JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Novel Zwitterionic Inorganic−Organic Hybrids: Kinetic and Equilibrium Model Studies on Pb^{2+} Removal from Aqueous Solution

Junsheng Liu,* Long Song, and Guoquan Shao

Key Laboratory of Membrane Materials & Processes, Department of Chemical and Materials Engineering, Hefei University, 373 Huangshan Road, Hefei 230022, China

ABSTRACT: Pb^{2+} removal from aqueous solution using zwitterionic hybrid polymers as adsorbents was studied. Influence factors such as solution temperature, initial pH, adsorption time, and solution concentration on Pb^{2+} adsorption were investigated. Adsorption kinetics data were modeled using four two-parameter kinetic equations (i.e., Lagergren first-order and second-order, Ritchie modified second-order, and intraparticle diffusion models). It was indicated that Pb^{2+} adsorption on these zwitterionic hybrid polymers followed the Lagergren second-order kinetic model. Meanwhile, the equilibrium adsorption data were analyzed using four two-parameter isotherm equations (i.e., Langmuir, Freundlich, Dubinin−Radushkevich, and Temkin isotherm models). The results reveal that the adsorption of Pb^{2+} ions followed the Langmuir isotherm model. The thermodynamic parameters ΔG, ΔH, and ΔS for Pb^{2+} removal from aqueous solution were also calculated. The negative values of ΔG and the positive values of ΔH are evidence that Pb^{2+} adsorption on these zwitterionic hybrid polymers is spontaneous and an endothermic process in nature. Moreover, the zwitterionic hybrid polymers produced reveal relatively high desorption efficiency in $1.0\ mol \cdot dm^{-3}$ aqueous HNO_3 solution, indicating that they can be recycled in industrial processes. These findings suggest that the zwitterionic hybrid polymers are promising adsorbents for Pb^{2+} removal from contaminated water.

1. INTRODUCTION

Water pollution caused by highly toxic heavy metals such as Pb^{2+}, Cu^{2+}, and Cd^{2+} has become a major environmental issue throughout the world. Especially with the rapid development of lead refineries and wide application of lead-acid rechargeable batteries, Pb^{2+} pollution has deserved increasing attention. Currently, it is well accepted that lead cannot be biodegraded and is easily accumulated in the vital organs in humans and animals to induce lead poisoning.[1−3] Removing Pb^{2+} from aqueous media or eliminating its pollution loading amount in water resources is thus significantly important and highly needed. Various innovative methods have recently been developed for Pb^{2+} removal from water. Among these, adsorption using functionalized hybrid materials as adsorbents is regarded as one of the most effective techniques.[4,5]

As one type of inorganic/organic hybrid material with functionalized ionic groups, zwitterionic hybrid polymers have attracted much interest in recent years.[6−8] This type of hybrid polymer not only combines the advantages of organic and inorganic materials but also exhibits some distinguished properties, such as structural flexibility and thermal and mechanical stability. Typically, its unique pendant-side structure allows its application in the separation and recovery of heavy metal ions from aqueous solution via an electrostatic effect between ionic groups and metal ions, exhibiting promising applications in the field of heavy metal removal. However, little work has been done so far to study the kinetic and equilibrium model of Pb^{2+} removal from water using a zwitterionic hybrid polymer as a sorbent.

Recently, much effort has been made to investigate the preparation, characterization, and applications of zwitterionic hybrid polymers and membranes in the separation field.[9−12] In previous articles,[11,12] a series of zwitterionic hybrid polymers were prepared from the ring-opening polymerization of pyromellitic acid dianhydride (PMDA) and phenylaminomethyl trimethoxysilane (PAMTMS) and a subsequent sol−gel process. Their applications for Cu^{2+} and Pb^{2+} removal from aqueous solution were examined. Especially, their adsorption kinetics and isotherms were modeled based on two-parameter kinetic and isotherm models. It was indicated that their adsorption behavior for Pb^{2+} ions fitted well with the Lagergren second-order kinetic and the Langmuir isotherm models. Our continuing interest in such zwitterionic hybrid polymers stimulates us to make further effort. Therefore, to continue the previous job and examine the adsorption properties of zwitterionic hybrid polymers with different molecular structures for heavy metal ions, herein, the kinetic and equilibrium data of zwitterionic hybrid polymers with a pendant-side structure for Pb^{2+} removal are investigated.

Compared with the previous articles,[11,12] the novelty of this investigation is that: (1) the anion-exchange (i.e., $-COOH$ and $-COO^-$) and cation-exchange groups located on the hybrid matrix are arrayed in the two sides of the polymer chain, indicating a pendant-side molecular structure, (2) the experimental data were modeled using four two-parameter kinetic (i.e., Lagergren first-order, Lagergren second-order, Ritchie modified second-order, and intraparticle diffusion models) and isotherm [i.e., Langmuir, Freundlich, Dubinin−Radushkevich (D−R), and Temkin isotherm models] equations to investigate the lead sorption mechanism; and (3) the thermodynamic parameter ΔG, ΔH, and ΔS values were calculated to evaluate the adsorption behavior of Pb^{2+} ions on these zwitterionic hybrid polymers.

Received: November 7, 2010
Accepted: March 18, 2011
Published: March 29, 2011

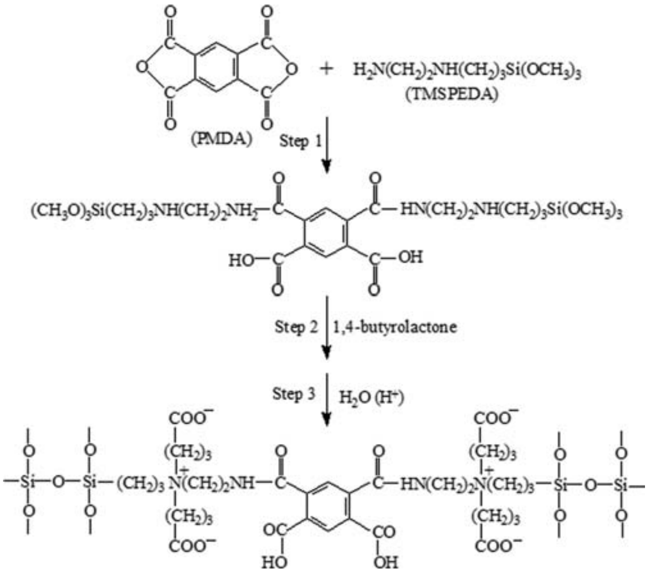
dx.doi.org/10.1021/je1011949 | *J. Chem. Eng. Data* 2011, 56, 2119–2127

Table 1. Composition and Ion-Exchange Capacities (IECs) of the Prepared Zwitterionic Hybrid Polymers[13]

sample	PMDA (mol)	TMSPEDA (mol)	BL (mol)	CIECs ($mmol \cdot g^{-1}$)	AIECs ($mmol \cdot g^{-1}$)	net charge[a]
A	0.1	0.1	0.01	9.55	6.28	3.27
B	0.2	0.1	0.01	9.13	5.92	3.21
C	0.3	0.1	0.01	9.83	4.97	4.86
D	0.4	0.1	0.01	11.49	5.82	5.67

[a] Net charge = CIEC − AIEC.

Scheme 1. Preparation Route of Zwitterionic Hybrid Polymers[a]



[a] Step 1 is the ring-opening polymerization of PMDA and TMSPEDA to produce the hybrid precursor. Step 2 is the zwitterionic process of 1,4-butyrolactone with amine groups to create ion pairs in the polymer chains. Step 3 is the hydrolysis and condensation of alkoxysilane by sol−gel reaction.[13]

This investigation will aid in the optimization design of the adsorption process and the effective disposal of contaminated water caused by heavy metal ions.

2. EXPERIMENTAL SECTION

2.1. Materials. *N*-[3-(Trimethoxysilyl)propyl] ethylene diamine (TMSPEDA, purity: ≥ 95.0 %) was purchased from the Silicone New Material Co., Ltd. of Wuhan University (Wuhan, China) and used without further purification. Pyromellitic acid dianhydride (PMDA, purity: ≥ 99.5 %) and 1,4-butyrolactone (BL, purity: ≥ 97.0 %) were purchased from the National Pharmaceutical Group Corporation of China (Shanghai, China) and used as received. Lead nitrate, $Pb(NO_3)_2$, and other reagents were of analytical grade.

2.2. Preparation of Zwitterionic Hybrid Polymers. In this work, four samples A to D were used as zwitterionic hybrid adsorbents to investigate the kinetic and equilibrium models of Pb^{2+} ions. The main difference in these samples is that different amounts of organic ingredient PMDA were incorporated into the hybrid matrix, which would give rise to different amounts of ionic groups in the polymer chains although they had a similar pendant-side molecular structure. The composition and ion-exchange capacities (IECs) of the prepared zwitterionic hybrid polymers used in this case are listed in Table 1. The preparation of these zwitterionic hybrid polymers was discussed in detail in a previous paper.[13] For the convenience of reference, the preparation route is also illustrated in Scheme 1. Moreover, compared with a previous study in our laboratory,[12] it can be found that the replacement of PAMTMS with TMSPEDA during the preparation of zwitterionic hybrid polymers, in which two types of anionic (i.e., $-COOH$ and $-COO^-$) groups are produced, will decrease the adsorption capacity of Pb^{2+} ions on these hybrid polymers. The significance of such modification with TMSPEDA will be confirmed, which is capable of giving insight into the preparation of hybrid adsorbents and adjusting the adsorption capacity of Pb^{2+} ions via different structural polymers.

2.3. Adsorption Experiments. The adsorption experiments of zwitterionic hybrid polymers for Pb^{2+} ions were conducted in a similar way to our previous studies, in which an aqueous solution containing Pb^{2+} ions was used as the adsorption medium.[11,14] The solution concentration of Pb^{2+} ions was determined using an EDTA solution ($0.1\ mol \cdot dm^{-3}$).

The adsorption capacity (q_{Pb2+}) of Pb^{2+} ions can be calculated by eq 1

$$q_{Pb^{2+}} = \frac{(C_0 - C_R)V}{W} \tag{1}$$

where V is the volume of aqueous solution; C_0 and C_R are the concentration of initial and remaining solution, respectively; and W is the weight of the sample.

The adsorption of Pb^{2+} from aqueous $Pb(NO_3)_2$ solution was initially studied at (35, 45, and 55) °C to optimize the adsorption temperature. The effect of initial pH on Pb^{2+} adsorption was conducted using $0.2\ mol \cdot dm^{-3}$ aqueous $Pb(NO_3)_2$ solution to determine the optimal initial solution pH. For adsorption kinetic studies, 1.0 g of sample was immersed in $0.2\ mol \cdot dm^{-3}$ aqueous $Pb(NO_3)_2$ solution for different adsorption times at pH 5. The experimental data were modeled using four two-parameter kinetic equations (i.e., Lagergren first-order and second-order, Ritchie modified second-order, and intraparticle diffusion models). The adsorption isotherm was conducted by changing the solution concentration ranging from (0.05, 0.1, to 0.206) $mol \cdot dm^{-3}$ (i.e., (10.36, 20.72, and 42.74) $mg \cdot mL^{-1}$) at 45 °C for 24 h at pH 5. The adsorption data were analyzed using four two-parameter isotherm equations [i.e., Langmuir, Freundlich, Dubinin−Radushkevich (D−R), and Temkin isotherm models]. On the basis of the adsorption data at different temperatures, the thermodynamic parameters ΔG, ΔH, and ΔS were calculated. In addition, the desorption efficiency was measured using HCl, H_2SO_4, and HNO_3 acidic solutions ($0.5\ mol \cdot dm^{-3}$) as desorbents.

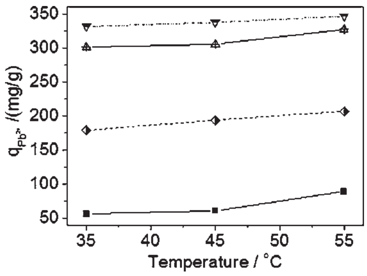


Figure 1. Adsorption capacity of Pb^{2+} ions on samples A (solid square), B (half-filled diamond), C (center triangle), and D (half-filled inverted triangle) vs solution temperature; 1.0 g samples were immersed in 20 dm^3 of aqueous $Pb(NO_3)_2$ solution (0.2 $mol \cdot dm^{-3}$) for 24 h.

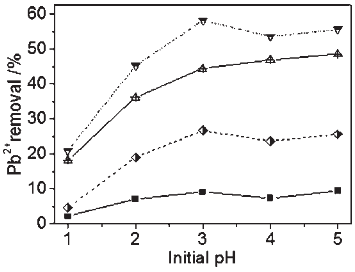


Figure 2. Initial pH vs the percent of Pb^{2+} removal on samples A (solid square), B (half-filled diamond), C (center triangle), and D (half-filled inverted triangle). The concentration of aqueous $Pb(NO_3)_2$ solution was 0.2 $mol \cdot dm^{-3}$ for 24 h at 45 °C.

3. RESULTS AND DISCUSSION

3.1. Effect of Temperature on Pb^{2+} Adsorption. It is well accepted that solution temperature is an important factor affecting the adsorption of divalent metal ions on an adsorbent. To select the optimal temperature for Pb^{2+} adsorption, the effect of solution temperature on Pb^{2+} adsorption was conducted and is presented in Figure 1.

As shown in Figure 1, it can be seen that the adsorption capacity of Pb^{2+} ions on samples A to D in aqueous $Pb(NO_3)_2$ solution increases with an increase in solution temperature, demonstrating that Pb^{2+} adsorption on these samples is endothermic, which can be confirmed by the enthalpy ΔH (as listed in Table 6, hereinafter). Moreover, it can also be seen that at the same temperature the adsorption capacity increases from samples A to D. Such an upward trend is consistent with an increase in the difference of net charge of these samples except that of sample B (cf. Table 1), suggesting that Pb^{2+} adsorption on these samples is related to the electric charge property of ionic groups, and a high difference of net charge will favor the adsorption of Pb^{2+} ions on these samples. The reason can be ascribed to the increasing amount of anionic (i.e., $-COOH$ and $-COO^-$) groups grafted on the polymer chains, leading to an increase in the electrostatic attraction between metal ions and ionic groups.

It should be pointed out that although a high temperature can increase the adsorption capacity of Pb^{2+} ions it also accelerates the evaporation of water from the aqueous $Pb(NO_3)_2$ solution. Therefore, 45 °C was selected as the solution temperature to investigate Pb^{2+} adsorption on these samples.

3.2. Effect of Initial pH. As reported,[15] the initial solution pH has an effect on the adsorption of heavy metal ions in aqueous solution. Since the hydroxide precipitation of metal ions may occur at high pH, the effect of initial pH on Pb^{2+} removal was thus conducted from (1 to 5 at 0.2) $mol \cdot dm^{-3}$ for 24 h at 45 °C. Figure 2 presents the dependence of initial pH on the percent of Pb^{2+} removal.

As shown in Figure 2, it can be seen that at the same initial pH value the adsorption capacity of Pb^{2+} ions increases from samples A to D. Nevertheless, for the individual sample, it indicates different change trends. For example, for samples A and C, the adsorption capacity of Pb^{2+} ions increases with the elevating initial solution pH in the pH range of 1 to 5 and reaches a peak at pH 5. However, for samples B and D, the highest adsorption capacity occurs at pH 3. These findings suggest that Pb^{2+} adsorption on samples A to D is pH dependent. Considering that the natural pH of Pb^{2+} solution is near 5.8[15] and the convenience of titrimetric analysis, the aqueous $Pb(NO_3)_2$ solution at pH 5 was thus chosen as the adsorption medium to study the adsorption behavior of Pb^{2+} ions on these samples.

To explain the effect of initial pH on Pb^{2+} adsorption on these samples, the interaction between Pb^{2+} ions and polymer active sits at different pHs can be theoretically analyzed as follows.

As presented in Scheme 1, the zwitterionic hybrid polymers produced simultaneously contain two types of anionic (i.e., $-COOH$ and $-COO^-$) groups and one type of cationic (i.e., $-N^+-$) group in the polymer chains. Thus, these ionic groups will play different roles in the adsorption of metal ions. Generally, $-COOH$ is partially dissociated in aqueous solution, and the partition degree increases as the pH is raised. Accordingly, the amount of $-COOH$ transformed into the $-COO^-$ group will be elevated. However, due to the existence of the $-COO^-$ group in the backbone of the polymers and the combination of $-COO^-$ groups with H^+, the dissociation of $-COOH$ will thus be blocked. Consequently, the opposite effect of $-COOH$ and $-COO^-$ groups will make the amount of anionic groups keep stability (i.e., a buffer function) and balance the electrostatic attraction of anionic groups for metal ions when the solution pH is changed. Moreover, the existence of the $-N^+-$ group in the backbone of polymers will also impact the adsorption of metal ions, which mainly prevents the adsorption of metal ions on the polymer surface due to the repulsive interaction of co-ions. As a result, Pb^{2+} adsorption on these zwitterionic hybrid polymers is pH dependent. For example, at lower pH, the amount of H^+ is relatively high, and the partition degree of the $-COOH$ group is lower. Meanwhile, the $-COO^-$ group possibly combines with H^+ to produce the $-COOH$ group. Thus, it will decrease the attraction of anionic groups for metal ions and prevent the adsorption of metal ions or ion-exchange. Therefore, at lower pH, the adsorption capacity of Pb^{2+} ions on these samples is lower. Nevertheless, at higher pH, the amount of H^+ is relatively low and the amount of OH^- larger, thus the partition degree of the $-COOH$ group becomes higher. On the other hand, the $-COO^-$ group is difficult to combine with H^+ to produce the $-COOH$ group. Thus, the attraction of anionic groups for metal ions is stronger. Consequently, the adsorption capacity of Pb^{2+} ions increases as solution pH is elevated. Moreover, at higher pH, the larger amount of OH^- possibly combines with the $-N^+-$ group and reduces its repulsion force to metal ions, which will favor the accessibility of metal ions to polymer active sites, leading to an increase in adsorption capacity of Pb^{2+} ions when solution pH is increased.

Furthermore, in comparison with the previous study,[12] it can be noted that the effect of both $-COOH$ and $-COO^-$ groups on the adsorption of metal ions in this case will obviously differ from that of the single $-COOH$ group. As discussed later, it will be confirmed

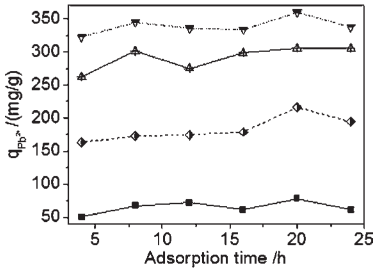


Figure 3. Adsorption capacity of Pb^{2+} ions on samples A (solid square), B (half-filled diamond), C (center triangle), and D (half-filled inverted triangle) vs adsorption time. The concentration of aqueous $Pb(NO_3)_2$ solution was 0.2 mol·dm^{-3} at 45 °C.

that two such types of anionic groups can balance the electrostatic attraction of anionic groups for metal ions and decrease the adsorption capacity of metal ions on the prepared polymers when compared with that of the single −COOH group, demonstrating the impact of molecular structure of zwitterionic hybrid polymers on the adsorption of metal ions in aqueous solution.

3.3. Adsorption Kinetics. To have an insight into the adsorption properties of zwitterionic hybrid polymers for metal ions, the effect of adsorption time on the adsorption capacity of Pb^{2+} ions was performed. Figure 3 illustrates the adsorption capacity of Pb^{2+} ions on samples A to D vs adsorption time.

As shown in Figure 3, it can be observed that at the same adsorption time the adsorption capacity of Pb^{2+} increases from samples A to D. However, for an individual sample, the time for adsorption equilibrium is different, indicating the influence of ionic groups on the adsorption of metal ions.

It is now well accepted that two-parameter adsorption kinetic equations (i.e., Lagergren first-order and second-order,[16,17] and Ritchie modified second-order[18]) are useful tools to describe the adsorption properties of an adsorbent. In addition, the adsorption mechanism can be predicted by the intraparticle diffusion model[19,20] or diffusion-controlled adsorption mechanism.[21] Consequently, the dependency of the adsorption capacity on adsorption time is analyzed using these models.

Currently, the Lagergren first-order and second-order equations can be linearly expressed as eqs 2b and 3b, respectively.

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2a}$$

or

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2b}$$

$$q_t = \frac{q_e^2 k_2 t}{(1 + q_e k_2 t)} \tag{3a}$$

or

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3b}$$

where k_1 and k_2 are the first-order and second-order rate constant, respectively; and q_t and q_e (mg·g^{-1}) are the adsorption capacity of the Pb^{2+} ion at time t and at the equilibrium state, respectively.

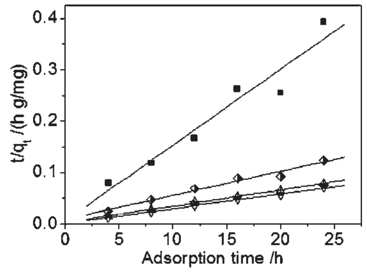


Figure 4. Lagergren second-order kinetic model for Pb^{2+} adsorption on samples A (solid square), B (half-filled diamond), C (center triangle), and D (half-filled inverted triangle).

Table 2. Lagergren Second-Order Kinetic Model Parameters for Pb^{2+} Adsorption

	k_2	h^a	q_e(exp.)	q_e(cal.)	
sample	(h·g·mg^{-1})	(h·mg·g^{-1})	(mg·g^{-1})	(mg·g^{-1})	R^2
A	0.0409	187.617	61.100	67.659	0.936
B	0.00251	114.810	215.928	213.675	0.974
C	0.00350	348.432	305.335	315.457	0.996
D	0.0115	1392.924	341.768	347.222	0.995

[a] Initial adsorption rate $(h) = k_2 q_e^2$.

Moreover, the Ritchie modified second-order model usually is used to determine the initial particle loading[17] and can be linearly expressed as eqs 4a and 4b

$$q_t = q_e\left\{1 - \left[\frac{1}{\beta + k_{2m}t}\right]\right\} \tag{4a}$$

or

$$\frac{q_e}{q_e - q_t} = \beta + k_{2m}t \tag{4b}$$

where k_{2m} is the Ritchie modified second-order rate constant of adsorption; β is a constant representing the initial particle loading; and q_t and q_e (mg·g^{-1}) are the adsorption capacity of Pb^{2+} ions at time t and at the equilibrium state, respectively.

It can be found that the Lagergren first-order and Ritchie modified second-order models for Pb^{2+} adsorption on samples A to D exhibited a poor regression coefficient (R^2) (the data were not presented in the text), suggesting that Pb^{2+} adsorption on these samples does not follow the Lagergren first-order kinetic and Ritchie modified second-order models. In contrast, the regression coefficient (R^2) of the Lagergren second-order model fitted well for these samples (Figure 4). Meanwhile, the experimental and calculated Lagergren second-order kinetic parameters for Pb^{2+} adsorption reveal approximate values (cf. Table 2).

On the basis of these data, it can be concluded that Pb^{2+} adsorption on these zwitterionic hybrid polymers followed the Lagergren second-order kinetic model. This finding is consistent with the result reported in our previous study,[12] demonstrating that zwitterionic hybrid polymers have the same adsorption kinetic behavior.

Furthermore, the effect of intraparticle diffusion on the adsorption rate can be calculated based on the relationship of the adsorption capacity and adsorption time, which can be expressed as eq 5[19,20]

$$q_t = x_i + k_p t^{0.5} \tag{5}$$

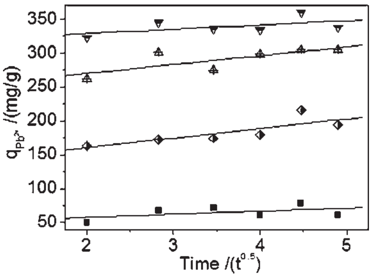


Figure 5. Intraparticle diffusion curves for Pb^{2+} adsorption on samples A (solid square), B (half-filled diamond), C (center triangle), and D (half-filled inverted triangle).

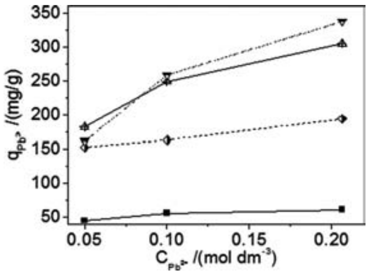


Figure 6. Adsorption capacity of Pb^{2+} on samples A (solid square), B (half-filled diamond), C (center triangle), and D (half-filled inverted triangle) vs initial solution concentration at pH 5. The sample was immersed in different concentration aqueous $Pb(NO_3)_2$ solution for 24 h, respectively.

where q_t is the adsorbed amount $(\text{mg}\cdot\text{g}^{-1})$ at time t; k_p is the intraparticle diffusion rate constant; and x_i is the intercept, which is related to the boundary layer thickness.[19,20]

Figure 5 illustrates the intraparticle diffusion curves for Pb^{2+} adsorption. It can be observed that the regression coefficient indicated a poor fit ($R^2 = 0.236, 0.649, 0.584$, and 0.298 for samples A to D, respectively). This finding reveals that Pb^{2+} adsorption on these samples is not governed by intraparticle diffusion. A diffusion-controlled adsorption mechanism might be the major process as reported in another article.[21] The reason might be related to the formation of a hybrid matrix and the different content of cationic and anionic groups in the polymer backbone.

3.4. Adsorption Isotherms. To further explain the above trends, an adsorption isotherm study of these zwitterionic hybrid polymers was conducted. Figure 6 illustrates the dependence of Pb^{2+} adsorption capacity on initial solution concentration. The equilibrium data were analyzed using four two-parameter isotherm equations (i.e., Langmuir, Freundlich, Dubinin−Radushkevich (D−R), and Temkin isotherm models).

Generally, the Langmuir isotherm equation is based on monolayer adsorption on the active sites of the adsorbent, which can be expressed as eq 6[16,19]

$$\frac{c_e}{q_e} = \frac{c_e}{Q_m} + \frac{1}{Q_m b} \tag{6}$$

where q_e and c_e are the equilibrium concentrations of metal ion in the adsorbed $(\text{mg}\cdot\text{g}^{-1})$ and liquid phases $(\text{mg}\cdot\text{mL}^{-1})$, respectively. Q_m and b are the Langmuir constants, which can be calculated from the intercept and slope of the linear plot based on c_e/q_e versus c_e.

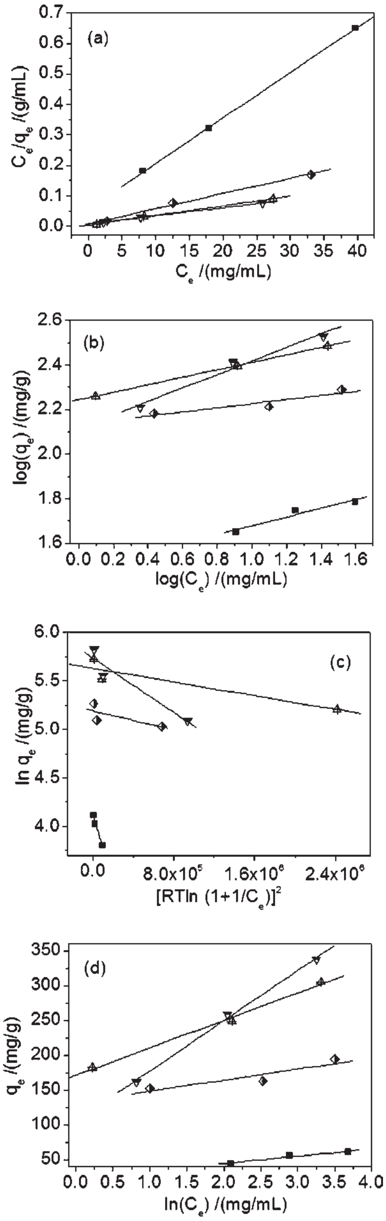


Figure 7. Adsorption isotherm of samples A (solid square), B (half-filled diamond), C (center triangle), and D (half-filled inverted triangle) for Pb^{2+} ions. (a) Langmuir, (b) Freundlich, (c) Dubinin−Radushkevich, and (d) Temkin isotherm model.

The Freundlich isotherm model is considered as the adsorption occurring on a heterogeneous surface with uniform energy, which can be expressed as eqs 7a and 7b[16,17]

$$q_e = k_F c_e^{1/n} \tag{7a}$$

or

$$\log q_e = \log k_F + \frac{1}{n} \log c_e \tag{7b}$$

where q_e and c_e are the equilibrium concentrations of metal ion in the adsorbed $(\text{mg}\cdot\text{g}^{-1})$ and liquid phases $(\text{mg}\cdot\text{mL}^{-1})$, respectively. Both k_F and n are the Freundlich constants, which can be calculated from the slope and intercept of the linear plot according to $\log(q_e)$ vs $\log(c_e)$.

Table 3. Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin Isotherm Parameters for Pb^{2+} Adsorption on Zwitterionic Hybrid Polymers

	values			
parameter	sample A	sample B	sample C	sample D
		Langmuir		
$Q_m/(mg \cdot g^{-1})$	67.204	202.020	320.512	380.228
$b/(mL \cdot mg^{-1})$	0.257	0.578	0.647	0.301
R^2	0.999	0.994	0.997	0.999
		Freundlich		
$k_F/(mg \cdot g^{-1})$	30.378	136.260	175.420	130.457
$n/(g \cdot mL^{-1})$	5.104	10.861	5.991	3.308
R^2	0.941	0.865	0.999	0.978
		Dubinin–Radushkevich		
$Q_{DR}/(mg \cdot g^{-1})$	61.026	179.454	278.681	308.903
$K_{DR}/(mol^2 \cdot J^{-2})$	$3.318 \cdot 10^{-6}$	$2.453 \cdot 10^{-7}$	$1.770 \cdot 10^{-7}$	$7.015 \cdot 10^{-7}$
$E/(J \cdot mol^{-1})$	388.157	1427.482	1680.636	844.222
R^2	0.987	0.561	0.867	0.925
		Temkin		
$b_T/(J \cdot mol^{-1})$	257.117	167.172	67.062	36.632
B_T	10.287	15.822	39.442	72.206
$K_T/(mL \cdot g^{-1})$	10.538	4438.299	76.898	4.298
R^2	0.957	0.847	0.993	0.997

To obtain the mean free energy of adsorption and further examine the adsorption behavior of the prepared polymers, the equilibrium adsorption data of Pb^{2+} ions were analyzed using the Dubinin–Radushkevich (D–R) isotherm equation, which can be expressed as eqs 8a and 8b[22,23]

$$q_e = Q_{DR} \exp\left(-K_{DR}\left[RT \ln\left(1+\frac{1}{C_e}\right)\right]^2\right) \tag{8a}$$

or

$$\ln q_e = \ln Q_{DR} - K_{DR} R^2 T^2 \left[\ln\left(1+\frac{1}{C_e}\right)\right]^2 \tag{8b}$$

where q_e is the amount of metal ions adsorbed $(mg \cdot g^{-1})$; Q_{DR} is the maximum adsorption capacity of metal ions $(mg \cdot g^{-1})$; K_{DR} is the Dubinin–Radushkevich isotherm constant $(mol^2 \cdot kJ^{-2})$; C_e is the equilibrium concentration of metal ions $(mg \cdot L^{-1})$; R is the gas constant $(8.314\ J \cdot mol^{-1} \cdot K^{-1})$; and T is absolute temperature (K).

The Dubinin–Radushkevich isotherm constant, K_{DR}, is related to the mean free energy of adsorption, E $(kJ \cdot mol^{-1})$, which can be obtained using the following relationship[22]

$$E = \frac{1}{\sqrt{2K_{DR}}} \tag{9}$$

To evaluate the adsorption heat, the equilibrium adsorption data of Pb^{2+} ions were analyzed using the Temkin isotherm equation, which can be expressed as eq 10[22,24]

$$q_e = \frac{RT}{b_T}\ln(K_T C_e) = B_T \ln(K_T C_e) \tag{10}$$

where constant $B_T = RT/b_T$, which is related to the adsorption heat; R is the gas constant $(8.314\ J \cdot mol^{-1} K^{-1})$; T is absolute temperature (K); b_T is the Temkin isotherm constant, which is the variation of adsorption energy $(J \cdot mol^{-1})$; and K_T is the equilibrium binding constant corresponding to the maximum binding energy. Both B_T and K_T can be calculated from the slope and the intercept of the linear plot based on q_e vs ln (C_e), respectively.

Figure 7(a) to (d) illustrates the Langmuir, Freundlich, Dubinin–Radushkevich (D–R), and Temkin adsorption isotherm of samples A to D for Pb^{2+} ions. The corresponding isotherm parameters for Pb^{2+} adsorption on zwitterionic hybrid polymers are summarized in Table 3.

As shown in Table 3, it can be seen that for samples A to D that the experimental data fitted well with the Langmuir isotherm model [i.e., the regression coefficient (R^2) values are in the range of 0.994 to 0.999]. In contrast, these experimental data were fitted worse with the Freundlich isotherm model [i.e., the regression coefficient (R^2) values are within 0.865 to 0.999], the Dubinin–Radushkevich isotherm model [i.e., the regression coefficient (R^2) values are within 0.561 to 0.987], and the Temkin isotherm model [i.e., the regression coefficient (R^2) values are within 0.847 to 0.997]. On the basis of these results, it can be concluded that the adsorption process of Pb^{2+} ions on zwitterionic hybrid polymers follows Langmuir monolayer adsorption, which is also in agreement with the outcome reported in a previous article.[12] The reason might be related to the following factors: the electrostatic attraction between the ionic groups and the metal ions, the content of ionic groups, etc.,[16] as well as the influence of the $-N^+-$ group on the adsorption of metal ions as discussed in previous papers.[11,12]

For the Langmuir isotherm model, the separation factor or equilibrium parameter (R_L) can be used to predict the favorability of adsorption, which is defined by eq 11[16,23]

$$R_L = \frac{1}{(1 + bC_0)} \tag{11}$$

where C_0 is the initial solution concentration and b is the Langmuir adsorption equilibrium constant. When the R_L value is within $0 < R_L < 1$, the adsorption of Pb^{2+} ions is favorable. Otherwise, the adsorption of Pb^{2+} ions is unfavorable.[21]

Table 4 lists the calculated R_L values based on the Langmuir isotherm parameters. Obviously, for samples A to D, these R_L values are all in the range of $0 < R_L < 1$, demonstrating that Pb^{2+} adsorption on these samples is favorable. Consequently, these zwitterionic hybrid polymers are promising adsorbents for Pb^{2+} removal from aqueous solution.

For comparison, Table 5 summarizes the maximum capacity, Q_m, of zwitterionic hybrid polymers with Q_m of other adsorbents reported in some articles.[3,19,23−25] It should be emphasized that the distinction in Pb^{2+} adsorption capacity can be ascribed to the difference in physicochemical properties of various adsorbents and the equilibrium condition conducted. Clearly, zwitterionic hybrid polymers exhibit high efficiency for Pb^{2+} removal, implying that they are promising in the separation and recovery of Pb^{2+} ions from waste chemicals and contaminated water of lead-acid rechargeable batteries.

3.5. Thermodynamic Parameters. As presented in Figure 1, it can be seen that for samples A to D the adsorption capacity of Pb^{2+} ions increases with an increase in solution temperature, suggesting that the adsorption process of Pb^{2+} ions is endothermic.[16] To further confirm such a trend, the thermodynamic parameters, Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS), are calculated.

Currently, the thermodynamic parameters ΔG, ΔH, and ΔS can be calculated from eqs 12 and 13[15]

$$\Delta G = -RT \ln K_c \tag{12}$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{13}$$

in which K_c is the equilibrium partition coefficient and can be calculated from eq 14[16]

$$K_c = \frac{C_s}{C_e} \tag{14}$$

where R is the gas constant ($8.314\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$); C_s and C_e are the equilibrium concentrations of Pb^{2+} ions in the adsorbent and solution, respectively; and T is the solution temperature (K). ΔH and ΔS can be calculated from the slope and intercept of the linear plot according to $\ln K_c$ vs $1/T$ (cf. Figure 8). The calculated results are presented in Table 6.

As shown in Table 6, the ΔG values are all negative, and the ΔH values are all positive, further corroborating that Pb^{2+}adsorption on zwitterionic hybrid polymers A to D is spontaneous and an endothermic process in nature.

Moreover, it can be noted that for individual samples these ΔG values become more negative with an increase in solution temperature, implying that the Pb^{2+} adsorption ability increases as the solution temperature was elevated. In addition, it can be found in Table 6 that the ΔS values are all positive, suggesting that the randomness increased during the adsorption of Pb^{2+} ions on samples A to D. These findings demonstrate that solution temperature and the content of ionic groups in the polymer chains have an active effect on Pb^{2+} adsorption.

The above trend can be ascribed to the electrostatic attraction between the Pb^{2+} ions and ionic groups in the zwitterionic hybrid polymers and the increasing dissociation degree of −COOH groups as solution temperature increases.[13,16] As discussed in a previous article,[13] at different adsorption periods, the effects of electrostatic attraction and intraparticle diffusion on adsorption process are different. In the early period of adsorption, electrostatic attraction is the major influencing factor. However, with the elapse of adsorption time, the intraparticle diffusion will govern the adsorption process as it reaches the final equilibrium state.

In comparison with our previous study,[12] it can be found that although the ΔG values of samples A to D prepared in this case are slightly higher than those in the previous work both ΔS and ΔH values in this case are all remarkably lower than the data obtained in the previous article, suggesting that Pb^{2+} adsorption on these zwitterionic hybrid polymers is easier. This improvement in Pb^{2+} adsorption ability would be very meaningful in the preparation of zwitterionic hybrid adsorbents for Pb^{2+} removal operating at high temperature in industry. The reason can be ascribed to the difference of various ionic groups being grafted on the polymer chains.

3.6. Desorption Experiment. Currently, for the removal of heavy metal ions, the desorption of a sorbent and reuse of metal ion in industrial processes rather than the simple adsorption and disposal is significant.[17] To regenerate and recycle the spent

Table 4. Calculated R_L Values Based on the Langmuir Isotherm Parameter

	R_L value			
$C_0/(\mathrm{mol \cdot dm^{-3}})$	sample A	sample B	sample C	sample D
0.05	0.272	0.142	0.129	0.242
0.10	0.157	0.0769	0.0693	0.138
0.206	0.0857	0.0400	0.0359	0.0741

Table 5. Comparison of Q_m of Zwitterionic Hybrid Polymers for Pb^{2+} with Those of Different Types of Sorbents in References

sorbent type	Q_m ($\mathrm{mg \cdot g^{-1}}$)	solution temperature (°C)	pH	ref
EMMB	333.0	room temperature	5.3	3
magnetic chelating resin	571.84 (2.76 $\mathrm{mmol \cdot g^{-1}}$)	45	6.0	19
metal-complexed chitosans	105.26	room temperature	5.0	23
moringa oleifera bark	34.60	25	5.0	24
fructose-mediated (polyethylene glycol/chitosan) membrane	185.18	30	6.0	25
PAN-oxime nanofibers	263.45	25	-	26
zwitterionic hybrid polymers	380.22	45	5.0	this work

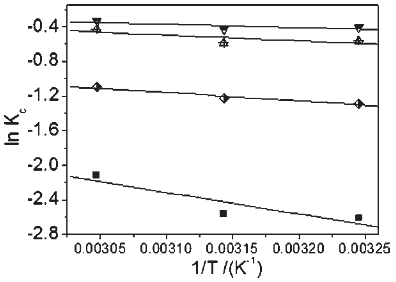


Figure 8. van't Hoff plot of Pb^{2+} adsorption on samples A (solid square), B (half-filled diamond), C (center triangle), and D (half-filled inverted triangle). The concentration of aqueous $Pb(NO_3)_2$ solution was 0.2 mol·dm^{-3} at (35, 45, and 55) °C for 24 h, respectively.

Table 6. Thermodynamic Data for Pb^{2+} Adsorption on Samples A to D

	temperature	ΔG	ΔS	ΔH
sample	(K)	(kJ·mol^{-1})	(J·mol^{-1}·K^{-1})	(kJ·mol^{-1})
A	308.15	−13.886	45.131	20.769
	318.15	−14.337		
	328.15	−14.789		
B	308.15	−4.688	15.241	8.030
	318.15	−4.841		
	328.15	−4.993		
C	308.15	−4.035	13.112	5.558
	318.15	−4.166		
	328.15	−4.297		
D	308.15	−2.058	6.690	3.150
	318.15	−2.125		
	328.15	−2.192		

adsorbent, a desorption experiment was conducted, and the related results are shown in Tables 7 and 8.

Obviously, among the desorbents of HCl, H_2SO_4, and HNO_3, the percent of desorption efficiency of sample D using 0.5 mol·dm^{-3} aqueous HNO_3 solution for 3 h could reachup to 49.35 % (cf. Table 8), indicating an effective regeneration cycle.

To further examine the effect of acid concentration on desorption efficiency, desorption was also performed using different concentrations of HNO_3. It can be found that the percent of desorption efficiency increases with an increase in acid concentration. With 1.0 mol·dm^{-3} aqueous HNO_3 solution, desorption efficiency was improved to 75.65 %. On the basis of these findings, it can be concluded that these zwitterionic hybrid polymers are promising adsorbents for Pb^{2+} removal from wastewater.

Note that this article mainly focuses on the kinetic and equilibrium model studies on Pb^{2+} removal using zwitterionic hybrid polymers as adsorbents, and little work is done to improve the desorption efficiency of these samples, which indicated unsatisfactory data in the desorbents of HCl, H_2SO_4, and HNO_3. However, it does not mean that this is less important. For their industrial application, further work is required to optimize the adsorption and desorption process to highly elevate the desorption efficiency of these zwitterionic hybrid polymers. We believe that a satisfactory desorption efficiency will be obtained with the further improvement on the properties of hybrid polymers and the optimization of operational parameters, which will be our future job.

Table 7. Desorption Efficiency of Sample D for Pb^{2+} Ions in Various Desorbents

	concentration of acid	desorption time	efficiency
desorbent	(mol·dm^{-3})	(h)	(%)
HCl	0.5	3	31.85
H_2SO_4	0.5	3	27.85
HNO_3	0.5	3	49.35

Table 8. Desorption Efficiency of Sample D for Pb^{2+} Ions in Different Concentration of HNO_3

concentration	desorption time	efficiency
(mol·dm^{-3})	(h)	(%)
0.1	3	18.06
0.5	3	49.35
1.0	3	75.65

4. CONCLUSIONS

The kinetic and equilibrium models of Pb^{2+} ions on zwitterionic hybrid polymers were investigated. It is confirmed that the Pb^{2+} adsorption on zwitterionic hybrid polymers followed the Lagergren second-order kinetic model and the Langmuir isotherm model, demonstrating that the adsorption mechanism followed Langmuir monolayer adsorption. The electrostatic attraction between the ionic groups and Pb^{2+} ions and the category difference of ionic groups might be responsible for such trends. The negative values of ΔG and the positive values of ΔH reveal that Pb^{2+} adsorption on these zwitterionic hybrid polymers is spontaneous and an endothermic process in nature. The percent desorption efficiency of sample D for Pb^{2+} in 1.0 mol·dm^{-3} aqueous HNO_3 solution for 3 h was 75.65 %, indicating an effective regeneration cycle. By comparison with other adsorbents reported in some articles, it is found that these zwitterionic hybrid polymers are promising sorbents and can be applied to remove and recover Pb^{2+} ions from aqueous solution.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +86-551-2158439. Fax: +86-551-2158437. E-mail: jsliu@hfuu.edu.cn.

Funding Sources

Financial support from the Natural Science Foundation of China (No. 21076055), Opening Project of Key Laboratory of Solid Waste Treatment and Resource Recycle (SWUST), Ministry of Education (No. 09zxgk03), Significant Foundation of Educational Committee of Anhui Province (No. ZD2008002-1), and Anhui Provincial Natural Science Foundation (No. 090415211) is highly appreciated.

■ ACKNOWLEDGMENT

Special thanks are given to the two anonymous reviewers for their insightful comments and suggestions. The authors also thank Editor Paul L. Brown for proof reading the manuscript.

REFERENCES

(1) Ju, X. J.; Zhang, S. B.; Zhou, M. Y.; Xie, R.; Yang, L. H.; Chu, L. Y. Novel heavy-metal adsorption material: ion-recognition P(NIPAM-co-BCAm) hydrogels for removal of lead(II) ions. *J. Hazard. Mater.* **2009**, *167*, 114–118.

(2) Zhao, X.; Jia, Q.; Song, N.; Zhou, W.; Li, Y. Adsorption of Pb(II) from an aqueous solution by titanium dioxide/carbon nanotube nanocomposites: kinetics, thermodynamics, and isotherms. *J. Chem. Eng. Data* **2010**, *55*, 4428–4433.

(3) Júnior, O. K.; Gurgel, L. V. A.; de Freitas, R. P.; Gil, L. F. Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse chemically modified with EDTA dianhydride (EDTAD). *Carbohydr. Polym.* **2009**, *77*, 643–650.

(4) Xia, K.; Ferguson, R. Z.; Losier, M.; Tchoukanova, N.; Brüning, R.; Djaoued, Y. Synthesis of hybrid silica materials with tunable pore structures and morphology and their application for heavy metal removal from drinking water. *J. Hazard. Mater.* **2010**, *183*, 554–564.

(5) Zhang, J. P.; Wang, A. Q. Adsorption of Pb(II) from aqueous solution by chitosan-g-poly(acrylic acid)/attapulgite/sodium humate composite hydrogels. *J. Chem. Eng. Data* **2010**, *55*, 2379–2384.

(6) Xuan, F. Q.; Liu, J. S. Preparation, characterization and application of zwitterionic polymers and membranes: Current developments and perspective. *Polym. Int.* **2009**, *58*, 1350–1361.

(7) Xu, T. W. Ion exchange membranes: State of their development and perspective. *J. Membr. Sci.* **2005**, *263*, 1–29.

(8) Liang, W. J.; Wu, C. P.; Hsu, C. Y.; Kuo., P. L. Synthesis, characterization, and proton-conducting properties of organic-inorganic hybrid membranes based on polysiloxane zwitterionomer. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3444–3453.

(9) Liu, J. S.; Xu, T. W.; Fu, Y. X. Fundamental studies of novel inorganic—organic charged zwitterionic hybrids. 2. Preparation and characterizations of hybrid charged zwitterionic membranes. *J. Membr. Sci.* **2005**, *252*, 165–173.

(10) Liu, J. S.; Xu, T. W.; Han, X. Z.; Fu, Y. X. Synthesis and characterizations of a novel zwitterionic hybrid copolymer containing both sulfonic and carboxylic groups via sulfonation and zwitterionic process. *Eur. Polym. J.* **2006**, *42*, 2755–2764.

(11) Liu, J. S.; Ma, Y.; Xu, T. W.; Shao, G. Q. Preparation of zwitterionic hybrid polymer and its application for the removal of heavy metal ions from water. *J. Hazard. Mater.* **2010**, *178*, 1021–1029.

(12) Liu, J. S.; Ma, Y.; Zhang, Y. P.; Shao, G. Q. Novel negatively charged hybrids. 3. Removal of Pb^{2+} from aqueous solution using zwitterionic hybrid polymers as adsorbent. *J. Hazard. Mater.* **2010**, *173*, 438–444.

(13) Dong, Q.; Liu, J. S.; Song, L.; Shao, G. Q. Novel zwitterionic inorganic—organic hybrids: Synthesis of hybrid adsorbents and their applications for Cu^{2+} removal. *J. Hazard. Mater.* **2011**, *186*, 1335–1342.

(14) Liu, J. S.; Wang, X. H.; Xu, T. W.; Shao, G. Q. Novel negatively charged hybrids. 1. Copolymers: Preparation and adsorption Properties. *Sep. Purif. Technol.* **2009**, *66*, 135–142.

(15) Atia, A. A.; Donia, A. M.; ELwakeel, K. Z. Adsorption behaviour of non-transition metal ions on a synthetic chelating resin bearing iminoacetate functions. *Sep. Purif. Technol.* **2005**, *43*, 43–48.

(16) Ramesh, A.; Hasegawa, H.; Maki, T.; Ueda, K. Adsorption of inorganic and organic arsenic from aqueous solutions by polymeric Al/Fe modified montmorillonite. *Sep. Purif. Technol.* **2007**, *56*, 90–100.

(17) Kumar, G. P.; Kumar, P. A.; Chakraborty, S.; Ray, M. Uptake and desorption of copper ion using functionalized polymer coated silica gel in aqueous environment. *Sep. Purif. Technol.* **2007**, *57*, 47–56.

(18) Anirudhan, T. S.; Radhakrishnan, P. G. Kinetic and equilibrium modelling of Cadmium(II) ions sorption onto polymerized tamarind fruit shell. *Desalination* **2009**, *249*, 1298–1307.

(19) Atia, A. A.; Donia, A. M.; Yousif, A. M. Removal of some hazardous heavy metals from aqueous solution using magnetic chelating resin with iminodiacetate functionality. *Sep. Purif. Technol.* **2008**, *61*, 348–357.

(20) Guibal, E.; Milot, C.; Tobin, J. M. Metal—anion sorption by chitosan beats: equilibrium and kinetic studies. *Ind. Eng. Chem. Res.* **1998**, *37*, 1454–1463.

(21) Zhao, L.; Mitomo, H. Adsorption of heavy metal ions from aqueous solution onto chitosan entrapped CM-cellulose hydrogels synthesized by irradiation. *J. Appl. Polym. Sci.* **2008**, *110*, 1388–1395.

(22) Ho, Y. S.; Porter, J. F.; Mckay, G. Equilibrium isotherm studies for the sorption of divalent metal ions onto peat; copper, nickel and lead single component systems. *Water, Air, Soil Pollut.* **2002**, *141*, 1–33.

(23) Chen, A.-H.; Yang, C.-Y.; Chen, C.-Y.; Chen, C.-Y.; Chen, C.-W. The chemically crosslinked metal-complexed chitosans for comparative adsorptions of Cu(II), Zn(II), Ni(II) and Pb(II) ions in aqueous medium. *J. Hazard. Mater.* **2009**, *163*, 1068–1075.

(24) Harikishore Kumar Reddy, D.; Seshaiah, K.; Reddy, A. V. R.; Madhava Rao, M.; Wang, M. C. Biosorption of Pb^{2+} from aqueous solutions by Moringa oleifera bark: Equilibrium and kinetic studies. *J. Hazard. Mater.* **2010**, *174*, 831–838.

(25) Wang, J.; Kuo, Y. Preparation of fructose-mediated (polyethylene glycol/chitosan) membrane and adsorption of heavy metal ions. *J. Appl. Polym. Sci.* **2007**, *105*, 1480–1489.

(26) Saeed, K.; Haider, S.; Oh, T.-J.; Park, S.-Y. Preparation of amidoxime-modified polyacrylonitrile (PAN-oxime) nanofibers and their applications to metal ions adsorption. *J. Membr. Sci.* **2008**, *322*, 400–405.