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Synthesis and characterization of a novel amino modified starch and its adsorption properties for Cd(II) ions from aqueous solution

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ABSTRACT

A new amino modified starch (AMS) has been synthesized via grafting polymerization and ring-opening reaction using cassava starch as raw material and used as an adsorbent for the removal of Cd(II) ions from aqueous solution. The adsorbent was characterized by infrared spectroscopy (FT-IR), X-ray diffraction (XRD) patterns, scanning electron microscopy (SEM). Batch adsorption experiments were carried out as a function of pH, adsorption time, initial Cd(II) ions concentration and temperature. Moreover, the equilibrium, thermodynamics and kinetics of the adsorption process were further investigated. It is found that the effect of pH on adsorption is visible and the optimum value is 6–7. The present adsorption system can be described more favorably by the pseudo-second-order kinetic model. The adsorption equilibrium data are correlated well with the Langmuir isotherm model. Furthermore, the adsorption is a spontaneous and endothermic process with increased entropy, and the rise of temperature will benefit the adsorption. In addition, the adsorption–desorption studies show that the AMS adsorbent can be reused almost without any loss in the adsorption capacity over three cycles.

1. Introduction

Environmental pollution arisen from industrial waste streams during the industrialization process is one of the major problems that has to be controlled (Ünlüa & Ersoz, 2006). Removal of toxic heavy metal ions such as copper, cadmium and lead from industrial wastewaters has received much attention in recent years because excessive heavy metal ions affect the environment and human life by joining the food chain (Benhammou, Yaacoubi, Nibou, & Tanouti, 2005; Ko, Porter, & McKay, 2003; Liu, Wang, & Li, 2005; Meena, Mishra, Rai, Rajagopal, & Nagar, 2005; Özcan, Özcan, Tunali, Akar, & Kiran, 2005; Prasad & Saxena, 2004). Some of these metal ions even in small concentration can cause severe physiological and health effects (Kadirvelu & Namasivayam, 2003; Rengaraj, Kim, Joo, & Yi, 2004). Therefore, different technologies and processes are currently used. Biological treatments, membrane processes, advanced oxidation processes, chemical and electrochemical techniques and adsorption procedures are the most widely used for removing metal ions from industrial effluents. Among all the treatments proposed, adsorption may be considered as preferable due to its economical advantages, high efficiency and applicability (Barrera-Díaz, Palomar-Pardavé, Romero-Romo, & Ureña-Nuñez, 2005; Mohan & Pittman, 2006).

However, conventional chemical precipitation method does not always provide better satisfactory removal effect to meet the demands of the pollution control. Further, the processes often result in secondary environmental pollution. Recently, efforts have been made to search for cheaper method of pollution control in order to solve the problems mentioned above (Acemioglu, Samil, Alma, & Gundogan, 2003; Alkan & Dogan, 2001; Chan & Wu, 2001; Kang, Choi, & Kweon, 1999; Sliba, Cauthier, & Guathier, 2000; Yang & Shao, 2000).

In this respect, many natural polysaccharides and their derivatives may have some potential because of an increasing interest in the synthesis of new cost-effective adsorbents. Recently, chitin, cellulose, starch and their derivatives with different functional groups have been investigated with respect to their ability to remove heavy metal ions from aqueous solution (Li, Xiang, & Ni, 2004). Starch is abundant, renewable and biodegradable resource and has the capacity to associate by physical and chemical interaction with a wide variety of molecules (Li et al., 2004; Polaczek, Starzyk, Malenki, & Tomasik, 2000). In recent years, many approaches have been made to utilize starch as a metal absorbent (Crini, 2005), by introducing various active groups, such as carboxylate (Khalil & Abdel-Halim, 2001; Xu, Feng, Peng, Wang, & Yushan, 2005), xanthate (Bose, Bose, & Kumar, 2002), acrylamide (Chauhan,

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Singh, & Sharma, 2006), acrylonitrile (Abdel-Aal, Gad, & Dessouki, 2006), tertiary amine (Xu, Feng, Yue, & Wang, 2004), phosphate (Guo, Zhang, Ju, & Yang, 2006) and dithiocarbamate (Yin, Ju, Zhang, Wang, & Yang, 2008). Some derivatives of starch dialdehyde like dihydrazone, semicarbazone, dithiosemicarbazone, and dioxime have also been prepared (Para & Karolczyk-Kostuch, 2002a; Para & Karolczyk-Kostuch, 2002b; Para, Karolczyk-Kostuch, & Fiedorowicz, 2004; Para, 2004). Nevertheless, these absorbents have low effective functional groups. In order to solve the problem, high content of functional groups are wanted to get by graft copolymerization. Adsorbent obtained by this method is more effective in removal heavy metal ions from aqueous solution.

Therefore, the objective of this study is to prepare a novel amino modified starch (AMS) and use it to remove Cd(II) ions from aqueous solutions. The adsorbent was characterized by FT-IR, X-ray diffraction (XRD), scanning electron microscopy (SEM). The equilibrium and kinetic data of the adsorption process were obtained to reveal the adsorption mechanism of Cd(II) ions on the adsorbent. Moreover, the adsorption isotherm and thermodynamics were also investigated.

2. Experimental

2.1. Materials

Cassava starch (food-grade) was dried at 105 °C before it was used, Glycidyl methacrylate (GMA, 97%, stabilized with inhibitor) was purchased from shanghai hersbit chemical Co. Ltd. Ethylenediamine (EDA), potassium persulfate (KPS), OP-10, ethanol, acetone, hydrochloric acid, nitric acid, sodium hydrate. All reagents used were of analytical reagent grade and used without further purification.

Solutions were prepared from $3CdSO_4 \cdot 8H_2O$ salt with distilled water and were diluted further to obtain the lower concentration solutions. All solutions and standards were prepared using distilled water.

2.2. Preparation of adsorbent

2.2.1. Synthesis of graft copolymer of glycidyl methacrylate (GMA) onto cassava starch (St-g-GMA)

The graft polymerization was carried out in a three-necked, round-bottom flask held in a constant-temperature water-bath. A portion (6.0 g) of dry cassava starch was mixed with 30 mL distilled water to prepare starch slurry. A known amount of glycidyl methacrylate (GMA) (12.0 g) monomer was added to this slurry, and a contact time of 15 min was allowed to facilitate formation of emulsion. This was followed by addition of a predetermined quantity of potassium persulfate (KPS) in solution (6 mmol L^{-1}) in order to form free radicals on the starch backbone and the volume of the reaction mixture was made to 120 mL with distilled water. All the experiments were conducted under a nitrogen atmosphere and with constant stirring. The graft polymerization proceeded generally for 3 h and at 60 °C. The sample was soaked in ethanol for 0.5 h with the purpose of separating the unreacted monomer and washed thoroughly with distilled water.

In addition, after the reaction period, the graft copolymer was extracted with acetone in a Soxhlet for 24 h in order to removal the homopolymer, and then dried under vacuum at 70 °C for 24 h.

2.2.2. Preparation of amino modified starch (AMS) with EDA

2.0 g of St-g-GMA graft copolymer and 30 mL of EDA were added to a reactor equipped with a magnetic stirrer and reflux condensator, and the mixture was stirred for 0.5 h. Then, about 1 mL of HCl aqueous solution was added to this mixture as activator. The reaction was performed for 12 h at 90 °C under stirring. Then the sample was extracted in ethanol for 0.5 h. After all, the product was washed thoroughly with distilled water, dried at 70 °C under vacuum for 24 h.

Three kinds of AMS were designated as AMS1, AMS2 and AMS3 with the nitrogen content 5.67, 8.26 and 13.01%, measured with the Kjeldahl method (GB/T12091-89).

2.3. Methods of characterization

The FT-IR spectra of starch, St-g-GMA and AMS were taken in the range 400–4000 cm^{-1} on a TENSOR27 FT-IR model with KBr pellets. The XRD patterns of the samples were recorded using a XD-3 X-ray unit with Nifiltered Cu Kα radiation. The SEMs (S-3400N) operated at 20 kV were used to probe the surface morphology of the samples.

2.4. Adsorption experiments

All the adsorption equilibrium experiments were conducted by batch method. A known volume of Cadmium solutions of varying initial concentrations, which was taken in 50 mL Erlenmeyer flasks, was shaken with a desired dose of adsorbent for a specified contact time in a thermostated shaking assembly. After the predetermined adsorption time, solution was filtered and the initial and equilibrium metal ion concentrations of Cadmium in the aqueous solutions were analyzed by the atomic adsorption spectra method (AAS). Initial pH of the solutions was adjusted to desired pH by adding 0.1 mol L^{-1} HCl and/or NaOH solutions to the medium to maintain a constant pH.

Temperature experiments were carried out from 25 to 55 °C at optimum pH for Cd(II) ions. All experiments were performed in duplicate at least and mean values were presented in this study.

The amount of Cadmium adsorbed (Q in mmol g^{-1}) was determined as follows.

$$Q = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where Q is the amount of metal ions adsorbed onto unit amount of the adsorbent (mmol g^{-1}), C_0 and C_t are the initial and terminal concentrations of Cadmium in solution (mmol L^{-1}), V is the volume of solution (L) and m is the mass of the adsorbent (g), respectively.

To examine the effect of solution pH values on Cd(II) ions adsorption, a 0.05 g amount of AMS was added into a series of 50 mL 0.9 mmol L^{-1} Cd(II) solutions prepared with pH adjusted to 2–8 using 0.1 mol L^{-1} HCl and/or NaOH solutions. The adsorption process was allowed for 2 h at room temperature. The initial and final Cd(II) ion concentrations in the solutions were analyzed with AAS.

Kinetic experiment was conducted with the following condition: 0.1 g of dry adsorbents was added to 200 mL of 0.9 mmol L^{-1} Cd(II) solution (pH 6.0) and the mixture was shaken continuously at room temperature. Samples were taken at different time intervals for the determination of Cd(II) ions concentration via AAS.

Adsorption isotherms were obtained by mixing 0.1 g of dry adsorbents in a series of flasks containing 50 mL of different initial metal ion concentrations varying from 0.2669 to 2.669 mmol L^{-1} for 4 h. The initial pH was adjusted to 6.0 for Cd(II) ions.

2.5. Desorption experiments

It is known that regeneration of adsorbents is an important aspect of adsorption study. In order to determine the reusability of the AMS, the adsorption–desorption process was repeated three times. A 1.0 g AMS adsorbents loaded about 0.5 mmol g^{-1} Cd(II) ions was put into 100 mL of 1% (v/v) HNO_3 solution for 0.5 h at room temperature. The adsorption performance in each cycle was measured. The desorption efficiency (DE) was calculated by the

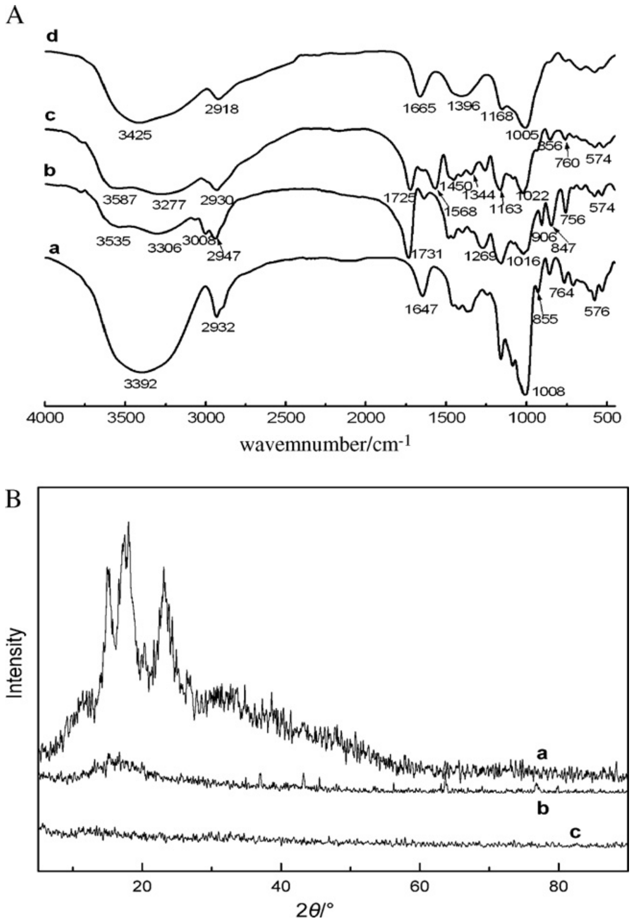

Fig. 1. FT-IR spectra (A) and X-ray diffraction patterns (B) of samples.

following equation:

$$DE = \frac{C_t V}{m_o} \times 100\% \tag{2}$$

where C_t (mmol L^{-1}) is the concentration of Cd(II) ions in the desorption solution at time t (min), V is the volume of the desorption solution, and m_0 (g) is the amount of Cd(II) ions adsorbed.

3. Results and discussion

3.1. Adsorbent characterization

The FT-IR spectra of the products are shown in Fig. 1A. Spectra a, b, c, d refer to cassava starch, St-g-GMA, AMS and Cd(II)-loaded AMS, respectively. The FT-IR spectra of cassava starch display the O—H stretching absorption at 3392 cm^{-1}, the C—H stretching at 2932 cm^{-1}, and the C—O stretching at 1008 cm^{-1}. For St-g-GMA, the peak at 1731 cm^{-1} can be assigned to the —C=O stretching vibration and that at 1016 cm^{-1} to the —C—O— stretching vibration, indicating the presence of the ester group of —COO—. The characteristic peaks at 1269, 906, 847 cm^{-1} correspond to the characteristic peaks of the epoxy group. After the ring-opening reaction with EDA, a strong broad band appeared in the range of 3200–3600 cm^{-1}, mainly attributes to the N—H stretching vibration (overlapped by ν_{OH}). The new peaks at 1568 cm^{-1} for the N—H bending vibration, and at 1163 cm^{-1} for the C—N stretching vibration have all supported the existence of amine groups on the AMS adsorbent. However, the characteristic peak for the epoxy group of St-g-GMA disappears, indicating that EDA reacts with the epoxy groups and changes the structure during the modification process. The asymmetrical stretching vibration at 3277 cm^{-1} is shifted to 3245 cm^{-1} for Cd(II)-loaded AMS. In addition, the peaks of N—H bending vibration and C—N stretching vibration are shifted to 1665 and 1168 cm^{-1} for Cd(II)-loaded AMS, respectively. The results indicate that the chemical interactions between the —OH, —C—N and —N—H groups of AMS and the Cd(II) ions are mainly involved in the adsorption of Cd(II) onto AMS.

The effect of graft copolymerization and ring-opening reaction on the crystallinity of starch and AMS was studied by XRD pattern (Fig. 1B). Pattern a, b and c refer to cassava starch, AMS and AMS adsorbed Cd(II) ions, respectively. The original starch shows scattering at $2\theta = 15.4°$, $17.15°$, $23.76°$, which are characteristic peaks of starch. The absence of the peak at $2\theta = 19.1°$ in AMS indicates that the intensity and sharpness of the reflections decrease, confirming the decrease in crystallinity. It is attributed to that the aggregation phase of original starch is changed from semicrystalline state to amorphous aggregation state during the graft polymerization and ring-opening reactions. However, after AMS adsorbed Cd(II) ions, the peak further becomes weaker rather than AMS which indicate that its crystallinity is further reduced. This is because the Cd(II) ions enter the inner of AMS, which destroy assignment and movement of the chain of AMS. In addition, coordination of Cd(II) ions with AMS would also destroy the intermolecular hydrogen bond, which causes the crystallinity of AMS adsorbed Cd(II) ions decrease.

Fig. 2 shows the SEMs of starch, AMS, and AMS adsorbed Cd(II) ions. The original starch particles (Fig. 2a) show dispersed and smooth. However, the particles of AMS (Fig. 2b and c) appear obviously diverse. Clearly, there are particle fragments and irregular structure on the surface. Such cracks and irregularities are beneficial for the metal ions to diffuse to the inner adsorption sites located in the interior portion of the adsorbent (Anirudhan, Unnithan, Divya, & Senan, 2007). Fig. 2d and e show micrographs of the AMS surface after adsorbed Cd(II) ions, which is covered with some small particulates on the surface, suggesting Cd(II) ions have been adsorbed.

3.2. Effect of pH on the adsorption

The solution pH plays an important role in adsorption process (Denizli, Salih, & Pişkin, 1997; Ücer, Uyanık, & Aygün, 2006). Thus, the effect of pH on adsorption capacities of Cd(II) ions is examined by varying the initial pH of the solutions. The results in Fig. 3 show that the adsorption capacities increase with the increase of pH. It may be attributed to the partial protonation of the amino groups, which hinder the AMS adsorbent/Cd(II) ion interaction as shown below:

$$\text{R-NH}_2 + \text{H}^+ \rightarrow \text{R} - \text{NH}_3{}^+ \tag{3}$$

The R-NH$_3{}^+$ sites on the AMS adsorbent repel the Cd(II) ions to be adsorbed due to the electrostatic repulsion. As the pH increases from 2.0 to 6.0, the active sites become increasingly ionized and the Cd(II) ions are more adsorbed. In the pH 6, the adsorbent has a stable maximum adsorption capacity, which involves competitive reactions of protonation and complex binding (Juang & Chen, 1996). However, beyond pH 7.0 both ions adsorption and Cd(OH)$_2$ precipitation jointly contribute to Cd(II) ions removal from solution. All three kinds of AMS have the same trends, and their adsorption capacities increase with the increase of nitrogen content in the same pH, i.e. AMS1 < AMS2 < AMS3. The maximum adsorption capacities can be achieved as 0.69, 0.49, 0.35 mmol g^{-1} for Cd(II) ions, respectively. For all subsequent experiments, the optimum pH value is used.

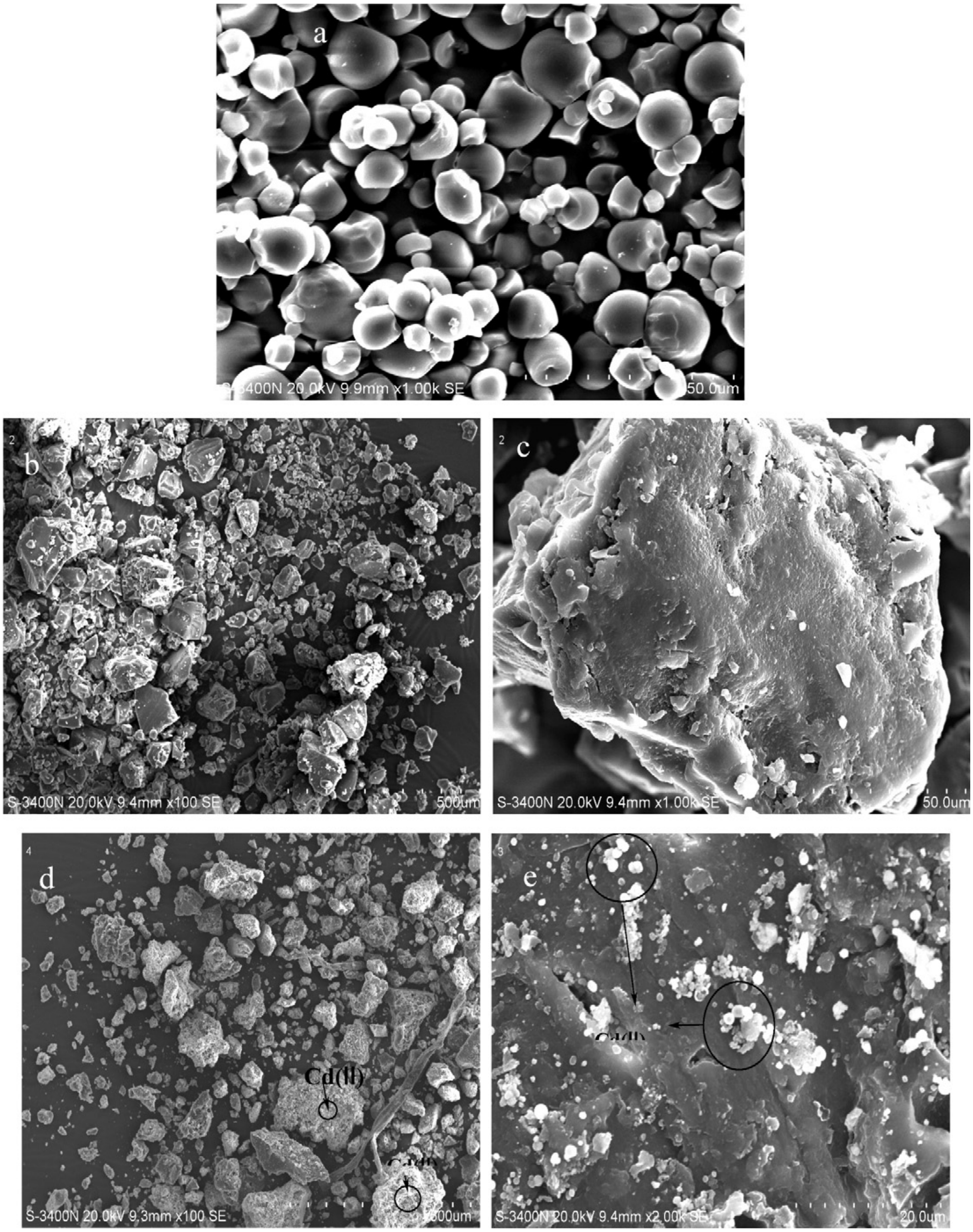

Fig. 2. SEMs of starch (a), AMS (b, c) and AMS-Cd(II) (d, e).

3.3. *The effect of contact time and adsorption kinetics*

In order to establish the equilibration time for maximum adsorption capacity and to know the kinetics of the adsorption process, adsorption capacities of Cd(II) are measured as a function of time and the results are shown in Fig. 4a. As it can be seen that the adsorption rate is initially rapid, with 50% of the adsorption capacity is complete within 20 min and adsorption equilibrium is attained within 2 h. Therefore, an equilibration time of 2 h is selected for all further experiments. Although the amounts of active amine groups are different, the equilibrium time is almost the same. The observed higher adsorption capacities of Cd(II) ions on AMS3 (0.70 mmol g^{-1}) compared to AMS2 (0.50 mmol g^{-1}), AMS1 (0.34 mmol g^{-1}) may be attributed to the higher concentration of amino groups.

It has been known that adsorption process could be controlled by various kinds of mechanisms, such as mass transfer, diffusion control, chemical reactions and particle diffusion (Ünlüa & Ersoz, 2006). In order to clarify the adsorption process, several adsorption models such as pseudo-first-order and pseudo-second-order models are used to identify the rate and kinetics of adsorption of Cadmium on the AMS adsorbent.

3.3.1. *Pseudo-first-order model*

The Lagergren's rate equation (Ho & McKay, 1998a; Ho & McKay, 1998b) is one of the most widely used adsorption rate equations to

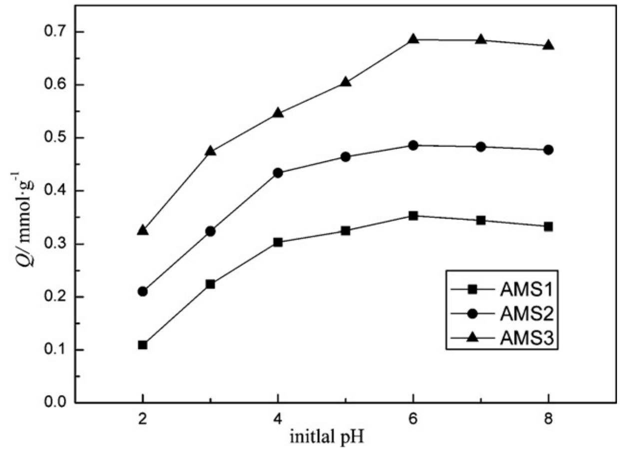

Fig. 3. Effect of pH of Cd(II) ions adsorption on the AMS adsorbents.

describe the adsorption of pollutants from aqueous solutions. The linear form of pseudo-first-order equation is given as below:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_f}{2.303}t \tag{4}$$

where Q_e and Q_t (mmol g^{-1}) are the amount of Cadmium adsorbed at equilibrium and at time t, respectively, and k_f is the pseudo-first-order rate constant. In fact, it is required that calculated equilibrium adsorption capacity values Q_e (cal.), should be in accordance with the experimental Q_e (exp.) values (Özacar & Sengil, 2003). A plot of linearized form of pseudo-first-order kinetic model of Cadmium adsorption on AMS adsorbent is showed (figure not shown).

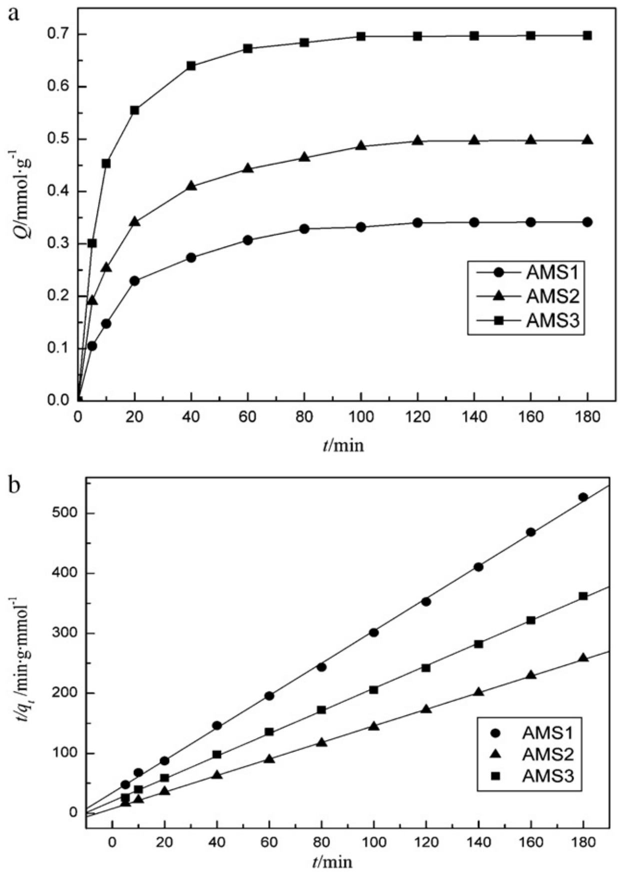

Fig. 4. Effect of contract time (a) and pseudo-second-order kinetic model plots (b) of Cd(II) ions adsorption on AMS adsorbents.

The slopes and intercept of $\log(Q_e - Q_t)$ versus t plot are used to calculate the pseudo-first-order rate constants (k_f) and Q_e (cal.), compiled in Table 1 along with correlation coefficients (R^2).

It can be seen from Table 1 that the theoretical Q_e (cal.) values calculated from the pseudo-first-order model and experimental ones Q_e (exp.) do not agree with each other. Further, all the correlation coefficients ($R^2 = 0.97664$, 98256, 98499 for AMS1, AMS2 and AMS3) are less than 0.99 implying the adsorption of Cd(II) ions on AMS adsorbent is not pseudo-first-order process.

3.3.2. *Pseudo-second-order model*

Ho's pseudo-second-order model has been successfully applied to the adsorption of pollutants, such as metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions. The pseudo-second-order model is fit for the chemisorption of divalent metal ions onto adsorbents with polar functional groups (Ho & McKay, 1998a; Ho & McKay, 1998b; Ho & McKay, 1999; Ho & McKay, 2000). The adsorption of Cd(II) on AMS mainly depends on the chemical bonding between the amine groups and Cd(II). Therefore, experimental data are also applied to the pseudo-second-order kinetic model that is generally expressed as (Ho, 2006; Ho & McKay, 1999):

$$\frac{t}{Q_t} = \frac{1}{k_s Q_e{}^2} + \frac{1}{Q_e}t \tag{5}$$

where Q_e and Q_t are the amount of Cadmium adsorbed (mmol g^{-1}) at equilibrium and at time t, respectively. k_s is the rate constant of pseudo-second-order kinetics.

It has been known that pseudo-second-order kinetic is applicable if the plot of t/Q_t versus t shows linearity. In addition, this process is more likely to predict the behavior of whole adsorption and in agreement with chemical adsorption being the rate-controlling step (Doğan, Alkan, Türkyilmaz, & Özdemir, 2004; Özacar & Sengil, 2003). The plots between t/Q_t and t are drawn and shown in Fig. 4b. The rate constants (k_s), correlation coefficients (R^2) of the plots together with the experimental and theoretical Q_e values are given in Table 1. It is clear from the results that the theoretical Q_e (cal.) values agree well with the experimental ones Q_e (exp.). Further, all the correlation coefficients (R^2) for the pseudo-second-order kinetic model are more than 0.99 (0.99964, 0.99977, 0.99988 for AMS1, AMS2 and AMS3), implying that the adsorption of Cd(II) ions can be described more favorably by pseudo-second-order process. Moreover, it indicates that chemisorption is the determining step of the adsorption process rather than mass transfer in solution. The similar results are obtained to adsorb Cd(II) ions from aqueous solution using adsorbents with active groups (Chiou & Li, 2002; Vitali, Laranjeira, Gonçalves, & Fávere, 2008).

3.4. *Effect of initial concentration and sorption isotherms*

In order to determine the adsorption efficacy of the AMS adsorbent for Cadmium adsorption, the effect of initial concentrations of Cd(II) ions is investigated by varying the initial concentrations of Cd(II) ions at optimum pH values and 2 h of equilibration time. The adsorption isotherms are shown in Fig. 5a. It is found that the isotherm initially rises sharply, indicating that a large quantity of readily active sites are available in the beginning of adsorption. However, when the AMS adsorbent becomes saturated, a plateau is reached suggesting that no more active sites are available. Similarly, it means that the adsorption process is highly concentration dependent. The three curves show that a common trend adsorption capacity increases with increasing of initial concentration of Cd(II) ions and the higher concentration of amino group benefits adsorption of Cd(II) ions. When the initial Cd(II) ion concentration increases from 0.26 to 2.6 mmol L^{-1}, the adsorption capacities of AMS1, AMS2 and AMS3 increase from 0.21 to 0.60 mmol g^{-1}, 0.26 to 0.78 mmol g^{-1}, and 0.26 to 1.20 mmol g^{-1}, respectively. This

Table 1
Pseudo-first-order and pseudo-second-order model parameters for the adsorption of Cd(II) ions on AMS adsorbents.

Sample	q_e (exp.) (mmol g^{-1})	Pseudo-first-order			Pseudo-second-order			
		q_e (cal.) (mmol g^{-1})	K_f (min^{-1})	R^2	q_e (exp.)/q_e (cal.)	q_e (cal.) (mmol g^{-1})	K_s (g mmol^{-1} min^{-1})	R^2
AMS1	0.3415	0.3924	0.04730	0.98499	0.8703	0.37051	0.21185	0.99964
AMS2	0.4972	0.5859	0.04917	0.97664	0.8486	0.53088	0.17746	0.99977
AMS3	0.6975	0.7615	0.04882	0.99256	0.9160	0.72460	0.24636	0.99988

increase in adsorption capacity with relation to the Cd(II) ion concentration can be explained with the high driving force for mass transfer. In fact, the more concentrated the solution is, the better the adsorption is.

The adsorption equilibrium data obtained from the effect of initial concentration on adsorption capacity are evaluated with the two popular adsorption models that are Langmuir and Freundlich models. The linearized forms of the equations representing the models are used.

3.4.1. Freundlich model

Freundlich equation is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces and described by the following equation (Freundlich, 1906):

$$\log Q_e = \log k_F + \frac{1}{n}\log C_e \tag{6}$$

where Q_e (mmol g^{-1}) is the amount adsorbed at the equilibrium concentration C_e (mmol L^{-1}), K_F represents the strength of the adsorptive bond, n is the heterogeneity factor which represents the bond distribution. According to this equation, the plot of the log q_e versus log C_e gives a straight line and K_F and n values can be calculated from the intercept and slope of the straight line, respectively. Experimental data obtained from the effect of initial concentrations of Cd(II) ions are also calculated by applying this equation and related constants are given in Table 2. The values of correlation coefficients are low (0.96018, 0.82423, 0.91698 for AMS1, AMS2 and AMS3) which shows that the Freundlich equation is not well fit with the adsorption process.

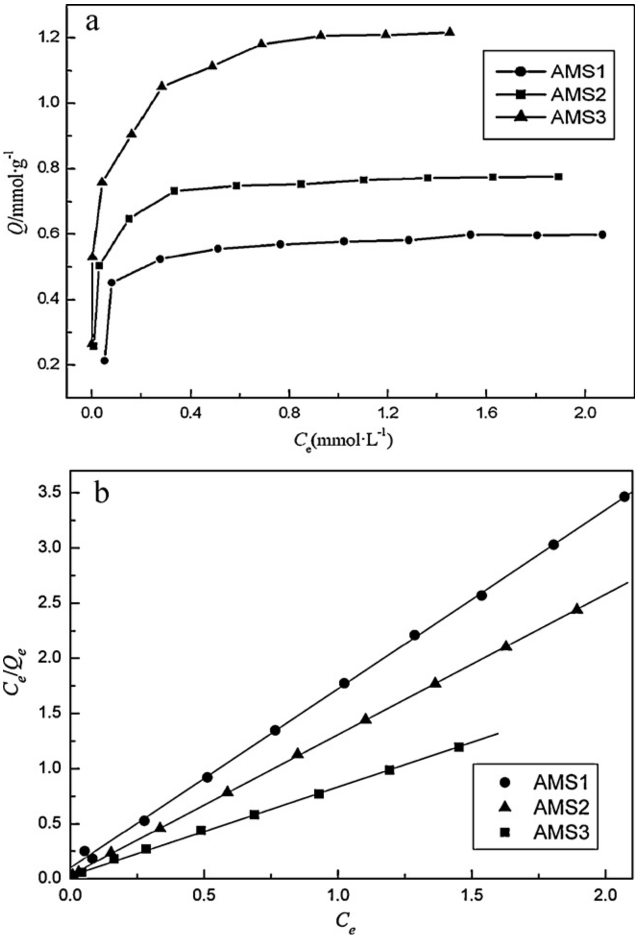

Fig. 5. Adsorption isotherms (a) and Langmuir isotherms (b) of Cd(II) ion adsorption on AMS adsorbents.

3.4.2. Langmuir model

Langmuir isotherm models the monolayer coverage of the adsorption surface. It assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface. The Langmuir adsorption model further assumes that all the adsorption sites are energetically identical and adsorption occurs on a structurally homogeneous adsorbent. The Langmuir equation is given below (Langmuir, 1918):

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \tag{7}$$

where Q_e (mmol g^{-1}) is the amount adsorbed at the equilibrium concentration C_e (mmol L^{-1}), Q_m (mmol g^{-1}) is the Langmuir constant related to the maximum adsorption capacity and b (L mol^{-1}) is the Langmuir constant representing energy of adsorption. The plots of C_e/Q_e as a function of C_e for the adsorption of Cd(II) ions are found linear (Fig. 5b), implying the applicability of Langmuir model in the present adsorption process. The maximum adsorption capacities of AMS1, AMS2 and AMS3 are 0.60, 0.78 and 1.21 mmol g^{-1}, respectively. The correlation coefficients (R^2 = 0.99937, 0.99966 and 0.99996 for AMS1, AMS2 and AMS3, respectively) confirm good agreement between the oretical models and our experimental results. The values of the monolayer capacity (Q_m) and equilibrium constant (b) have been calculated from the intercept and slope of these plots and given in Table 2. It is found that monolayer capacity (Q_m) of the AMS adsorbent for the Cadmium is comparable to the maximum adsorption obtained from the adsorption isotherms. A higher content of amino groups leads to a higher Q_m and b, and it corresponds to the above-mentioned conclusion that a higher content of amino groups results in a higher adsorption capacity.

3.5. Thermodynamics of the adsorption

The thermodynamics for adsorption of Cd(II) ions on AMS are carried out at different temperature. It is found that the adsorption capacity increases with increase in temperature and that shows the

Table 2
Freundlich and Langmuir parameters for the adsorption of Cd(II) ions on AMS adsorbents.

Sample	Langmuir			Freundlich		
	Q_m (mmol g^{-1})	b	R^2	n	K_F	R^2
AMS1	0.6160	16.3301	0.99966	4.9444	0.5690	0.82423
AMS2	0.7844	39.9383	0.99996	5.6699	0.7728	0.91698
AMS3	1.2364	32.2886	0.99937	5.0355	1.2542	0.96018

Table 3
Thermodynamic parameters for the adsorption of Cd(II) on AMS adsorbents.

Sample	T (K)	Q_e (mmol g^{-1})	K_D (L g^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
AMS1	298	0.6128	2.2131	−2.0048	3.8833	19.7587
	308	0.6286	2.4075	−2.2024		
	318	0.6354	2.4986	−2.4000		
	328	0.6398	2.5602	−2.5976		
AMS2	298	0.7373	4.8374	−3.9326	4.5668	28.5214
	308	0.7486	5.3055	−4.2178		
	318	0.7513	5.4285	−4.5030		
	328	0.7586	5.7864	−4.7882		
AMS3	298	0.8466	19.6519	−7.4959	16.6305	80.9612
	308	0.8586	27.6077	−8.3055		
	318	0.8621	31.2355	−9.1152		
	328	0.8664	37.1846	−9.9248		

endothermic nature of the adsorption with the temperature in the range of 298–328 *K*.

Thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) are estimated using the following equations. The Gibb's free energy change of the process is related to the distribution coefficient (K_D) by the equation (Donat, Akdogan, Erdem, & Cetisli, 2005; Tahir & Rauf, 2003):

$$K_D = \frac{Q_e}{C_e} \tag{8}$$

$$\Delta G = \Delta H - T\,\Delta S \tag{9}$$

$$\log K_D = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \tag{10}$$

where K_D is the distribution coefficient (cm^3 g^{-1}), and R is gas constant (kJ mol^{-1} K^{-1}). According to Eq. (9), the values of ΔH and ΔS can be calculated from the slopes ($\Delta H/2.303R$) and intercepts ($\Delta S/2.303R$) of $\log K_D$ versus $1/T$ plots. The calculated values of thermodynamic parameters are given in Table 3.

As it can be seen from Table 3, ΔH values are found to be positive for all cases due to adsorption is endothermic. Although there are no certain criteria related to the ΔH values that define the adsorption type, it is obvious from the ΔH value obtained for Cd(II) that chemisorption also takes part in the adsorption process with chelating effects of the functional groups available on the surface of AMS. Negative values of ΔG indicate the spontaneous nature of the reaction. The values of ΔG become more negative with increase temperature, which means that the adsorption process is more favorable at high temperature. The similar results are found in the studies of Wang and Qin (Wang & Qin, 2006) and Rakhshaee et al. (Rakhshaee, Khosravi, & Ganji, 2006). The positive value of ΔS indicates that there is an increase in the randomness in the system solid/solution interface during the adsorption process (Fig. 6).

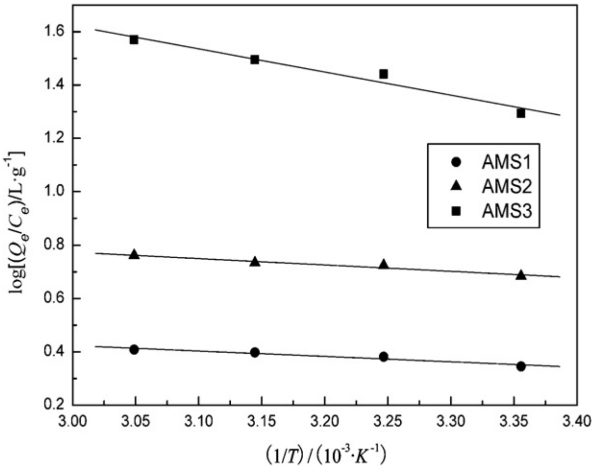

Fig. 6. The plots of $\log K_D$ versus $1/T$ for the adsorption of Cd(II) on AMS adsorbents.

3.6. *Desorption studies*

An important characteristic of adsorbents is the desorption efficiency. The results in Fig. 7 show the amounts of Cd(II) ions adsorbed on AMS from three repeated adsorption–desorption cycles. It is found that the adsorbents can be used repeatedly without changing significantly their adsorption capacities with high desorption percentages 98% for Cd(II) ions studied here.

3.7. *Comparison with other adsorbents*

In order to justify the validity of AMS as an adsorbent of Cd(II), its adsorption potential must be compared with other various adsorbents reported in literature. Table 4 shows the values of maximum adsorption capacity on different adsorbents cited in the literature compared with that of the present study. It shows that AMS3 has good adsorption capacity when compared with other adsorbents.

Table 4
Maximum adsorption capacity and residual concentration for the adsorption of Cu(II), Pb(II) and Cd(II) onto various adsorbents.

Adsorbents	Q_m (mmol g^{-1})			C_r^{*a} (mmol L^{-1})			Refs.
	Cu(II)	Cd(II)	Pb(II)	Cu(II)	Cd(II)	Pb(II)	
Cellulose-g-acrylic acid copolymer	0.286	0.296	0.240	0.242	0.348	0.603	Guclu, Gurdag, and Ozgumus (2003)
Starch-g-acrylic acidcopolymer	0.080	0.603	0.170	0.507	0.412	0.347	Keles and Guclu (2006)
Crosslinked carboxymethyl KGM	0.434	0.201	0.208	0.213	0.311	0.418	Niu, Wu, Wang, Li, and Wang (2007)
Amino-functionalized silica	–	0.279	0.161	–	0.669	0.761	Heidari, Younesi, and Mehraban (2009)
Amberlite IR-120 resin	0.334	0.406	0.899	0.544	0.347	0.203	Demirbas, Pehlivan, Gode, Altun, and Arslan (2005)
Scoria	0.023	0.033	0.021	0.301	0.312	0.358	Kwon, Yun, Lee, Kim, and Jo (2010)
AMS3	0.686	0.481	1.200	0.197	0.295	0.069	Present work

[a] The initial concentration of metal ions is 1.000 mmol L^{-1}.

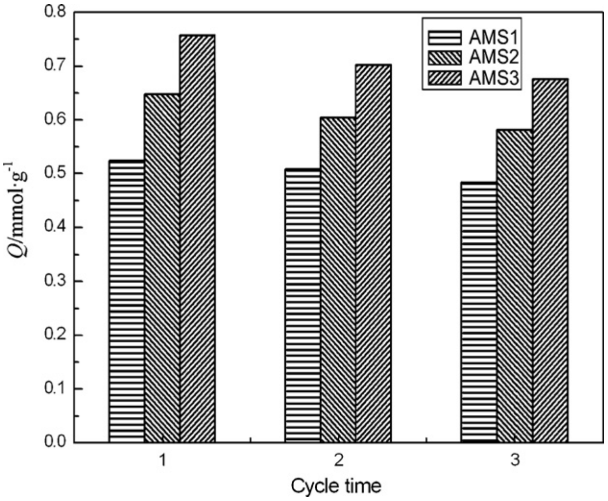

Fig. 7. Amounts of Cd(II) ions adsorbed on the AMS adsorbent in three adsorption–desorption cycles.

4. Conclusions

The results of this study show that the amino modified starch (AMS) can be successfully used for the adsorption of Cd(II) ions from aqueous solution. Pseudo-first-order and pseudo-second-order kinetic models are tested to investigate the adsorption mechanism. The pseudo-second-order kinetic model fits very well with the adsorption behavior of Cd(II) ions. The adsorption process can be well described by Langmuir isotherm with a maximum adsorption capacity 0.60, 0.78 and 1.21 mmol g^{-1} for AMS1, AMS2, AMS3, respectively. The values of ΔG become more negative with increase temperature, which indicates that the adsorption process is more favorable at high temperature. The small values of ΔH mean weak electrovalent bond interactions between amino groups and Cd(II) ions in the adsorption process. The AMS may be used as effective and biodegradable adsorbent for the removal of Cd(II) ions from wastewater.

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References

Abdel-Aal, S. E., Gad, Y. H., & Dessouki, A. M. (2006). Use of rice straw and radiation-modified maize starch/acrylonitrile in the treatment of wastewater. *Journal of Hazardous Materials*, *129*, 204–215.

Acemioglu, B., Samil, A., Alma, M. H., & Gundogan, R. (2003). Copper (II) removal from aqueous solution by organosolv lignin and its recovery. *Journal of Applied Polymer Science*, *89*, 1537–1541.

Alkan, M., & Dogan, M. (2001). Adsorption of copper(II) onto Perlite. *Journal of Colloid and Interface Science*, *243*, 280–291.

Anirudhan, T. S., Unnithan, M. R., Divya, L., & Senan, P. (2007). Synthesis and characteriztion of polyacrylamide-grafted coconut coir pith having carboxylate functional group and adsorption ability for heavy metal ions. *Journal of Applied Polymer Science*, *104*, 3670–3681.

Barrera-Díaz, C., Palomar-Pardavé, M., Romero-Romo, M., & Ureña-Nuñez, F. (2005). Lead removal from wastewater using Cu(II) polymethacrylate formed by gamma radiation. *Journal of Polymer Research*, *12*, 421–428.

Benhammou, A., Yaacoubi, A., Nibou, L., & Tanouti, B. (2005). Adsorption of metal ions onto Moroccan stevensite: Kinetic and isotherm studies. *Journal of Colloid and Interface Science*, *282*, 320–326.

Bose, P., Bose, M. A., & Kumar, S. (2002). Critical evaluation of treatment strategies involving adsorption and chelation for wastewater containing copper, zinc and cyanide. *Advances in Environmental Research*, *7*, 179–195.

Chan, W. C., & Wu, J. Y. (2001). Dynamic adsorption behaviors between Cu(II) ion and water-insoluble amphoteric starch in aqueous solutions. *Journal of Applied Polymer Science*, *81*, 2849–2855.

Chauhan, G. S., Singh, B., Sharma, R. K., et al. (2006). Use of biopolymers and acrylamide-based hydrogels for sorption of Cu2+, Fe2+ and Cr6+ ions from their aqueous solutions. *Desalination*, *197*, 75–81.

Chiou, M. S., & Li, H. Y. (2002). Equilibrium and kinetic modeling of adsorption of reactive dye of cross-linked chitosan beads. *Journal of Hazardous Materials*, *93*, 233–248.

Crini, G. (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science*, *30*, 38–70.

Demirbas, A., Pehlivan, E., Gode, F., Altun, T., & Arslan, G. (2005). Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin. *Journal of Colloid and Interface Science*, *282*, 20–25.

Denizli, A., Salih, B., & Pişkin, E. (1997). New sorbents for removal of heavy metal ions: Diamine-glow-discharge treated polyhydroxyethylmethacrylate microspheres. *Journal of Chromatography A*, *773*, 169–178.

Doğan, M., Alkan, M., Türkyilmaz, A., & Özdemir, Y. (2004). Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *Journal of Hazardous Materials B*, *109*, 141–148.

Donat, R., Akdogan, A., Erdem, E., & Cetisli, H. (2005). Thermodynamics of Pb2+ and Ni2+ adsorption onto natural bentonite from aqueous solutions. *Journal of Colloid and Interface Science*, *286*, 43–52.

Freundlich, H. M. F. (1906). Über die Adsorption in Lösungen. *Zeitschrift fur Physikalische Chemie*, *57A*, 385–470.

Guclu, G., Gurdag, G., & Ozgumus, S. (2003). Competitive removal of heavy metal ions by cellulose graft copolymers. *Journal of Applied Polymer Science*, *90*, 2034–2039.

Guo, L., Zhang, S. F., Ju, B. Z., & Yang, J. Z. (2006). Study on adsorption of Cu(II) by water-insoluble starch phosphate carbamate. *Carbohydrate Polymers*, *63*, 487–492.

Heidari, A., Younesi, H., & Mehraban, Z. (2009). Removal of Ni(II), Cd(II), and Pb(II) from a ternary aqueous solution by amino functionalized mesoporous and nano mesoporous silica. *Chemical Engineering Journal*, *153*, 70–79.

Ho, Y. S. (2006). Review of second-order models for adsorption systems. *Journal of Hazardous Materials*, *136*, 681–689.

Ho, Y. S., & McKay, G. (1998a). A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Safety and Environment*, *76B*, 332–340.

Ho, Y. S., & McKay, G. (1998b). Sorption of dye from aqueous solution by peat. *Chemical Engineering Journal*, *70*, 115–124.

Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*, *34*, 451–465.

Ho, Y. S., & McKay, G. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Research*, *34*, 735–742.

Juang, R. S., & Chen, M. N. (1996). Measurement of binding constants of poly(ethylenimine) with metal ions and metal chelates in aqueous media by ultrafiltration. *Industrial and Engineering Chemistry Research*, *35*, 1935–1943.

Kadirvelu, K., & Namasivayam, C. (2003). Activated carbon from coconut coir pith as metal adsorbent: Adsorption of Cd(II) from aqueous solution. *Advances in Environmental Research*, *7*, 471–478.

Kang, D. W., Choi, H. R., & Kweon, D. K. (1999). Stability constants of amidoximated chitosan-g-poly (acrylonitrile) copolymer for heavy metal ions. *Journal of Applied Polymer Science*, *73*, 69–472.

Keles, S., & Guclu, G. (2006). Competitive removal of heavy metal ions by starch-graft-acrylic acid copolymers. *Polymer - Plastics Technology and Engineering*, *45*, 365–371.

Khalil, M. I., & Abdel-Halim, M. G. (2001). Preparation of anionic starch containing carboxyl groups and its utilization as chelating agent. *Starch*, *53*, 35–41.

Ko, D. C. K., Porter, J. F., & McKay, G. (2003). Mass transport model for the fixed bed sorption of metal ions on bone char. *Industrial and Engineering Chemistry Research*, *42*, 3458–3469.

Kwon, J. S., Yun, S. T., Lee, J. H., Kim, S. O., & Jo, H. Y. (2010). Removal of divalent heavy metals (Cd, Cu, Pb, and Zn) and arsenic(III) from aqueous solutions using scoria: Kinetics and equilibria of sorption. *Journal of Hazardous Materials*, *174*, 307–313.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, *40*, 1361–1403.

Li, Y. J., Xiang, B., & Ni, Y. M. (2004). Removal of Cu (II) from aqueous solutions by chelating starch derivatives. *Journal of Applied Polymer Science*, *92*, 3881–3885.

Liu, C. C., Wang, M. K., & Li, Y. S. (2005). Removal of nickel from aqueous solution using wine processing waste sludge. *Industrial and Engineering Chemistry Research*, *44*, 1438–1445.

Meena, A. K., Mishra, G. K., Rai, P. K., Rajagopal, C., & Nagar, P. N. (2005). Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent. *Journal of Hazardous Materials B*, *122*, 161–170.

Mohan, D., & Pittman, C. U. (2006). Activated carbons and low cost adsorbents for remediation of tri- and hexa-valent chromium from water. *Journal of Hazardous Materials*, *137*, 762–811.

Niu, C., Wu, W., Wang, Z., Li, S., & Wang, J. (2007). Adsorption of heavy metal ions from aqueous solution by crosslinked carboxymethyl konjac glucomannan. *Journal of Hazardous Materials*, *141*, 209–214.

Özacar, M., & Sengil, I. A. (2003). Adsorption of reactive dyes on calcined alunite from aqueous solutions. *Journal of Hazardous Materials B*, *9*, 8–11.

Özcan, A., Özcan, A. S., Tunali, S., Akar, T., & Kiran, I. (2005). Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper(II) ions onto seeds of capsicum annuum. *Journal of Hazardous Materials B*, *124*, 200–208.

Para, A. (2004). Complexation of metal ions with dioxime of dialdehyde starch. *Carbohydrate Polymers*, *57*, 277–283.

Para, A., & Karolczyk-Kostuch, S. (2002a). Semicarbazone of starch dialdehyde and its complexes with metal ions. *Carbohydrate Polymers*, *48*, 55–60.

Para, A., & Karolczyk-Kostuch, S. (2002b). Metal complexes of starch dialdehyde thiosemicarbazone. *Carbohydrate Polymers*, *50*, 151–158.

Para, A., Karolczyk-Kostuch, S., & Fiedorowicz, M. (2004). Dihydrazone of dialdehyde starch and its metal complexes. *Carbohydrate Polymers*, *56*, 187–193.

Polaczek, E., Starzyk, F., Malenki, K., & Tomasik, P. (2000). Inclusion complexes of starches with hydrocarbons. *Carbohydrate Polymers*, *43*, 291–297.

Prasad, M., & Saxena, S. (2004). Sorption mechanism of some divalent metal ions onto low-cost mineral adsorbent. *Industrial and Engineering Chemistry Research*, *43*, 1512–1522.

Rakhshaee, R., Khosravi, M., & Ganji, M. T. (2006). Kinetic modeling and thermodynamic study to remove Pb(II), Cd(II), Ni(II) and Zn(II) from aqueous solution using dead and living Azolla filiculoides. *Journal of Hazardous Materials*, *134*, 120–129.

Rengaraj, S., Kim, Y., Joo, C. K., & Yi, J. (2004). Removal of copper from aqueous solution by aminated and protonated mesoporous aluminas: Kinetics and equilibrium. *Journal of Colloid and Interface Science*, *273*, 14–21.

Sliba, R., Cauthier, H., Guathier, R., et al. (2000). Automotive clear coat damage due to oviposition of dragonflies. *Journal of Applied Polymer Science*, *751*, 624–1631.

Tahir, S. S., & Rauf, N. (2003). Thermodynamic studies of Ni(II) adsorption onto bentonite from aqueous solution. *Journal of Chemical Thermodynamics*, *35*, 2003–2009.

Ücer, A., Uyanık, A., & Aygün, S. F. (2006). Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by tannic acid immobilised activated carbon. *Separation and Purification Technology*, *47*, 113–118.

Ünlüa, N., & Ersoz, M. (2006). Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions. *Journal of Hazardous Materials*, *136*, 272–280.

Vitali, L., Laranjeira, M. C., Gonçalves, N. S., & Fávere, V. T. (2008). Spray-dried chitosan microspheres containing 8-hydroxyquinoline-5-sulphonic acid as a new adsorbent for Cd(II) and Zn(II) ions. *International Journal of Biological Macromolecules*, *42*, 152–157.

Wang, X. S., & Qin, Y. (2006). Removal of Ni(II), Zn(II) and Cr(VI) from aqueous solution by Alternanthera philoxeroides biomass. *Journal of Hazardous Materials*, *138*, 582–588.

Xu, S. M., Feng, S., Peng, G., Wang, J. D., & Yushan, A. (2005). Removal of Pb (II) by crosslinked amphoteric starch containing the carboxymethyl group. *Carbohydrate Polymers*, *60*, 301–305.

Xu, S. M., Feng, S., Yue, F., & Wang, J. D. (2004). Adsorption of Cu (II) ions from an aqueous solution by crosslinked amphoteric starch. *Journal of Applied Polymer Science*, *92*, 728–732.

Yang, Y., & Shao, Y. (2000). Synthesis of sulfhydryl chitin and its adsorption properties for heavy metal ions. *Journal of Applied Polymer Science*, *77*, 151–155.

Yin, Q. F., Ju, B. Z., Zhang, S. F., Wang, X. B., & Yang, J. Z. (2008). Preparation and characteristics of novel dialdehyde aminothiazole starch and its adsorption properties for Cu (II) ions from aqueous solution. *Carbohydrate Polymers*, *72*, 326–333.