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Removal of Lead(II) from Aqueous Solution by Adsorption Using Zwitterionic Hybrid Copolymers

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Lead(II) pollution has become a severe environmental problem. It is confirmed that inorganic-organic hybrid materials can be effectively used to eliminate such heavy-metal pollution by adsorption. For such application, the adsorption properties of zwitterionic hybrid copolymers prepared from different reaction steps for removal of lead(II) ions are investigated, which primarily focus on two dominating factors *i.e.*, pH value and initial solution concentration. Moreover, the adsorption isotherm model of these samples was calculated to evaluate the adsorption behaviours of lead(II) ions on these zwitterionic hybrid copolymers. It is found that the adsorption of lead(II) ions on these zwitterionic hybrid copolymers followed the Freundlich isotherm model, suggesting that lead(II) adsorption on these samples is heterogeneous surface rather than Langmuir monolayer adsorption. This finding is valuable in the separation and recovery of lead(II) ions from aqueous solution using zwitterionic hybrid copolymers.

Key Words: Hybrid copolymer, Adsorption, Lead(II) removal, Zwitterionic copolymer.

INTRODUCTION

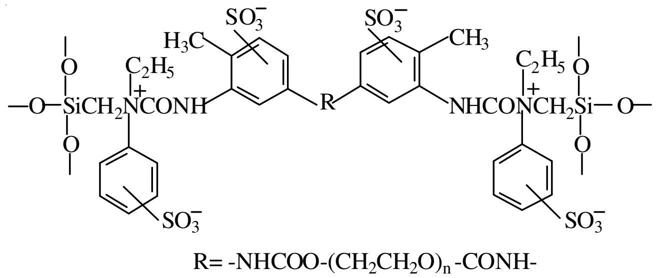
Water contamination caused by heavy-metal ions, such as Cu^{2+}, Pb^{2+}, *etc*., has become a major environmental issue[1,2]. Especially, with the rapid development of electronic industry and large application of lead-acid battery as a new power source, the demand for lead is elevated to a new level. Accordingly, the amount of wastewater from lead refinery and the abandoned battery is increased. The environment around us is thus deteriorating at a rapid pace. Water pollution from toxic lead(II) becomes a severe environmental problem and catches much public attention in recent years. Presently, it is well accepted that the toxic lead(II) cannot be biodegraded and can easily be accumulated in human body to induce various diseases[3,4]. Consequently, lead(II) removal from wastewater is significantly important and highly needed.

To eliminate or reduce lead(II) pollution, various innovative methods was developed[5-9]. Among these, the method using functionalized hybrid materials has significant advantages over others. However, the removal of lead(II) ions using these functionalized hybrid materials mainly depends the attractive effect of counter-ions on lead(II) ions, little work is done so far to examine the effect of both counter-ions and co-ions on lead(II) removal from wastewater. These previous studies are thus unsatisfactory. Further work is needed to investigate the effect of co-ions on the adsorption of lead(II) from aqueous solution using hybrid materials.

Recently, much effort is made to prepare zwitterionic hybrid materials and membranes. Such functionalized hybrid materials simultaneously containing anionic and cationic groups have revealed excellent adsorption properties for heavy-metal ions in aqueous solution[4,10]. Our continuing interest in these zwitterionic hybrid materials stimulates us to do further work. Consequently, to investigate the effect of both counter-ions and co-ions on the adsorption of hybrid materials for lead(II) removal, herein, two zwitterionic hybrid copolymers prepared from different reaction steps are used to adsorb lead(II) from aqueous solution. Their adsorption properties for removal of lead(II) in aqueous solution will be evaluated.

EXPERIMENTAL

Samples: The molecular structure of zwitterionic hybrid copolymers used in this study is presented in **Scheme-I**, in which both anionic and cationic groups are grafted on the chains of copolymer matrixes. Their preparation steps were described in detail in a previous article[11]. Namely, sample (a) is the zwitterionic hybrid copolymer, PEG-$[Si(OEt)_3]_2SO_3^-$-$N^+C_2H_5$, which was derived from the sulfonation and a subsequent quarteramination process, *i.e.*, **sulfonation-quarteramination Route I**;



Scheme-I: Molecular structure of zwitterionic hybrid copolymers (a) and (b)[11]

its thermal degradation temperature is 418 ºC. In contrast, sample (b) is the zwitterionic hybrid copolymer, PEG-[Si(OEt)$_3$]$_2$-N$^+$ C$_2$H$_5$-SO$_3^-$, which was prepared from the quarteramination and a subsequent sulfonation process, *i.e.*, **quarteramination-sulfonation Route II**; its thermal degradation temperature is 405 ºC, which is clearly lower than that of sample (a). The fundamental physicochemical parameters of these samples are listed in Table-1.

TABLE-1
SULFONATION DEGREE AND ANION-EXCHANGE CAPACITY OF SAMPLES[11]

Sample	(a)	(b)
Sulfonation degree (mmol/g)	0.128	0.244
Anion-exchange capacity (mmol/g)	0.168	0.136
Net charge (mmol/g)	-0.040	0.108

*(a) is the zwitterionic hybrid copolymer, PEG–[Si(OEt)$_3$]$_2$SO$_3^-$-N$^+$C$_2$H$_5$, which was synthesized from the sulfonation-quarteramination Route I, (b) is the zwitterionic hybrid copolymer, PEG-[Si(OEt)$_3$]$_2$-N$^+$C$_2$H$_5$-SO$_3^-$, which was prepared from the quarteramination-sulfonation Route II. Net charge = sulfonation degree – anion-exchange capacity.

Adsorption experiment: To have an insight into the adsorption properties of these zwitterionic hybrid copolymers for lead(II) ions in aqueous solution system, adsorption experiment using zwitterionic hybrid copolymers as adsorbents for lead(II) ions was conducted.

The adsorption capacity ($q_{Pb^{2+}}$) of Pb^{2+} ions on these samples can be calculated by eqn. 1:

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

where V is the volume of aqueous Pb(NO$_3$)$_2$ solution, C$_0$ and C$_R$ are the concentration of initial and remaining Pb(NO$_3$)$_2$, respectively; W is the weight of copolymer.

The effects of pH and initial solution concentration on adsorption capacity of lead(II) ions were determined. Meanwhile, adsorption isotherm model was calculated by changing the initial solution concentration ranging from 0.003, 0.006, 0.008, 0.01 mol/L at room temperature for 7 h at pH 6. The adsorption data were analyzed using the Langmuir and Freundlich isotherm models.

RESULTS AND DISCUSSION

Effect of the pH on lead(II) adsorption: Currently, it is well accepted that pH is an important factor affecting the adsorption of heavy metal ions[12]. Meanwhile relatively high pH value will result in the sedimentation of lead(II) in aqueous solution. Considering both the convenience of titration for determining the adsorption capacity of lead(II) at different pH values and avoiding lead(II) precipitation in aqueous solution, pH is thus only chosen within 5 and 6. The relationship between the adsorption capacity ($q_{Pb^{2+}}$) of Pb^{2+} ions *versus* pH values is presented in Fig. 1.

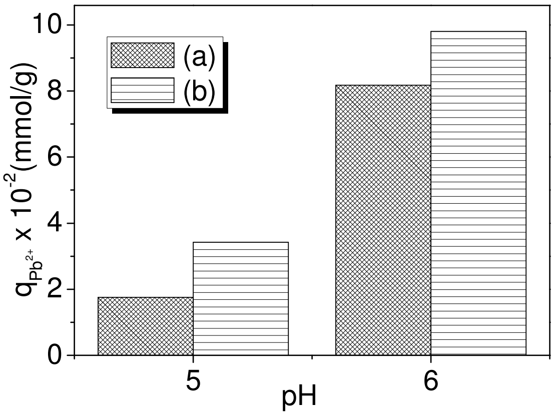


Fig. 1. pH *versus* adsorption capacity of lead(II) on samples (a) and (b). The sample was immersed in 0.01 mol/L aqueous Pb(NO$_3$)$_2$ solution for 24 h

It can be seen that the adsorption capacity of samples (a) and (b) also increased with the elevating pH values in aqueous solution. Clearly, pH = 6 is more suitable for lead(II) adsorption on these zwitterionic hybrid copolymers. Consequently, pH = 6 was chosen to investigate the adsorption property of lead(II) on the tested samples (a) and (b).

Effect of initial solution concentration on lead(II) adsorption: Fig. 2 illustrates the effect of initial solution concentration on lead(II) adsorption. It can be seen that for the individual samples, the adsorption capacity of lead(II) increases with the elevated initial solution concentration. The reason can be ascribed to the increasing amount of lead(II) ions in water. Whereas, for different samples (a) and (b), the adsorption capacity of lead(II) on sample (b) is clearly larger than that of sample (a), suggesting that sample (b) has relatively higher affinity for lead(II) ions. Two dominating factors might be responsible for such trend. One can be ascribed to the large net charge of sample (b) (Table-1), which conduces to the adsorption of lead(II) ions on sample (b) due to the attractive effect of counter-ions between -SO$_3$H groups and Pb^{2+} ions. Another can be assigned to the electrostatic repulsion between -N$^+$- groups and Pb^{2+} ions, which will block the adsorption of lead(II) ions on sample (a) due to the effect of co-ions. Moreover, the pendant-side structure of -SO$_3$H groups will also favour lead(II) adsorption on sample (b).

Adsorption isotherm model: To examine the adsorption properties of samples (a) and (b), Langmuir and Freundlich isotherm models are used to analyze the obtained adsorption data.

The Langmuir isotherm model, which describes the monolayer adsorption on the active sites of the adsorbent, can be expressed as eqn. 2[13-15]:

$$\frac{c_e}{q_e} = \frac{c_e}{Q_m} + \frac{1}{Q_m b} \qquad (2)$$

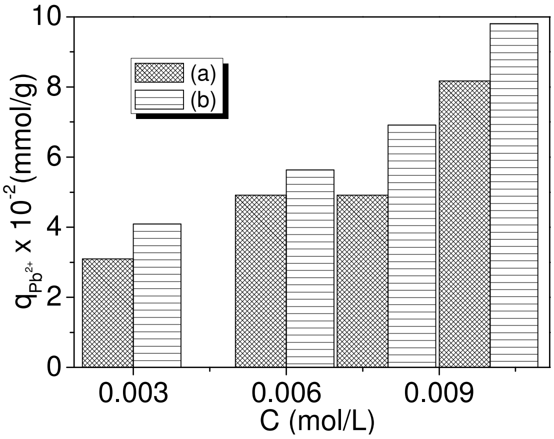


Fig. 2. Adsorption capacity of lead(II) *versus* the initial solution concentration at pH 6. The sample was immersed in different concentrations of aqueous $Pb(NO_3)_2$ solution for 7 h

The Freundlich isotherm model, which is considered as the adsorption occurred on a heterogeneous surface with uniform energy, can be expressed as eqn. 3[13-15]:

$$\log(q_e) = \log k_F + \frac{1}{n}\log(c_e) \qquad (3)$$

where q_e and c_e are the equilibrium concentrations of lead(II) in the adsorbed and liquid phases, 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. 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) *versus* log (c_e).

Fig. 3(a-b) illustrates the Langmuir and Freundlich adsorption isotherm of samples (a) and (b) for lead(II) adsorption. Meanwhile, the Langmuir and Freundlich isotherm parameters are listed in Table-2.

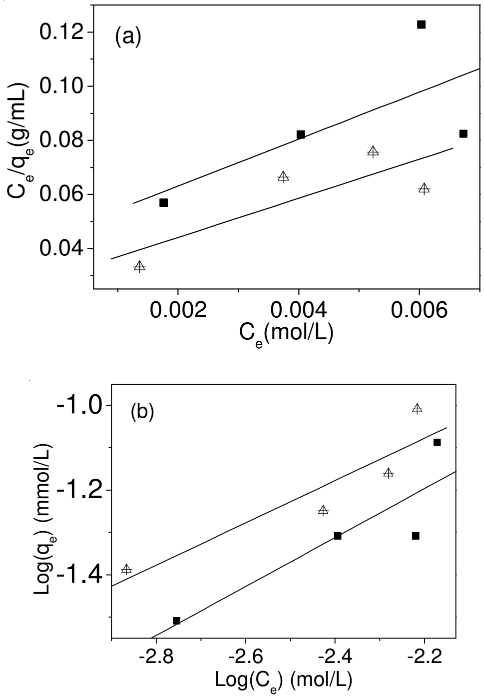


Fig. 3. Adsorption isotherm of lead(II) ions on samples (a) (solid square) and (b) (center uptriangle); (a) Langmuir and (b) Freundlich models

TABLE-2
LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS FOR LEAD (II) ADSORPTION ON SAMPLES (a) AND (b)

Sample	Langmuir			Freundlich		
	Q_m (mmol/g)	b (L/mol)	R	k_F	n	R
(a)	0.115	189.434	0.711	1.195	1.726	0.888
(b)	0.138	243.888	0.816	1.054	1.999	0.920

As shown in Fig. 3(a-b), it can be observed that the experimental data fitted better with Freundlich isotherm model [the regression coefficient (R) values are within the range of 0.88-0.92]. In contrast, these experimental data fitted worse with Langmuir isotherm model [the regression coefficient (R) values are within 0.71-0.81]. Considering such outcomes, it can be concluded that the adsorption process follows the Freundlich heterogeneous surface rather than Langmuir monolayer adsorption. In addition, compared the experimental data of sample (b) with those of sample (a), it can be noted that lead(II) adsorption on sample (b) is more fitted with Freundlich isotherm model, suggesting that the performance property of these zwitterionic hybrid copolymers has dominating influences on lead(II) adsorption.

Several reasons might be responsible for such trend. One can be assigned to the electrostatic attraction between the $-SO_3H$ groups and the lead(II) ions. Another is related to the net charge difference of anionic and cationic groups. Furthermore, the pendant-side structure of $-SO_3H$ groups in the copolymer chains will also conduce to on lead(II) adsorption on these zwitterionic hybrid copolymers.

From the results discussed above, it can be deduced that these zwitterionic hybrid copolymers are promising adsorbent for lead(II) removal and have potential applications in the separation and recovery of divalent metal ions from contaminated water.

Conclusion

Adsorption property of zwitterionic hybrid copolymers (a) and (b) for lead(II) ions removal was performed *via* two dominating influencing factors, pH value and initial solution concentration. Adsorption experiment demonstrates that lead(II) adsorption on zwitterionic hybrid copolymer (b) followed the Freundlich isotherm model, suggesting that both net charge property and molecular structure of a zwitterionic hybrid copolymer has some effects on lead(II) adsorption. The kinetic model of lead(II) adsorption on these samples will be our next study.

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