Removal of Pb(II) from Aqueous Solutions by D113 Resin Kinetics and Isotherms Study

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Summary: In this study, the adsorption and desorption properties of Pb(II) on D113 resin have been investigated. The different variables affecting the adsorption capacity have been also studied, such as pH of the solution, contact time, Pb(II) concentrations, resin amounts and temperatures, which indicate that D113 resin could be used effectively for the removal of Pb(II) ions from aqueous solution. The results show that the optimal pH for the adsorption of Pb(II) is 5.73 and the maximum saturated adsorption capacity is 598.3 mg/g at 298K. The apparent activation energy *E*a and adsorption rate constant k_{298K} values are 16.5 kJ/mol and 1.89×10^{-5} s^{-1}, respectively. The adsorption of Pb(II) follows the Langmuir isotherm and Freundlich isotherm, and the correlation coefficients have been evaluated. Thermodynamic parameters which ΔS value of 0.241 kJ/(mol K) and ΔH value of 55.18 kJ/mol indicate the endothermic nature of the adsorption process, and a decrease of Gibb's free energy (ΔG) with increasing temperature indicates the spontaneous nature of the adsorption process. The resin can be regenerated through desorption of the Pb(II) using 0.5 mol/L HCl solution and can be reused to adsorb again.

Keywords: D113 resin; Pb(II); Removal; Adsorption; Kinetics; Thermodynamic.

Introduction

Recently, chemical and industrial processes cause environmental contamination and treatment of these pollutions has been receiving tremendous attention [1, 2]. Lead is among those contaminants that must be removed from wastewater, due to its high toxicity and tendency to accumulate in tissues of living organisms [3]. Many industries, such as battery manufacturing, ammunition, tetraethyl lead manufacturing, ceramic and glass industries printing, and the painting and dying industry, represent significant sources of lead release into the environment [4-6]. It is a very toxic element that can damage the nervous system, kidneys and reproductive system. Consequently, separation and removal of lead from industrial effluent and drinking water systems has become of great importance.

There are many different methods for treating wastewaters. In comparison with such conventional methods as precipitation [7], chemical oxidation [8], and membrane separation [9], adsorption is regarded as one of the most effective and attractive processes with several advantages associated with no chemical sludge and high removal efficiency [21]. A number of investigators have studied the removal of lead from aqueous solution using different adsorbents [10–15], but with low adsorption capacity. D113 resin is a polymeric material containing a functional group (–COOH). It not only has proton which can exchange with cation, but also oxygen atom that can coordinate directly with metal ions. Therefore, D113 resin is widely used in the remove of metal ions from aqueous solutions due to its high exchange capacity and good ability of regeneration.

The objectives of this study are to investigate the adsorption behaviors of Pb(II) on the commercial adsorbents (D113 resin), and evaluate their feasibility for Pb(II) removal from aqueous solutions. The adsorption kinetics and adsorption isotherms for D113 resin was studied in detail. The possible interactions between the adsorbents and adsorbates were also discussed.

Experimental

Experimental Materials

D113 resin was provided by Nankai University, activated before use. Its properties are shown in Table-1. Double distillated water was used in all experiments. Solutions of 0.1M HAc and NaAc were used for pH adjustment. The stock solutions of Pb(II) was prepared from $Pb(NO_3)_2$ of AR grade. All other chemicals were of reagent grade.

Apparatus

A flame atomic absorption spectrophotometer (M6 Thermo) was used for metal

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ion concentration determination (with the operating condition for the lamp current 5.0 mA, slit width 0.5nm, wavelength 283.3nm). A mettler Toledo delta 320 pH meter was used for measuring pH. The sample was shaken in the DSHZ-300A and THZ-C-1 temperature constant shaking machine. The IR spectrum was detected on Nicolet 380 FT-IR spectrometer. The water used in the present work was purified using Mol research analysis-type ultra-pure water machine.

Table-1: General description and properties of D113 resin.

Items	Properties
Trade name	D113 resin
Functional group	−COOH
Structure	Macroporous
Exchange capacity (mmol/g)	≥ 10.8
Containing moisture (%)	45−52
Wet superficial density (g/mL)	0.74−0.80
True wet density (g/mL)	1.15−1.20

Adsorption Experiments

Adsorption experiments were performed under kinetic and equilibrium conditions. 15.0 mg D113 resin was weighed and added into a conical flask, in which a desired volume of acetic acid-sodium acetate (HAc–NaAc) buffer solution was added. After 24 h, a required amount of standard solution of Pb(II) was put in. The flask was shaken in a shaker at constant temperature. The upper layer of clear solution was taken for analysis until adsorption equilibrium reached. The procedure of kinetic tests was identical to that of the equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of Pb(II) were similarly measured by a flame atomic absorption spectrophotometer. The adsorption capacity (Q, mg/g) and distribution coefficient (D, mL/g) were calculated with the following formulas:

$$Q = \frac{C_0 - C_e}{W} V \qquad D = \frac{C_0 - C_e}{C_e} \frac{V}{W}$$

where C_0 is the initial concentration of Pb(II) (mg/mL); C_e is the residual concentration of Pb(II) in solution (mg/mL); V the volume of the solution used; (mL), W is the weight of the resin beads (g).

Desorption Experiments

An amount of resin (about 15.0 mg), loaded with a known amount of Pb(II) , was placed in a series of flasks containing 20 mL eluents of different concentration, then the mixture was shaken at 25°C for 4 h. The resin which had adsorbed Pb(II) was shaken with the eluant. After reaching equilibrium, the concentration of Pb(II) in the aqueous phase was determined and then the percentage of elution was obtained.

Results and Discussion

*Influence of pH on the distribution coefficient of Pb***(II)**

In this work, the effect of pH on the adsorption of Pb(II) ions was tested at different pH values (2.63–5.73) using amount of the resin (15.0 mg) at constant Pb(II) ions concentration (8.0mg/30.0mL) and room temperature to reach equilibrium absorption, and the results was shown in Fig. 1. The study was limited to a maximum pH of 5.73 to avoid the hydrolysis of the metal ion. The results indicated that the distribution coefficient of the resin increased with increase in pH of the aqueous solution and the maximum uptake of Pb(II) ions occurred at initial pH of 5.73. Hence, all the following experiments were carried out at pH 5.73.

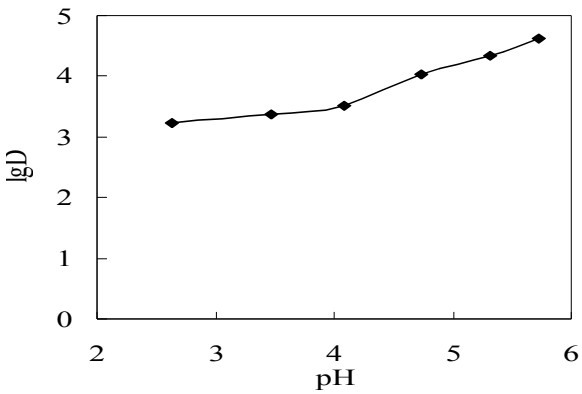


Fig. 1: Effect of pH on the distribution coefficient of D113 resin for Pb(II), resin 15.0 mg, [Pb^{2+}]$_0$=8.0 mg/30.0 mL, T = 298 K, 100 rpm.

Determination of Adsorption Rate Constant and Apparent Activation Energy

The metal ion uptake at different time intervals by D113 resin was evaluated for the Pb(II) ions concentration of 20.0mg/50.0mL with 30.0 mg D113 resin at 298K. At predetermined intervals, aliquots of 1.0 mL solution were taken out for analysis and the concentration of metal ion was determined. After the remains kept constant and volume was corrected, a series of data were obtained (Fig. 2). The removal increases with time and almost reaches the equilibrium in 50 h.

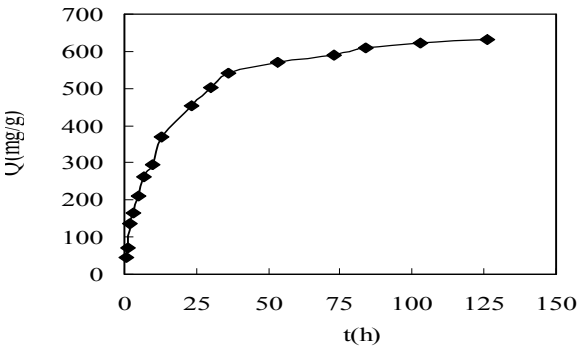


Fig. 2: Effect of contact time on adsorption of D113 resin for Pb(II), resin 30.0 mg, $[Pb^{2+}]_0$=20.0 mg/50.0 mL, pH = 5.73, 100 rpm.

According to the Brykina method, the adsorption rate constant k can be calculated from $-\ln(1-F)=kt$, (where $F = Q_t/Q_e$, Q_t and Q_e are respectively the adsorption amounts at time t and at equilibrium). The experimental results accord with the equation and a straight line was obtained by plotting $-\ln(1-F)$ versus t (Fig. 3), yields the adsorption rate constant k at the various temperatures ($k_{291K}=1.59\times10^{-5}$ s^{-1}; $k_{298K}=1.89\times10^{-5}$ s^{-1}; $k_{308K}=2.50\times10^{-5}$ s^{-1}; $k_{318K}=2.89\times10^{-5}$ s^{-1}). According to Boyd's liquid film spreading equation, it can be deduced from the linear relationship between $-\ln(1-F)$ and t, that liquid film spreading is the predominant step of the sorption process [16].

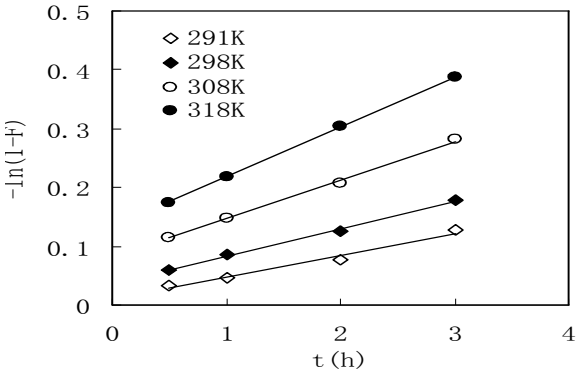


Fig. 3: Determination of rate content of D113 resin for Pb(II).

According to the Arrhenius equation:

$$\log k = -\frac{E_a}{2.303RT} + \log A$$

where E_a is the Arrhenius activation energy for the adsorption process indicating the minimum energy that reactants must have for the reaction to precede, A is the Arrhenius factor, R is the gas constant (8.314 J/(mol K)), k is the adsorption rate constant and T is the solution temperature.

The slope of straight line was made by plotting–log k versus $1/T$ (Fig. 4) and calculated by linear fitting, yields the apparent activation energy of E_a = 16.5 kJ/mol, which could be considered as a low energy barrier in this study. It can be deduced that the adsorption speed accelerated when the temperature rose within the scope of experimental temperature [17].

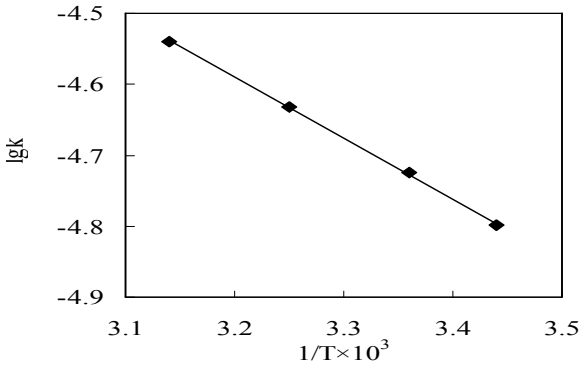


Fig. 4: Determination of activation energy of D113 resin for Pb(II).

Adsorption Isotherm

Adsorption isotherms are very powerful tools for the analysis of adsorption process. Adsorption isotherms establish the relationship between the equilibrium pressure or concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. In this study, The Langmuir and Freundlich isotherms are studied by varying the resin amount (10.0mg, 15.0mg, 20.0mg, 25.0mg, and 30.0mg) and the Pb(II) ions concentration of 14.3mg/30.0mL at 298K.

Langmuir model suggests a monolayer adsorption with no lateral interaction between the sorbed molecules. The Langmuir equation is expressed as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}$$

where Q_e is the amount of Pb(II) adsorbent at equilibrium (mg/g), the constant Q_m gives the theoretical monolayer adsorption capacity (mg/g) and K_L is the Langmuir constant which reflects quantitatively the affinity between the D113 resin and Pb(II) ions.

Freundlich model assumes heterogeneous adsorption due to the diversity of sorption sites or the diverse nature of the adsorbate adsorbed, free or hydrolyzed species. The Freundlich equation is expressed as:

$$\lg Q_e = \frac{1}{n}\lg C_e + \lg K_F$$

where K_F is Freundlich constant and n (dimensionless) is the heterogeneity factor which can be related to the capacity and intensity of adsorption. The n values of between 1 and 10 represent a favorable adsorption [18].

The linearize Langmuir and Freundlich adsorption isotherms are given in Figs. 5 and 6, respectively. According to the results, R^2 values of 0.9995 and 0.9991 were obtained from Langmuir model and the Freundlich model for Pb(II) ions respectively, suggested the equilibrium data fit well both the Langmuir and Freundlich isotherm model. The Langmuir adsorption capacity Q_m for the Pb(II) ions was found to be 666.7 mg/g, which in close agreement with the real experiments value (598.3 mg/g). The n value is 6.74 indicates that the resin has followed a favorable adsorption and effective interaction between adsorbent and the adsorbate at the studied temperatures.

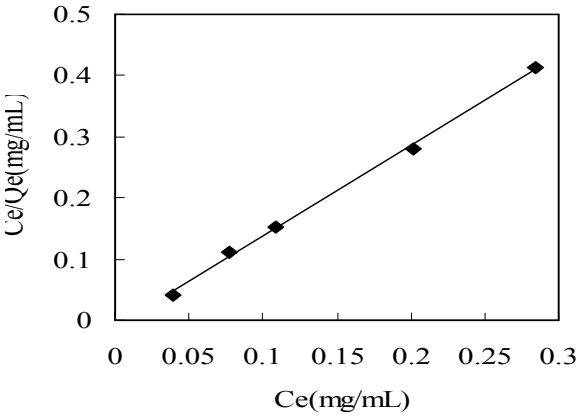


Fig. 5: Langmuir isotherm curve.

Effect of Temperature and Thermodynamic Parameters

Temperature of this adsorption experiment was varied to study thermodynamic feasibility of adsorption process. Adsorption of 10.0mg/30mL of Hg(II) was performed (with 15.0 mg resin) at 291K, 298K, 308K, 318K. Thermodynamic parameters including Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) associated to the adsorption process were estimated by the following equations:

$$\lg D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad ; \quad \Delta G = \Delta H - T\Delta S$$

where R is the gas constant (8.314 J/(mol K)) and T is the absolute temperature (K). A linear plot was obtained by plotting lg$D$ versus $1/T\times10^3$ (Fig. 7). The negative value of ΔG = -16.70 kJ/mol, confirms the spontaneity of the adsorption process with increasing temperature and the positive value of the enthalpy ΔH=55.18 kJ/mol indicates that the adsorption is endothermic. The positive entropy (ΔS) value was 0.241 kJ/mol corresponds to an increase in randomness at the solid–liquid interface and may be significant changes occur in the internal structure of the adsorbent through the adsorption of Pb(II) ions onto resin. [19, 20]

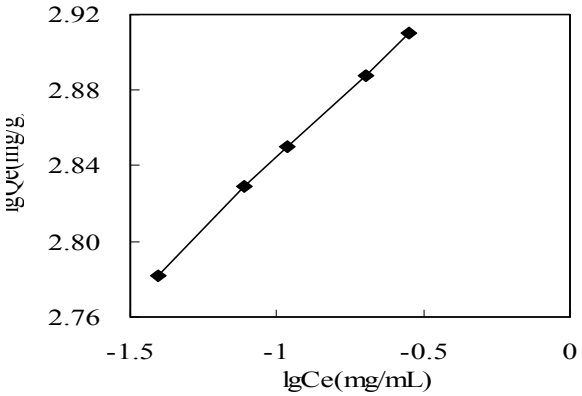


Fig. 6: Freundlich isotherm curve.

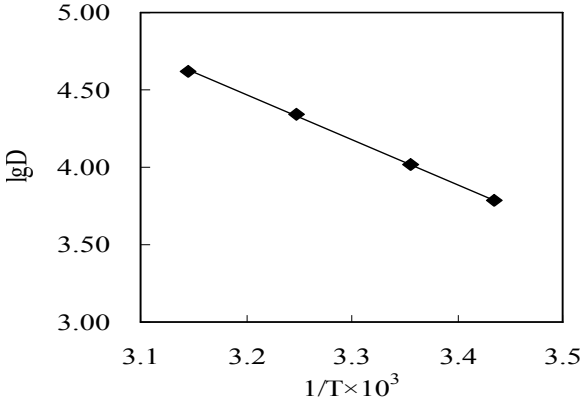
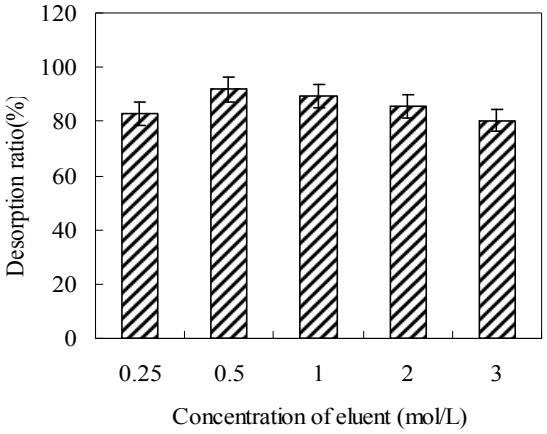


Fig. 7: Effect of temperature on distribution ratio of D113 resin for Pb(II).

Elution and Regeneration of Resin

Whether an adsorbent is economically attractive in removal of metal ions from aqueous solution depends not only on the adsorptive capacity,

but also on how well the adsorbent can be regenerated and used again. Therefore, different concentrations of HCl solutions (0.25 to 3.0 mol/L) were used to perform desorption tests in order to choose proper desorption solution. The results showed that the eluting rate reaches 91.90% with 0.5 mol/L HCl was listed in Fig 8. The fraction eluted was calculated from the amount of ions adsorbed onto the resin and the final ion concentration in the desorption medium. In order to examine the practical value of HCl as an eluant, the elution rate in 0.5 mol/L HCl was determined, using the same method above, and found to fast with $t_{1/2}$ equal to 18 min. Three tests of regeneration were also carried out which showed no change in the adsorption capacity of D113 resin, therefore allowing the resin to be regenerated and reused.



Influence of temperature on distribution ratio of D113 resin for Pb(II)

Fig. 8: Desorption of Pb(II) from D113 resin by HCl eluent solutions in varying concentrations.

Infrared Spectra Analysis

From the results above, it can be deduced that the adsorption of Pb(II) by D113 resin ($\Delta H > 0$) belongs to a chemical adsorption. It shows that the functional group of resin forms a chemical bond with Pb(II). To identify the possibility of Pb(II) bonding to resin, IR spectra were obtained for D113 resin before and after Pb(II) adsorption. The results indicated that characteristic adsorption peak (υ=1718cm^{-1}) of C=O vanished after adsorbing Pb(II), and anti-symmetric and symmetric flex vibration sorption peaks of carboxy group were found (υ_{as}=1526cm^{-1}, υ_s=1397cm^{-1}, $\Delta\upsilon$=129cm^{-1}), These results show that there are coordination bonds between oxygen atoms and Pb(II) and that H of C-OH has been exchanged with the formation of a complex compound.

Conclusion

The adsorption kinetics and isotherms of Pb(II) ions on D113 resin were investigated and the resin exhibited a high adsorption capacity for Pb(II) ions. The adsorption kinetic results reveal that the adsorption equilibrium of Pb(II) on the D113 resin was achieved after at 50 h, and the apparent activation energy *E*a and adsorption rate constant k_{298K} values were 16.5 kJ/mol and 1.89×10^{-5} s^{-1}, respectively. The adsorption isotherms show that the equilibrium data fit both the Langmuir and Freundlich model, and the maximum adsorption capacity was 598.3 mg/g according to the Langmuir model. The Pb(II) adsorbed on D113 resin can be eluted by using 0.5 mol/L HCl solution as an eluant indicating that the resin can be regenerated and reused. The IR spectra of D113 resin before and after the adsorption of Pb(II) showed that hydrogen and oxygen atoms in the −OH and C=O groups were involved in Cu(II) adsorption. So D113 resin is a promising adsorbent for Pb(II) ions removal from water and industrial wastewater.

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