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Equilibrium isotherm and mechanism studies of Pb(II) and Cd(II) ions onto hydrogel composite based on vermiculite

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ABSTRACT

In the present work, the abilities of chitosan-*g*-poly(acrylic acid)/ vermiculite (CTS-*g*-PAA/VMT) hydrogel composites to remove Pb(II) and Cd(II) ions from aqueous solutions were compared. Batch adsorption studies were carried out to examine the influence of various parameters such as the VMT content, the initial pH value, the contact time, the initial metal ion concentration on adsorption capacities. Adsorption of Pb(II) and Cd(II) ions on the composite showed a pH-dependent profile. The maximum adsorption capacity for both metal ions was found to lie between 5.5 and 6.00. The adsorption processes were all relatively fast. Over 90% of the total adsorption was reached in around 3 min for both Pb(II) and Cd(II) adsorption at 303 K, and the equilibrium was reached after about 15 min of contact time. The adsorption data for the composite fitted well not only the Langmuir model but also the Freundlich model. The maximum Pb(II) adsorption capacity (3.0774 mol/g) of the composite is only a little more than that of Cd(II) (2.9817 mmol/g) at 303 K, however, the desorption efficiency of Pb(II) loaded sample (63.27%) is much lower than that of Cd(II) loaded sample (86.26%) when 0.1 mol/L HNO_3 solution was used as the elutent. The adsorption of Pb(II) and Cd(II) ions by the composite seemed to involve ion exchange, chelation, electrostatic attraction or adsorption. $–NH_2$, –COOH and –OH groups are all involved in the adsorption processes. Moreover, there are only few of $–NH_2$ groups participating in the reaction with Pb(II) ions.

Keywords: Chitosan; Vermiculite; Hydrogel composite; Pb(II); Cd(II); Adsorption mechanism

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1. Introduction

Pollution of metal ions has become a major issue throughout many countries because the serious threat of high level heavy metals to human health. In recent years, one of the main goals regarding heavy metal removal from wastewater rests with the reduction of these pollutants at very low levels. Conventional techniques such as chemical precipitation, ion-exchange processes, membrane separation, reverse osmosis, evaporation, and electrochemical treatment are not useful when the metals are present at concentrations between 1 and 100 mg/L. One of the most important alternatives available to solve such problems is the use of adsorption processes.

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Adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions [1]. Adsorption processes can be widely used with a variety of solid sorbents to remove certain classes of chemical pollutants from wastewater. The success of this adsorption process depends directly on the sorbent properties, which could be expected to be inexpensive and not require any additional pre-treatment step before its application [2].

Hydrogels with three-dimensional cross-linked polymeric networks, are well documented to be used for the removal of metal ions from aqueous solutions [3–6]. However, the conventional hydrogels are based on expensive petroleum-based polymer. Their production consumes lots of petroleum and their usage can also cause ineluctable environmental problems [7]. New types of hydrogels by introducing naturally available raw materials such as polysaccharide and clay as additives drawn particular attention [8–10], because that incorporation of raw material into other synthetic polymers not only reduces our dependence on petrochemical-derived monomers but also can provide materials which show improved performance, and low-cost and environmental friendly characteristics [11,12].

Clay minerals are layer aluminosilicates in which isomorphous substitution generates permanent negative charges, which vary from material to material and are balanced in the natural state by inorganic cations. Under certain circumstances the inorganic cations may be replaced by other cations [13]. There is therefore considerable scope for utilizing the interior of clay–organic composites for a variety of scientific and technological purposes, some examples of which are removal of organic contaminants [14,15] and heavy metals [16–18], use as templates for the preparation of porous materials [19], or for *in situ* polymerization to make composite clay–polymer materials [20].

In our previous study, we have prepared a series of chitosan-*g*-poly (acrylic acid)/clay hydrogel composites via *in situ* copolymerization in aqueous solution, using chitosan as the backbone to graft poly (acrylic acid) to enhance the affinity for water and clay micro-powders (for example: montmorillonite, attapulgite, and vermiculite) being introduced into composites to improve the swelling degree of hydrogel composites in water [21–23]. We have investigated the adsorption capacity of chitosan-*g*-poly(acrylic acid)/attapulgite hydrogel composites for heavy metal ions (Cu(II), Cd(II), Hg(II), Pb(II)), and found that such a series of hydrogel composites are very excellent and potential adsorbents for heavy metal ions [16,17,24]. Vermiculite (VMT) has very high cation exchange capacity (120–150 meq/100 g), and swell less than smectites because of their higher charge in the tetrahedral sheets and possess higher elasticity and plasticity than kaolin and mica [25]. So, to discover whether the hydrogel composites containing VMT are also excellent adsorbents for heavy metal ions, on the basis of our previous work on preparing chitosan-*g*-poly(acrylic acid)/vermiculite (CTS-*g*-PAA/VMT) hydrogel composites, we investigated the adsorption of CTS-*g*-PAA/VMT composites for Pb(II) and Cd(II) ions in this work. The adsorption experiments were carried out in single component. The adsorption process has been analyzed through batch experiments with regard to the influence of VMT content (wt.%), the initial pH value (pH_0), the contact time (t), the initial concentration (C_0) and temperature (T). Both kinetic and equilibrium models were used to investigate the adsorption behaviours, and the regeneration abilities of Pb(II) or Cd(II) loaded composite have also been studied. FTIR spectra were also used to identify the adsorption mechanisms.

2. Experimental

2.1. Materials

Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Ammonium persulphate (APS, analytical grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), *N*,*N*′-methylenebisacrylamide (MBA, chemically pure, Shanghai Yuanfan additives plant, Shanghai, China), and chitosan (CTS, with an degree of deacetylation of 0.90 and average molecular weight of 3×10^5, Zhejiang Yuhuan Ocean Biology Co., Zhejiang, China) were used as received. Vermiculite (VMT, Longyan Colloidal Co., Ltd., Fujian, China) milled through a 320-mesh screen before used with a chemical composition of analytical SiO_2 44.23 wt.%, Al_2O_3 15.10 wt.%, Fe_2O_3 14.26 wt.%, MgO 16.69 wt.%, CaO 4.02 wt.%, TiO_2 0.92 wt.%, MnO 0.13 wt.%, K_2O 3.64 wt.%, Na_2O 0.24 wt.%, and P_2O_5 0.06 wt.%.

Cd(II) solution was prepared by dissolving certain amount of $Cd(CH_3COO)_2{\cdot}2H_2O$ (analytical grade reagent, supplied by Shanghai Chemical Reagent Factory, Shanghai, China) in distilled water. Pb(II) solution was prepared by dissolving $Pb(CH_3COO)_2{\cdot}3H_2O$ (analytical grade reagent, supplied by Xi’an Chemical Reagent Factory, Xi’an, China) in distilled water. Other reagents used were all of analytical grade reagents and all solutions were prepared with distilled water.

2.2. Preparation of CTS-g-PAA/VMT hydrogel adsorbents

CTS-*g*-PAA/VMT hydrogel composite was prepared according to our previous report [23]. Typically, 0.5 g 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. 0.10 g APS was added into the flask to initiate CTS to produce radicals after being purged with nitrogen for 30 min to remove oxygen dissolved in the system. Ten minutes later, the mixture of 3.60 g AA, 0.25 g MBA, different amounts of VMT and 10 ml water was added. The water bath was kept at 343 K for 3 h to accomplish the reaction, then the resulting product was washed with distilled water to remove residual reactants and shifted into 1 mol/L NaOH solution to be neutralized to pH = 7 until swelling equilibrium was achieved and then dehydrated with industrial ethanol. The sample was dried to a constant weight at 343 K and then milled. The sample with a particle size ranging from 80 to 160 mesh was selected for the adsorption experiment. CTS-*g*-PAA hydrogel was prepared according to a similar procedure except without VMT.

2.3. Batch adsorption experiments

The adsorption experiments of Pb(II) and Cd(II) ions were performed by batch technique. Twenty five5 milliliter of the test solution, which has been adjusted to the desired pH value (adjusted with acetic acid or sodium hydroxide solutions by using a Mettler Toledo 320 pH meter) and concentration of the metal ion, was contacted with 0.1000 g sample. The mixture was shaken in a thermostatic shaker bath (THZ-98A) at a speed of 120 rpm under the desired temperature for a given time. And then the suspensions after adsorption were centrifuged at 5000 rpm for 10 min. The pH value of each suspension was determined by a pH meter. Considering the high adsorption capacity of the composite for Pb(II) and Cd(II) ions, very high initial Pb(II) and Cd(II) concentrations were selected in the study. The concentrations of Pb(II) and Cd(II) were all analyzed by EDTA titrimetric method, using 0.0050 mol L^{-1} EDTA solution as the standard solution and 0.5% xylenol orange solution as the indicator. The adsorbed amount of Pb(II) or Cd(II) ions per unit weight of adsorbent at time *t* or at equilibrium was calculated from the mass balance equation as

$$q = [V(C_0 - C)] / m \tag{1}$$

And the removal efficiency of adsorbent for heavy metal ions was calculated from the following equation:

$$r = [(C_0 - C) / C_0] \times 100\% \tag{2}$$

where q is the amount of metal ions adsorbed at time t or at equilibrium (mmol/g). r is the removal efficiency of adsorbent for heavy metal ions. C_0 is the initial concentration of metal ions solution (mmol/L). C is the liquid-phase metal ions concentration at time t or at equilibrium during adsorption process (mmol/L). m is the mass of adsorbent used (g) and V is the volume of metal ions solution used (L).

To study the optimum adsorption conditions of the sample for Pb(II) and Cd(II) ions, batch adsorption experiments were carried out at different initial pH values (Pb(II): 2.00–5.80; Cd(II): 3.00–7.00) at a known initial concentration (Pb(II): 22.2086 mmol/L; Cd(II): 19.8148 mmol/L). Batch kinetic experiments were carried out at different temperatures for predetermined time intervals (1, 3, 5, 8, 12, 15, 30 and 60 min) and the initial concentrations of 22.5309 mmol/L for Pb(II) and 19.8148 mmol/L for Cd(II) were selected, respectively. For equilibrium adsorption experiments at different temperatures, various initial concentrations of Pb(II) and Cd(II) solutions were also used.

2.4. Desorption and regeneration experiments

Pb(II) or Cd(II) loaded sample was prepared by mixing 0.1000 g CTS-*g*-PAA/30%VMT composite and 25 mL of Cd(II) or Pb(II) solution with the desired pH value and concentration (Cd(II): pH_0 6.50, C_0 20.1960 mmol/L; Pb(II): pH_0 5.50, C_0 20.0980 mmol/L) and shaking the mixture at 303 K for 240 min. Then the sample was separated from the solution by centrifugation and washed with distilled water for three times to scour off Pb(II) or Cd(II) ions, and then dried for reuse. For the desorption study, Pb(II) or Cd(II) loaded sample was agitated with a 25 mL nitric acid solution with a concentration of 0.10 mol/L (dose: 0.1000 g/20mL) on a magnetic agitator with 220 rpm for 30 min at room temperature. The desorption efficiency of Pb(II) or Cd(II) loaded sample by nitric acid solution was calculated from the following equation:

$$R = C' / (C'_0 - C) \times 100\% \tag{3}$$

where R is the desorption efficiency of Pb(II) or Cd(II) loaded sample; C' is the liquid-phase metal ions concentration after desorption (mmol/L); C'_0 is Pb(II) or Cd(II) concentration used in adsorption experiments (i.e. Cd(II): 20.1960 mmol/L; Pb(II): 20.0980 mmol/L); C is the liquid-phase metal ions concentration at equilibrium during adsorption process (mmol/L).

2.5. FTIR spectroscopy

Infrared spectra of samples with or without adsorbed metal ions were obtained by a Thermo Nicolet NEXUS TM spectrophotometer. Pressed pellets were prepared by grinding the powder specimens with IR grade KBr in an agate mortar. The spectrum was collected 32 times and corrected for the background noise.

3. Results and discussion

3.1. Effect of VMT content

In clay–organic composite materials, clay content is a very important factor influencing the property of materials. The increase of clay content may directly result in the decrease of the amount of organic functional groups in clay–organic composite materials, which are directly responsible for the adsorption of the material for metal or other ions. Meanwhile, the increase of clay content may increase the crosslinking density of clay–organic composite materials and then decrease the elasticity of the polymer chains [16]. To evaluate the extent of the effect of VMT content on the adsorption capacity of CTS-*g*-PAA/VMT composites for Pb(II) and Cd(II) ions, we examined the adsorption capacity of the composites with different VMT content. The results are shown in Fig. 1. Just as what we expected, the equilibrium adsorption capacity of the composites decreased with the increase of VMT content. However, when VMT content reaches to 30 wt.%, the adsorption capacity of the composite for Pb(II) and Cd(II) ions can still reach to 2.9938 mmol/L and 2.8549 mmol/L, respectively, which is much higher than that the values of 0.336 and 0.397 mmol/g for Pb(II) and Cd(II), respectively, reported by Sağlam et al. [26] and is equivalent to the values reported in our previous work [24]. Moreover, we found that the experimental adsorption capacities of the composites are obviously higher than that calculated by the adsorption capacities of VMT and CTS-*g*-PAA, presuming that VMT and CTS-*g*-PAA were only compounded mechanically or physically, which indicated that the introduction of VMT into the polymer may improve the adsorption ability of the polymer to some extent. In practical industrial production, one of the most important purposes of the addition of clay into polymers is to largely reduce the cost of adsorbents. Therefore, considering the economic advantage and the very high adsorption capacity, CTS-*g*-PAA/VMT composites can be very promising and potential adsorbents for Pb(II) and Cd(II) ions. In the following adsorption experiments, CTS-*g*-PAA/30%VMT composite was selected as the adsorbent for further study.

3.2. Effect of the initial pH

In adsorption process, variation in pH can affect the surface charge of the adsorbent and the degree of ionization and speciation of the metal adsorbate [27]. If the metal binding groups in the material are weakly acidic or basic, the availability of free sites is dependent on the pH of solution [28]. Meanwhile, hydrogen ions themselves are strongly competing adsorbate. Because there are some amino groups and carboxyl groups in CTS-*g*-PAA/30%VMT composite, it can be expected that the adsorption capacity of the composite may be strongly depend on equilibrium solution pH values. Therefore, characterization of its effect on adsorption studies is necessary for an accurate evaluation of equilibrium parameters. Fig. 2 shows the experimental results of

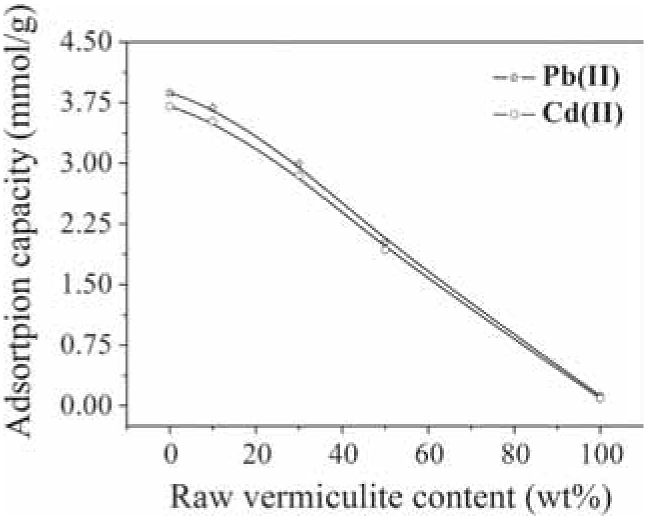

Fig. 1. Effect on VMT content in CTS-*g*-PAA/VMT composites on the adsorption of Pb(II) and Cd(II) ions (adsorption conditions—(i) Pb(II): pH_0: 5.50; C_0: 22.5309 mmol/L; sample dose: 0.1000 g/25mL; temperature: 303 K; contact time: 60 min; (ii) Cd(II): pH_0: 6.00; C_0: 18.4568 mmol/L; sample dose: 0.1000 g/25 mL; temperature: 303 K; adsorption time: 60 min).

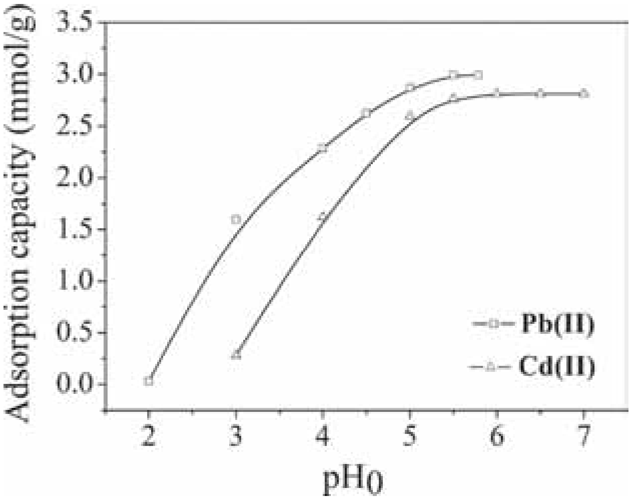

Fig. 2. Effect of the initial solution pH values (pH_0) on Pb(II) and Cd(II) adsorption by the composite (adsorption conditions—(i) Pb(II): C_0: 22.2086 mmol/L; sample dose: 0.1000 g/25 mL; pH_0 range: 2.00–5.80; temperature: 303 K; adsorption time: 60 min; (ii) Cd(II): C_0: 19.8148 mmol/L; sample dose: 0.1000 g/25 mL; pH_0 range: 3.00–7.00; temperature: 303 K; adsorption time: 60 min).

the amounts of Pb(II) and Cd(II) ions adsorbed on CTS-*g*-PAA/30%VMT composite under various initial pH values at adsorption equilibriums. It can be seen that the amounts of Pb(II) and Cd(II) ions adsorbed on the composite all increased with the increase of pH in the pH range we studied. At solution pH_0 values greater than 5.50 for Pb(II) and 6.00 for Cd(II), the increase in the metal uptake is almost insignificant, and the uptake reaches a plateau. At solution pH_0 values below 2 for Pb(II) solution and 3 for Cd(II) solution, the metal uptake is small, but not negligible, which may be attributed to the protonation of the lone pair of electrons on nitrogen and the lower dissociation extent of the carboxyl group, which hinder the interaction of metal ion. Meanwhile, in acidic media, hydrogen ions may the compete with Pb(II) or Cd(II) ions for the same binding sites on the adsorbent. Increasing the initial pH value of the solution may cause the overall surface charge on the composite more negatively, and therefore increases the interactions of divalent metal ions with the composite. In solution which pH value is beyond the neutral pH, the uptake of the metal ions is not only attributed to the interaction of the free metal ions with the active sites on the composite, but also be attributed to the formation of soluble or insoluble metal hydroxide species [29]. So, in the following experiments, pH_0 5.50 for Pb(II) and pH_0 6.00 for Cd(II) were selected.

In the adsorption processes of the composites for Pb(II) and Cd(II) ions, the same phenomenon reported in our previous paper [16] was observed again. i.e., the pH values of the suspension decreased rapidly when contact time increased from 0 to 20 min, and then decreased quite little. After the adsorption equilibrium was set up, the pH values of all suspensions did not change any more. The decrease of the suspension value is mainly due to the dissociation of the carboxyl grou3.3. Kinetic studies

Kinetic studies of Pb(II) and Cd(II) adsorption by CTS-*g*-PAA/30%VMT composite were developed in order to determine minimum necessary time to achieve the adsorption equilibrium. Moreover, in order to obtain the dependence of Pb(II) and Cd(II) adsorption on the temperature, a temperature range from 293 to 333 K was tested in kinetic experiments.

The results of Pb(II) and Cd(II) adsorption kinetics on the composite showed that the adsorption rate increased sharply at the beginning of the process, followed by a slower uptake rate as equilibrium is approached. Fig. 3 showsthat over 90% of the total adsorption is reached in around 3 min for both Pb(II) and Cd(II) adsorption at 303 K, and equilibrium was reached after about 15 min of contact. Such a fast metal uptake observed for the composite is quite important for the process designation and operation in practical application. As the adsorption equilibrium may be influenced by the temperature, in order to ensure all adsorption processes reach equilibrium adequately, equilibrium adsorption experiments were conducted for 60 min.

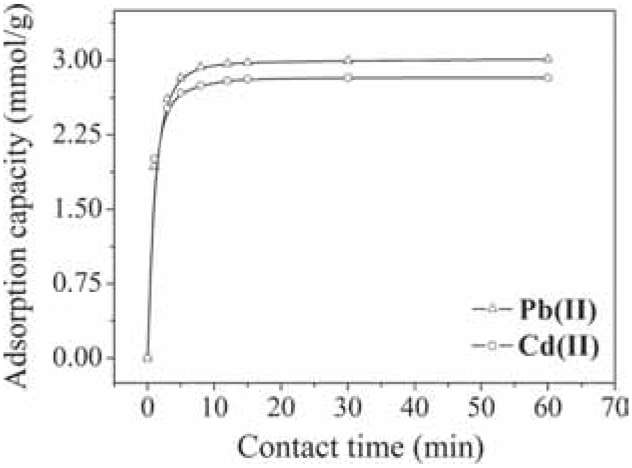

Fig. 3. Effect of contact time on Pb(II) and Cd(II) adsorption by the composite (adsorption conditions—(i) Pb(II): pH_0: 5.50; C_0: 22.5309 mmol/L; sample dose: 0.1000 g/25 mL; temperature: 303 K; (ii) Cd(II): pH_0: 6.00; C_0: 19.8148 mmol/L; sample dose: 0.1000 g/25 mL; temperature: 303 K).

The study of sorption kinetics can provide valuable insights into the reaction pathway and into the mechanism of sorption reactions. In addition, the kinetics describes the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid–solution interface [30]. Various models have been used to analyze the kinetics of sorption process, e.g., Elovich, diffusion, pseudo-first and pseudo-second order equations. Among these models, only the pseudo-second order equation proposed by Ho et al. is able to fit for the whole data range studied [31,32]. It is in agreement with chemisorption being the rate controlling step. And it does not have the problem of assigning an effective capacity, i.e., the sorption capacity, the rate constant and the initial sorption rate can be determined from equation without the knowledge of any parameter beforehand [32]. In the present study, the pseudo-second order kinetic model was used to simulate the adsorption kinetics.

The linear form of Ho and McKay's pseudo-second order kinetic model [31] can be expressed as:

$$t/q_{\mathrm{t}} = 1/(k_2 q_{\mathrm{e}}^2) + t/q_{\mathrm{e}} \qquad (4)$$

where q_e and q_t are the amount of metal ions adsorbed at equilibrium and time *t* (mmol/g), respectively. k_2 is the equilibrium rate constant of the pseudo-second order adsorption (g /(mmol min)). The calculated equilibrium adsorption capacity, $q_{e,cal}$, and the pseudo-second order rate constant, k_2, were experimentally determined from the slope and the intercept of straight-line plots of t/q_t against t. The values obtained at different temperatures were summarized in Table 1, where the good regression coefficients attained are shown. And the values of $q_{e,cal}$ of the composite for all temperatures also agreed very well with the experimental data $q_{e,exp}$. These indicate that all of the adsorption processes of Pb(II) and Cd(II) on CTS-*g*-PAA/30%VMT composite conformed to the pseudo-second order kinetic model. Therefore, chemical sorption or chemisorption, may be the rate limiting step, and k_2 was the adsorption rate constant. Here, it must be mentioned that these parameters can change depending on experimental conditions as it was found by Lodeiro et al. [33], who obtained simple empirical equations to derive the dependence of k_2 and $q_{e,cal}$ on ionic strength, algal mass and initial metal concentration.

From Table 1, it can also be seen that the adsorption capacities of Pb(II) and Cd(II) all showed a slight increase as temperature increases. However, the phenomenon that an initial increase in the corresponding pseudo-second order rate constants was followed by a subsequent reduction with increasing temperature were also observed in Pb(II) and Cd(II) adsorption processes. On the whole, the changes in temperature did not produce any significant difference in Pb(II) and Cd(II) uptake or its corresponding pseudo-second order rate constants.

The effect of temperature on the adsorption process found in the literature presents different and opposite behaviors. Lodeiro et al. [28] reported a slight increase in Pb(II) and Cd(II) uptake on the alga *C. baccata*. A more complex situation that an initial increase in the adsorption capacity of Cd(II) ions by chitin followed by a subsequent reduction was described by Benguella and Benaissa [34].

3.4. Equilibrium adsorption isotherms

The equilibrium isotherms are very important in designing adsorption systems. To estimate the adsorption characteristics of an adsorbent, the adsorption isotherm of that adsorbent with a specific adsorbate is registered. Concentration variation method is used to calculate the adsorption characteristic of adsorbent. It is mainly carried out by selecting an appropriate concentration range of the adsorbate with a fixed mass of adsorbent. In the present study, the ratio of adsorbent mass and the volume of solute solution were 0.1:25 (g/mL). Fig. 4 shows the adsorption capacity of the composite changing with the initial concentrations of Pb(II) and Cd(II) at 303 K. The adsorption capacities of

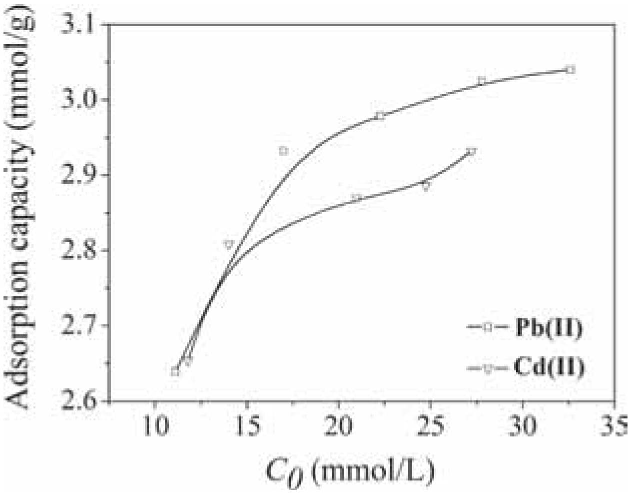

Fig. 4. Effect of the initial metal ion concentration (C_0) on Pb(II) and Cd(II) adsorption by the composite (adsorption conditions—(i) Pb(II): sample dose: 0.1000 g/25mL; pH_0: 5.50; temperature: 303 K; contact time: 60 min; (ii) Cd(II): sample dose: 0.1000 g/25 mL; pH_0: 6.00; temperature: 303 K; contact time: 60 min).

Table 1
Parameters related to the pseudo-second order kinetic model of Pb(II) and Cd(II) adsorption on CTS-*g*-PAA/30%VMT composite (T: K; $q_{e,exp}$: mmol/g; $q_{e,cal}$: mmol/g; k_2: g/(mmol·min))

T	Pb(II)				Cd(II)			
	$q_{e,exp}$	$q_{e,cal}$	k_2	R^2	$q_{e,exp}$	$q_{e,cal}$	k_2	R^2
293	2.9784	3.0201	0.5113	0.9999	2.8086	2.8326	0.8984	1
303	3.0093	3.0315	0.8616	1	2.8240	2.8424	1.1794	1
313	3.0247	3.0397	1.1800	1	2.8395	2.8566	1.1990	1
323	3.0556	3.0703	1.1896	1	2.8549	2.8699	1.3793	1
333	3.071	3.0859	1.1767	1	2.8858	2.9008	1.2913	1

the composite for Pb(II) and Cd(II) all increased with increasing the initial metal concentration, because the increase in Pb(II) and Cd(II) concentrations accelerates the diffusion of Pb(II) and Cd(II) ions onto the adsorbent, with the result of the increase in the driving force of concentration gradient. To investigate the adsorption isotherm, the Langmuir and the Freundlich equilibrium isotherm models were analyzed.

The Langmuir sorption isotherm has been successfully applied to many pollutants sorption processes and has been the most widely used sorption isotherm for the sorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. It is then assumed that once a metal ion occupies a site, no further sorption can take place at that site. The linear form of the Langmuir model is represented as follows [35]:

$$C_e / q_e = 1/\left(q_m b\right) + C_e / q_m \tag{5}$$

where q_e is the amount of metal ions adsorbed at equilibrium (mmol/g), C_e is the liquid-phase metal ions concentration at equilibrium (mmol/L), q_m is the maximum adsorption capacity of the adsorbent (mmol/g), and b is the Langmuir adsorption constant related to the energy of adsorption and affinity of the sorbent (L/mmol). The linear plot of C_e/q_e versus C_e is obtained from the model, and the values of q_m and b can be determined from the slope and intercept, respectively.

The Freundlich model is applied to describe heterogeneous system characterized by a heterogeneity factor of $1/n$. This model was raised in 1906 when Freundlich studied the sorption of a material onto animal charcoal [36]. He found that if the concentration of solute in the solution at equilibrium, C_e, was raised to the power $1/n$, the amount of solute sorbed being q_e, then $C_e^{1/n}/q_e$ was a constant at a given temperature. This fairly satisfactory empirical isotherm can be used for non-ideal sorption and is expressed by the following equation:

$$q_e = KC_e^{1/n} \tag{6}$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\log(q_c) = \log K + 1/n \log(C_e) \tag{7}$$

where K is the Freundlich isotherm constant ((mmol/g) (L/mmol)$^{1/n}$) which is a indicator of the adsorption capacity and n refers to adsorption tendency. By plotting $\log(q_e)$ versus $\log(C_e)$, it is possible to obtain the value of K and $1/n$ from the slope and the intercept. The value of $1/n$ is indicative of the relative energy distribution on the adsorbent surface.

The fit of two models to the experimental data obtained from the adsorption isotherms was checked and the results are shown in Tables 2 and 3. The quite high values of the correlation coefficients at different temperatures indicate that the adsorption of Pb(II) and Cd(II) onto CTS-*g*-PAA/30%VMT hydrogel composite fitted not only the Langmuir model but also the Freundlich model. The same result was also obtained in the Cd(II) adsorption by CTS-*g*-PAA/30%APT composite in our previous study [24]. The Langmuir monolayer saturation capacities, q_m, for Pb(II) and Cd(II) at 303 K are 3.0576 and 2.9386 mmol/g, respectively.

The value of monolayer saturation capacity is the ultimate sorption capacity at high concentrations. It can be used to estimate the specific surface area, S, of CTS-*g*-PAA/30%VMT composite towards Pb(II) or Cd(II) binding, using the following equations. And the results are showns in Table 2 and 3.

Table 2

Langmuir and Freundlich isotherm constants and Gibbs free energy changes associated with the adsorption of Pb(II) onto CTS-*g*-PAA/30%VMT composite at different temperatures (T: K; $q_{m,exp}$: mmol/g; b: L/mmol; $q_{m,cal}$: mmol/g; S: m^2/g; ΔG: kJ/mol; ΔH: kJ/mol; ΔS: kJ/(mol K); K: (mmol/g)(L/mmol)$^{1/n}$)

T	$q_{m,exp}$	Langmuir equation			S	R_L	ΔG	ΔH	ΔS	Freundlich equation		
		b	$q_{m,cal}$	R^2						K	$1/n$	R^2
293	3.0247	5.1753	3.0454	1	81.5819	0.0171–0.0059	−6.717	6.34	0.0446	2.6690	0.0442	0.9887
303	3.0401	5.6987	3.0576	1	81.9111	0.0156–0.0054	−7.119			2.7131	0.0398	0.9928
313	3.0556	5.9809	3.0718	1	82.2910	0.0148–0.0051	−7.575			2.7377	0.0384	0.9939
323	3.0710	6.2874	3.0859	1	82.6692	0.0141–0.0049	−7.963			2.7629	0.0369	0.9950
333	3.0864	7.1300	3.1002	1	83.0513	0.0125–0.0043	−8.571			2.7904	0.0356	0.9955

Table 3
Langmuir and Freundlich isotherm constants and Gibbs free energy changes associated with the adsorption of Cd(II) onto CTS-*g*-PAA/30%VMT hydrogel composite at different temperatures (T: K; $q_{\mathrm{m,exp}}$: mmol/g; b: L/mmol; $q_{\mathrm{m,cal}}$: mmol/g; S: m^2/g; ΔG: kJ/mol; ΔH: kJ/mol; ΔS: kJ/(mol K); K: (mmol/g)(L/mmol)$^{1/n}$)

T	$q_{\mathrm{m,exp}}$	Langmuir equation			S	R_{L}	ΔG	ΔH	ΔS	Freundlich equation		
		b	$q_{\mathrm{m,cal}}$	R^2						K	$1/n$	R^2
293	2.9012	6.1947	2.9176	1	51.8137	0.0135–0.0059	–7.051	11.773	0.0638	2.6280	0.0363	0.9659
303	2.9321	6.6155	2.9386	1	52.1866	0.0127–0.0055	–7.475			2.6684	0.0333	0.9592
313	2.9475	7.4727	2.9587	1	52.5435	0.0112–0.0049	–8.057			2.7020	0.0317	0.9781
323	2.9630	8.9179	2.9697	1	52.7389	0.0094–0.0041	–8.799			2.7435	0.0279	0.9719
333	2.9784	10.7903	2.9809	1	52.9378	0.0078–0.0034	–9.609			2.7838	0.0243	0.9632

$$S = \left(q_{\mathrm{m}} NA\right)/1000 \tag{8}$$

where S is the specific surface area of the composite for metal ions binding (m^2/g); q_{m} is the monolayer adsorption capacity (mmol/g); N is Avogadro number, 6.02×10^{23} mol^{-1}; A is the cross sectional area of metal ion (m^2). According to the radius of Pb(II) and Cd(II) (1.19×10^{-10} m [37] and 0.97×10^{-10} m (Pauling), respectively), the cross sectional areas of Pb(II) and Cd(II) have been determined to be 4.45×10^{-20} m^2 and 2.95×10^{-20} m^2, respectively. Therefore, the specific surface areas of the composite towards Pb(II) or Cd(II) binding at different temperature can be calculated, and the results are shown in Tables 2 and 3. It can be seen that the specific surface area of the composite towards metal ions binding increased with increasing temperatures. And the specific surface area of the adsorbent towards metal ions binding tends to increase the adsorption capacity.

The effect of isotherm shape can be used to predict whether a sorption system is “favourable” or “unfavourable” both in fixed bed systems [38] as well as in batch processes [39]. According to Hall et al. [40], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_{L}, which is defined by the following relationship:

$$R_{\mathrm{L}} = 1/\left(1 + bC_0\right) \tag{9}$$

where R_{L} is the dimensionless constant separation factor, C_0 is the initial concentration of metal ions solution (mmol/L), b is the Langmuir constant (L/mmol). For favourable adsorption process, the value of R_{L} should be in the range between 0 and 1. If the value of R_{L} is beyond one, it implies that the adsorption process is unfavourable.

The values of R_{L} for Pb(II) and Cd(II) changing with the initial concentration of metal ions solution at different temperatures are shown in Figs. 5 and 6, and the results of the range of the R_{L} values for Pb(II) and Cd(II) at different temperatures are given in Tables 2 and 3. The R_{L} values indicate that adsorption is more favourable for the higher initial metal ion concentrations than for the lower ones, and the adsorption is more favourable at higher temperatures than at lower ones, which indicates that the adsorption processes of the composite for Pb(II) and Cd(II) may be endothermic. Referring to the results of the range of R_{L} values given in Tables 2 and 3 and the values of q_{m}, it is obvious that the composite is a very excellent adsorbent for

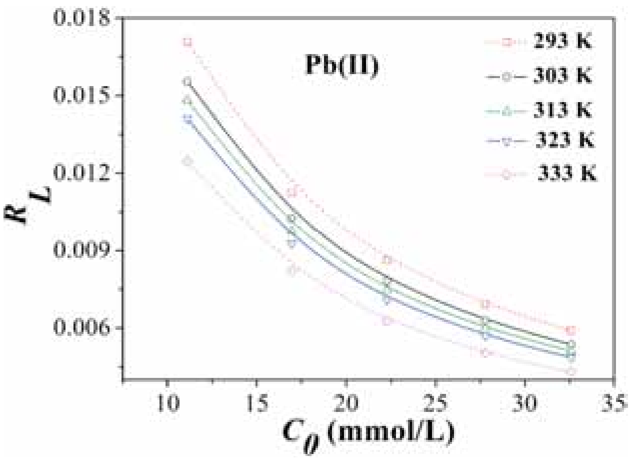

Fig. 5. Plot of R_{L} against the initial concentration of Pb(II) ions at different temperatures (adsorption conditions—sample dose: 0.1000 g/25 mL; pH$_0$: 5.50; temperature range: 293–303 K; contact time: 60 min).

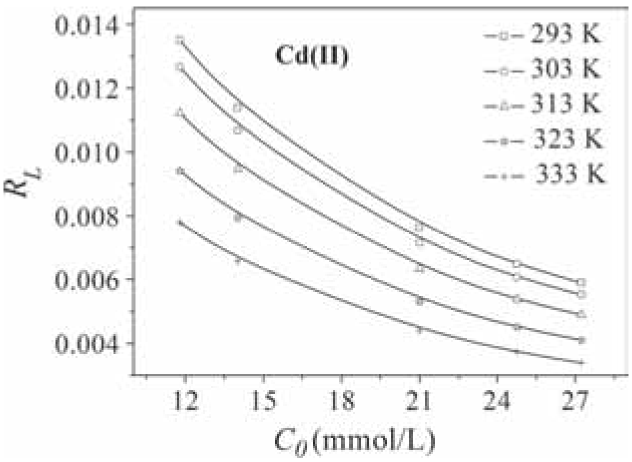

Fig. 6. Plot of R_L against the initial concentration of Cd(II) ions at different temperatures (adsorption conditions—sample dose: 0.1000 g/25 mL; pH_0: 6.00; temperature range: 293–303 K; contact time: 60 min).

Pb(II) and Cd(II). Meanwhile, it can also be seen that the adsorption system is more favourable for Cd(II) than for Pb(II).

3.5. Desorption studies

Desorption studies can help to recover metal ions from the composite and regenerate the composite, so that it can be used again to adsorb metal ions. Desorption studies can also help to elucidate the nature of the adsorption process. Table 4 showed the results of consecutive adsorption–desorption experiments. It was clear that the maximum Pb(II) adsorption capacity (3.0774 mol/g) of the composite is only a little more than that of Cd(II) (2.9817 mmol/g) at 303 K, however, the desorption efficiency of Pb(II) loaded sample (63.27%) is much lower than that of Cd(II) loaded sample (86.26%) when 0.1 mol/L HNO_3 solution was used as the elutent, which suggested that the adsorption of Cd(II) onto the composite carried out mainly by electrostatic attraction.

Table 4
Results of the consecutive adsorption–desorption experiment

Ions	Adsorption experiment *q* (mmol/g)	Desorption experiment *R* (%)
Pb(II)	3.0774	63.27
Cd(II)	2.9817	86.26

3.6. Proposed mechanisms of adsorption

Understanding the mechanisms of the solute adsorption onto CTS-*g*-PAA/VMT hydrogel composite surfaces is essential for the removal of Pb(II) and Cd(II) from aqueous solution. The driving force for adsorption results from: (i) specific character of the solute relative to the particular solvent (i.e. solubility); (ii) specific affinity of the solute for the solid. This kind of attraction may be predominantly one of electrical, Van der Waals, or of a chemical nature [41]. CTS-*g*-PAA/VMT hydrogel composite is formed by the graft polymerization among CTS, VMT and AA. $-NH_2$, $-NHCOCH_3$ and –OH groups from CTS polymeric chain and Si–OH group on the surface of VMT micro-powders all participated in the graft polymerization [23]. The introduction of VMT makes the structure of the composite very loose and porous. CTS-*g*-PAA/VMT hydrogel composite not only possesses $-NH_2$, $-NHCOCH_3$ and –OH groups from CTS polymeric chain, and –COOH groups from poly(acrylic acid), which can be beneficial for trapping metal ions through chelation or complexation, but also possesses VMT which have very high cation exchange capacities (120–150 meq/100 g) due to substitutions of Mg(II) and Fe(II) in place of Al(III) in the octahedral positions, to a higher degree, to substitutions of Al(III) in place of Si(IV) in the tetrahedral positions [25]. The pH dependence of the binding showed that ion exchange, electrostatic interactions and other phenomena are involved in the binding mechanism of Pb(II) and Cd(II) by the composite. In addition, adsorption and/or chelation involving amines, carboxyl groups and/or hydroxyl functions may increase the binding level of Pb(II) and Cd(II) ions on to the composite in addition to the electrostatic interactions taking place [42]. Thus, Pb(II) and Cd(II) ions uptake on to the composite may involve complexation, chelation, ion exchange, electrostatic attraction or adsorption.

The solubility of a metal is an essential property to enable the metal to penetrate into the porous structure of the composite. The concentrations of metal species (i.e. MOH^+, $M(OH)_2$, $M(OH)_3^-$, and $M(OH)_4^{2-}$) are too small to affect the concentrations of M^{2+} in this study. Although many metal species can be viewed as potential sorbates in the uptake of M^{2+} from solution, the data presented in this study suggest that, under experimental conditions (pH < 6 for Pb(II) and pH < 7 for Cd(II)), the M^{2+} is the predominant species responsible for the removal of M^{2+} in the species distribution [43]. Thus, sorption can be explained by elucidating the mechanism whereby the M^{2+} molecules are accommodated by the composite surface.

FTIR spectroscopy is a useful tool for studying the interaction between an adsorbate and the active groups on the surface of the adsorbent. To understand the nature of Pb(II) and Cd(II) adsorption and identify

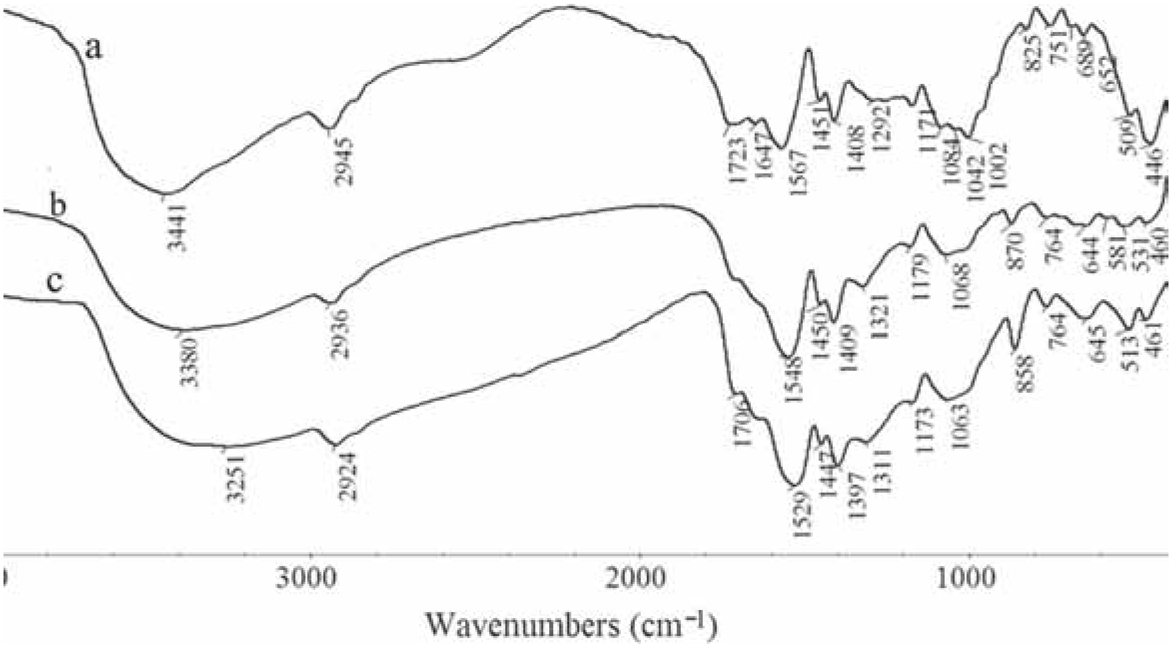

Fig. 7. FTIR spectra of the typical CTS-g-PAA/30%VMT composite before and after Pb(II) and Cd(II) adsorption. (a) CTS-g-PAA-30%VMT; (b) after Cd(II) adsorption; (c) after Pb(II) adsorption.

the possible sites of Pb(II) and Cd(II) binding to CTS-*g*-PAA/30%VMT composite, FTIR spectra were obtained for the composite before and after adsorption in solutions with the initial pH 5.50 for Pb(II) and pH 6.00 for Cd(II) (shown in Fig. 7). Since there is a possibility of overlapping between the N–H and the O–H stretching vibrations, the strong broad band at the wavenumber region of 3300–3500 $\mathrm{cm^{-1}}$ is characteristic of the N–H and the O–H stretching vibration. The significant decrease of transmittance in this band region after Pb(II) and Cd(II) adsorption indicates that the N–H and the O–H vibrations were affected due to Pb(II) and Cd(II) adsorption. However, from the equilibrium adsorption capacities of raw material CTS used in this study (0.0343 mmol/g for Pb(II) and 0.7606 mmol $\mathrm{g^{-1}}$ for Cd(II)), it can be concluded that both $-\mathrm{NH_2}$ groups and –OH groups did not react with Pb(II) and Cd(II) equally. There are only few of $-\mathrm{NH_2}$ groups participating in the reaction with Pb(II) ions. And the significant decrease of transmittance in this band region after Pb(II) adsorption may be mainly due to the participation of –OH groups in the reaction with Pb(II) ions, which can also be identified by the transmittance of C–H vibration adsorption band.

The FTIR data showed that the C=O of –COOH groups strong stretching vibration wavenumbers at 1723 $\mathrm{cm^{-1}}$ disappeared almost completely after Pb(II) and Cd(II) adsorption, and the C=O of $-\mathrm{COO^-}$ groups strong stretching vibration wavenumbers at 1567 $\mathrm{cm^{-1}}$ were enhanced obviously and shifted to the lower wavenumbers after Pb(II) and Cd(II) adsorption. These indicates that lots of –COOH groups dissociated into $-\mathrm{COO^-}$ groups during Pb(II) and Cd(II) adsorption on to the composite. Pb(II) and Cd(II) ions may be attached to $-\mathrm{COO^-}$ groups through electrostatic attraction.

Another major change in the transmittance can also be observed at the wavenumbers of 2945 $\mathrm{cm^{-1}}$ after Pb(II) and Cd(II) adsorption. This band region may be assigned to both C–H (variable) and O–H (weak-broad) stretching vibration. As Pb(II) and Cd(II) ions are unlikely to be attached to a carbon atom, such results further suggest that oxygen atoms in the hydroxyls could also be involved in Pb(II) and Cd(II) adsorption.

Based on the above analysis, it can be said that $-\mathrm{NH_2}$, –COOH and –OH groups are all involved in the adsorption process of CTS-*g*-PAA/30%VMT composite for Pb(II) and Cd(II). However, there are only few of $-\mathrm{NH_2}$ groups participating in the reaction with Pb(II) ions.

4. Conclusions

The sorption of Pb(II) and Cd(II) by CTS-*g*-PAA/30%VMT composite seemed to involve adsorption phenomenon in addition to ion exchange, and electrostatic interactions may be completed by chelation for the binding of Pb(II) and Cd(II) ions. $-\mathrm{NH_2}$, –COOH and –OH groups are all involved in the adsorption process of CTS-*g*-PAA/30%VMT composite for Pb(II) and Cd(II). However, there are only few of $-\mathrm{NH_2}$ groups participating in the reaction with Pb(II) ions. The sorption of Pb(II) and Cd(II) by the composite is pH-dependent, and the maximum adsorption for both metal ions was found to lie between 5.5 and 6.00 for the composite. Both Pb(II) and Cd(II) sorption by the composite is very quick at different temperature under the experimental conditions used. The adsorption data for the composite fitted well not only the Langmuir model but also the Freundlich model. The maximum Pb(II) adsorption capacity (3.0774 mol/g) of the composite is only a little more than that of Cd(II) (2.9817 mmol/g) at 303 K, however, the desorption efficiency of Pb(II) loaded sample (63.27%) is much lower than that of Cd(II) loaded sample (86.26%) when 0.1 mol/L HNO_3 solution was used as the eluting agent. This type of investigation enables an accurate prediction of metal binding properties of CTS-*g*-PAA/30%VMT composite. All these parameters help to better understand the metal binding process onto the composite. Meanwhile, the results showed in this study also suggest that such a composite may be a potential substitute for removing Pb(II) and Cd(II) ions from polluted effluents.

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Symbols

q	the amount of metal ions adsorbed at time *t* or at equilibrium (mmol/g);
r	the removal efficiency of adsorbent for heavy metal ions (%);
C_0	the initial concentration of metal ions solution (mmol/L);
C	the liquid-phase metal ions concentration at time *t* or at equilibrium during adsorption process (mmol/L)
m	the mass of adsorbent used (g);
V	the volume of metal ions solution used (L);
R	the desorption efficiency of Pb(II) or Cd(II) loaded sample;
C'	the liquid-phase metal ions concentration after desorption (mmol/L);
$C_0{}'$	Pb(II) or Cd(II) concentration used in adsorption experiments (i.e. Cd(II): 20.1960 mmol/L; Pb(II): 20.0980 mmol/L);
t	the contact time (min);
q_e	the amount of metal ions adsorbed at equilibrium (mmol/g);
q_t	the amount of metal ions adsorbed at time *t* (mmol/g);
k_2	the equilibrium rate constant of the pseudo-second order adsorption (g /(mmol min));
C_e	the liquid-phase metal concentration at equilibrium (mmol/L);
q_m	the maximum adsorption capacity of the adsorbent (mmol/g);
b	the Langmuir adsorption constant (L/mmol);
K	the Freundlich isotherm constant ((mmol/g)(L/mmol)$^{1/n}$);
n	Freundlich isotherm constant;
S	the specific surface area of the composite for metal ions binding (m^2/g);
q_m	the monolayer adsorption capacity (mmol/g);
N	Avogadro number, 6.02×10^{23} mol^{-1};
A	the cross sectional area of metal ion (m^2);
R_L	the dimensionless constant separation factor;
C_0	the initial concentration of metal ions solution (mmol/L);
b	the Langmuir constant (L/mmol);

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