adsorption capacity of the composite is low, which may be because the functional groups responsible for the adsorption of Cd(II) ions decrease as a result of the introduction of APT. However, an adsorption capacity of 323.18 mg g^{−1} is much higher than that reported for activated carbon (93.4 mg g^{−1} [20], 67 mg g^{−1} [21]), which indicates that the composite could become a potential adsorbent for the removal of Cd(II).

Desorption studies

The regeneration of the adsorbent may be crucially important for keeping the process costs down and for the possible recovery of the pollutant extracted from the solution [13]. Except in the case of precious metals for which the cost of the sorbent is not a limiting criterion, the recycling of the sorbent is a required step in the design of the process. Furthermore, the recovery of metals is an important parameter for the economics of the process [22]. To evaluate the reuse value of the composite, a consecutive adsorption–desorption process was performed five times. Hydrochloric acid solution (0.05 mol L^{−1}) was used as the desorbing reagent. The relationship between the number of times of reuse and the Cd(II) adsorption capacity of the composite is shown in Table 4. It can be seen that the adsorption capacity of the composite for Cd(II) decreased slightly when it was reused for a second time, and then increased slowly with the increase in the number of times reused. The same tendency was also observed in our previous work about copper ions [11]. Such a result may be caused by the acid-treated process and the heat-treated process within each adsorption–desorption process, because both the acid-treated process and the heat-treated process may

Table 4. Relationship between the number of times reused and the Cd(II) adsorption capacity of the composite.

No. times reused	Adsorption capacity (mg g ^{−1})
1	335.9
2	321.9
3	346.1
4	366.7
5	401.0

increase the adsorption capacity of APT in the composite [6]. During the five-times consecutive adsorption–desorption process, the average desorption percentage of the composite was 75.9%, which indicated that the composite has the potential for regeneration and reuse.

Conclusions

The adsorption of Cd(II) on to CTS-g-PAA/30%APT composite was investigated in the present study. The following conclusions can be drawn on the basis of experimental results.

- (1) The species of cadmium salts can affect Cd(II) adsorption on to the composite, and the existence of CH_3COO^- anions in the solution may be more propitious to the complexation reaction of the composite for Cd(II) than that of SO_4^{2-} , NO_3^- and Cl^- anions. Complexation may be the main mechanisms responsible for Cd(II) adsorption. Carboxyl groups may be the main groups responsible for the Cd(II) adsorption. Meanwhile, the ion-exchange mechanism may be also responsible for Cd(II) adsorption because of the existence of APT in the composite.
- (2) The Cd(II) adsorption rate on CTS-g-PAA/30%APT composite was fast and more than 90% of Cd(II) adsorption occurred within the initial 3 min. The adsorption process can be better described by the pseudo-second-order kinetic model. The equilibrium adsorption isotherm was fitted for not only the Langmuir model but also the Freundlich model.
- (3) The adsorption was a spontaneous and endothermic process.
- (4) The high adsorption capacity and average desorption percentage obtained from the consecutive five-times adsorption–desorption study implied that the composite possesses the potential for regeneration and reuse.

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