



## Removal of some heavy metal cations by synthetic resin purolite C100

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### ABSTRACT

The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. These pollutants are introduced into the aquatic systems significantly as a result of various industrial operations. This paper describes the adsorption behaviour of cation exchange resin purolite C100 with respect to  $Ce^{4+}$ ,  $Fe^{3+}$  and  $Pb^{2+}$  in order to consider its application to purify metal finishing wastewaters. The batch method has been employed, using metal concentrations in solution ranging from 2.65 to 265 mg/L. The adsorption percentages (%) and distribution coefficient ( $K_d$ ) were determined for the adsorption system in the aqueous media as a function of sorbate concentration. The experimental isotherm data were analyzed using the Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich (DKR) equations. It was found that the adsorption phenomena depend on charge density and hydrated ion diameter. According to the equilibrium studies, the metal ions sequence can be given as  $Ce^{4+} > Fe^{3+} > Pb^{2+}$ . These results show that cation exchange resin purolite C100 holds great potential to remove cationic heavy metal species from polluted wastewater.

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### 1. Introduction

Nowadays heavy metals are among the most important pollutants in source of treated water and are becoming severe public health problem. Industrial wastewater contains the major source of various kinds of metal pollution in natural water [1,2]. The heavy metal ions are stable with persistent environment contaminations, since they cannot be degraded and destroyed. These metal ions can be harmful to aquatic life and causing serious soil pollution [3]. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver and other vital organs. Allergies are not uncommon and repeated long term contact with some metals or their compounds may even cause cancer. In small quantities, certain heavy metals are nutritionally essential for a healthy life. These metals are commonly found naturally in foodstuffs. Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, and steel [4].

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Heavy metals may enter the human body through food, water, air or absorption through the skin when they come in contact with humans in agriculture and in manufacturing pharmaceutical, industrial, or residential set-

tings.  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Hg^{2+}$ ,  $Al^{3+}$  and  $Cr^{3+}$  are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders [5,6]. They are also common groundwater contaminants at industrial and military installations [7]. Research on  $Pb^{2+}$  has become a dominant topic for environmental and medical scientists for two obvious reasons: (i) it has no known biological use and (ii) it is toxic to most living things [8]. Adsorption processes have been and actually are the most frequently applied method in the industries, and consequently the most extensively studied ones [9]. Adsorption process could be preceded by the following mechanisms [10]:

- 1 Ion-exchange reactions.
- 2 Physical adsorption.
- 3 Molecular sorption of electrolytes.
- 4 Complex formation between the counterion and the functional group.
- 5 Hydrate formation at the surface or in the pores of the adsorbent.

The most common methods for the removal of heavy metals are ion exchange and chemical precipitation. The main advantages of ion exchange over chemical precipitation are recovery of metal value, selectivity, less sludge volume produced and the meeting of strict discharge specifications. In ion-exchange systems, polymeric resins are usually employed [11–13]. Cation exchange resin purolite C100 is a simple, fast and economic means for separating lead quantitatively from aluminium, trivalent iron and barium [7]. Ion exchange removes unwanted ions from solution by transferring

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**Table 1**  
Physical and chemical properties of the cation exchange resin purolite C100.

Properties	Description or values
Matrix	Polystyrene-divinyl benzene, gel type
Functional group	Sulfonic acid, $-\text{SO}_3^-$
Ionic form	$\text{H}^+$
Exchange capacity (equiv./L)	2.0
Moisture content (%)	51–55%
Specific gravity	1.21
Effective size	0.5 mm

them to a solid material called an ion exchange which accepts them while giving back an equivalent number of desirable species stored on the ion-exchange skeleton. It should be remembered that the usual synthetic organic ion exchanger consists of relatively large porous particles, the pores or capillaries of which are filled with aqueous solution in terms of the base exchange reaction [14]. Thus, the purpose of our project is to test the influence of ionic charge on the removal of some metal ions from aqueous systems by using metal ions of different charges [15]. An additional goal is to establish the ability of three two-parameter equations the Langmuir, Freundlich and Dubinin Radushkevich isotherms to model the equilibrium sorption data [16]. To achieve these goals a batch sorption technique over a wide range of initial metal ion concentrations on the ability of purolite C100 cation exchange resin for the removal of  $\text{Ce}^{4+}$ ,  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  from aqueous systems was tested [17].

## 2. Materials and methods

### 2.1. Resins and reagents

The cation exchange resin purolite C100 with sulfonic acid  $\text{SO}_3\text{H}$  group from Purolite International Limited, Hounslow, Middlesex, UK, was used in this work. The physical and chemical properties of the resin were listed in Table 1 [18,19]. Prior to use, the resin was washed with  $\text{HCl}$  ( $1 \text{ mol/dm}^3$ ) and deionized water until all chloride ions were removed and was dried in a vacuum oven at  $25^\circ\text{C}$ .

Analytical reagent grade  $\text{Ce}^{4+}$ ,  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  as nitrates were purchased from Merck Co. They were used without further purification.

### 2.2. Experimental procedures

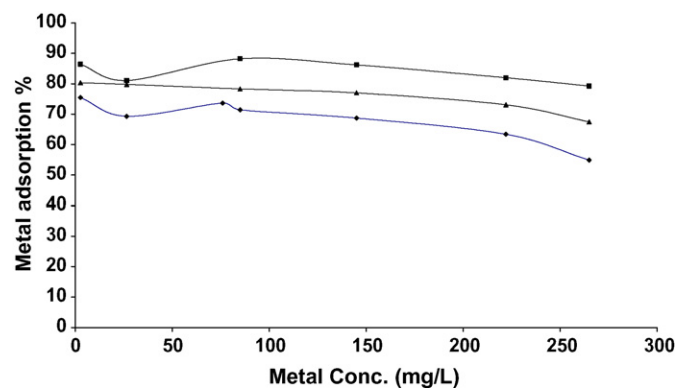
Ion exchange equilibrium experiments were determined by the batch equilibrium method. Each experiment was performed by the aliquot of the dry resins, 1 g and  $40 \text{ cm}^3$  of the aqueous solution were placed in a  $100\text{-cm}^3$  glass stoppered flask, and were equilibrated for 24 h. The aqueous solutions always consisted of a varying equimolar amount of each metal ions ( $C_0$ ). The temperature of water bath was controlled at  $25^\circ\text{C}$  and the experiment was carried at solution pH. After equilibrium, the aqueous-phase concentrations of each metal ions were determined using an atomic absorption spectrophotometer (POEMS III) with Merck 23 elements multielement stander.

The influence of initial metal ion concentration in aqueous media was investigated. The results were expressed as the adsorption (%) and distribution coefficient  $K_d$  which were defined as

$$\text{adsorption (\%)} = \frac{C_0 - C_1}{C_0} \times 100 \quad (1)$$

$$K_d = \frac{\text{amount of metal ion in adsorbent}}{\text{amount of metal ion in solution}} \times \frac{V}{m} \quad (\text{ml/g}) \quad (2)$$

where  $C_0$  and  $C_1$  are the initial and equilibrium concentrations of cation solution (ppm), respectively.  $V$  is the volume of the solution (ml) and  $m$  is the weight of adsorbent (g).



**Fig. 1.** Adsorption percent of metal ions by 1 g of cation exchange resin purolite C100 as a function of initial ion concentration in aqueous solution at  $25^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Metal ions adsorption percentage (%)

For a solid–liquid sorption process, the solute transfer is usually characterized by external mass transfer (boundary layer diffusion), or intraparticle diffusion, or both. The adsorption of metal ions onto ion exchange resin may be controlled due to film diffusion at earlier stages and later by the particle diffusion [20]. The effects of  $\text{Ce}^{4+}$ ,  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  metal ion concentrations on the sorption behaviour of the cation exchange resin purolite C100 was studied. The experiments were done using 1 g of resin with different metal ion concentrations varied from 2.65 to 265.00 mg/L for each metal cation in aqueous solutions at  $25^\circ\text{C}$ . The sorption reactions were consistent with the following ion exchange process [21]:



As hydrogen ions in the sulfonic group ( $-\text{SO}_3\text{H}$ ) of the resin can serve as exchangeable ions with metal cations. Fig. 1 represents that the increase in initial metal ion concentration decreases the adsorption percent and increases the amount of metal sorption per unit weight of the sorbent. This may be due to the fact that at lower concentrations almost all the ions were adsorbed very quickly and further increases in initial metal ion concentrations led to saturation of resin surface and energetically less favorable sites become involved. The maximum cation exchange resin adsorption percent was obtained as 86.42%, 80.38% and 75.47% for  $\text{Ce}^{4+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ , respectively.

The adsorption phenomena depend on the charge density of cations and the diameter of hydrated cations. The charges of metal ions are different (+4, +3 and +2), therefore  $\text{Ce}^{4+}$  ions give the maximum adsorption efficiency while  $\text{Pb}^{2+}$  ions give the minimum adsorption efficiency. The diameter of hydrated cations is very important, therefore  $\text{Ce}^{4+}$  ions ( $1.010 \text{ \AA}$ ) with the smallest diameter have maximum adsorption, while  $\text{Pb}^{2+}$  ions with the biggest diameter ( $1.200 \text{ \AA}$ ) have minimum adsorption [22].

### 3.2. Equilibrium distribution coefficient, $K_d$

The distribution coefficient,  $K_d$ , is defined as the ratio of metal ion concentration on the resin to that in the aqueous solution and can be used as a valuable tool to study metal cation mobility. High values of distribution coefficient,  $K_d$  indicate that the metal has been retained by the solid phase through sorption reactions, while low values of  $K_d$  indicate that a large fraction of the metal remains in solution. Table 2 and Fig. 2 show that the distribution coefficient  $K_d$  values decrease with the increase in concentration of metal ions. In the case of low concentrations, the ratio of the initial number of

**Table 2**  
Distribution coefficient ( $K_d$ ) of some metal ions at different concentrations in aqueous medium using cation exchange resin purolite C100 ( $H^+$  form)  $25 \pm 0.1^\circ C$ .

Cations	$K_d$ in aqueous media		
	2.65 (mg/L)	26.5 (mg/L)	265 (mg/L)
$Ce^{4+}$	254.55	171.53	152.77
$Fe^{3+}$	163.87	158.12	83.08
$Pb^{2+}$	123.07	90.38	48.69

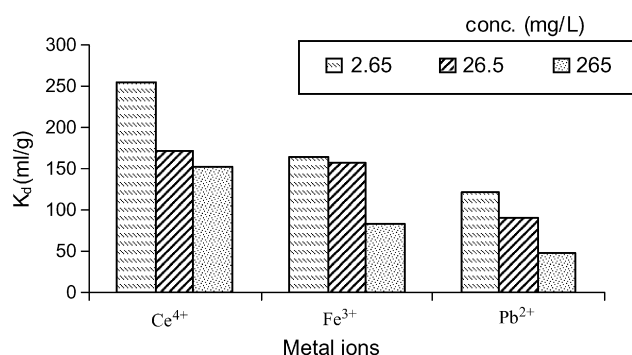
moles of each metal ion to the available surface area is larger and subsequently, the fractional ion exchange becomes independent of initial concentrations [23]. The rapid metal sorption has significant practical importance, as this will facilitate with the small amount of resins to ensure efficiency and economy.

### 3.3. Sorption isotherms

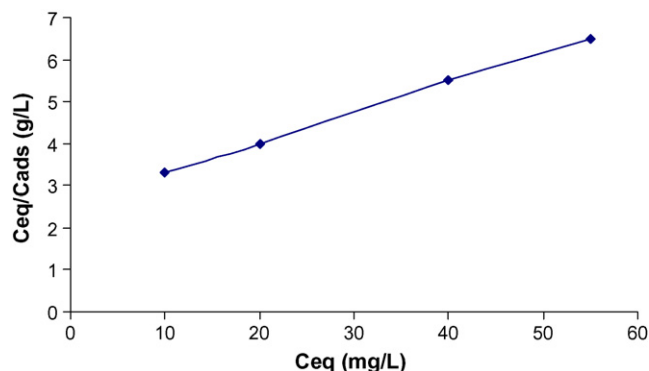
Equilibrium data, commonly known as sorption isotherms, are basic requirements for the design of sorption system. These data provide information on the capacity of the sorbent or the amount required to remove a unit mass of pollutant under the system conditions. The sorption of  $Ce^{4+}$ ,  $Fe^{3+}$ , and  $Pb^{2+}$  from aqueous solutions on cation exchange resin purolite C100 as a function of their concentrations was studied at  $25^\circ C$ . The sorption data have been subjected to different sorption isotherms, namely, Langmuir, Freundlich, and Dubinin–Kaganer–Radushkevich (DKR). The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the resin surface. The equilibrium data for metal cations concentration range (2.65–265.00 mg/L) have been correlated with the Langmuir isotherm [22]:

$$\frac{C_{eq}}{C_{ads}} = \frac{1}{Qb} + \frac{C_{eq}}{Q} \quad (4)$$

where  $C_{eq}$  is the equilibrium concentration of metal ions in solutions (mg/L),  $C_{ads}$  is the number of metal ions sorbed on cation exchange resin purolite C100,  $Q$  and  $b$  are Langmuir constants related to sorption capacity and sorption energy, respectively. Maximum sorption capacity ( $Q$ ) represents monolayer coverage of sorbent with sorbate and  $b$  represents enthalpy of sorption and should vary with temperature. A linear plot is obtained when  $C_{eq}/C_{ads}$  is plotted against  $C_{eq}$  over the entire concentration range of metal ions investigated as shown in Fig. 3. The Langmuir model parameters and the statistical fits of the sorption data to this equation are given in Table 3. The Langmuir model effectively described the sorption data with all correlation coefficient values  $> 0.95$ . According to the  $Q$  (mg/g) parameter, sorption of heavy metal ions on cation exchange resin purolite C100 listed in Table 3

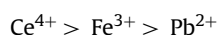


**Fig. 2.** Distribution coefficient,  $K_d$  of metal ions by cation exchange resin purolite C100 as a function of initial concentrations.



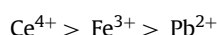
**Fig. 3.** Langmuir plots for  $Ce^{4+}$  ions adsorption on cation exchange resin purolite C100 ( $H^+$  form) at  $25 \pm 0.1^\circ C$ .

indicates the following metal ions sequence:



Since the sorption phenomena depend on the charge density of cations, the diameter of hydrate cations is very important,  $Pb^{2+}$  ions with the smallest diameter have maximum adsorption. Therefore  $Pb^{2+}$  ions with the biggest diameter (1.2 Å) have minimum adsorption. The  $Ce^{4+}$  has maximum sorption than  $Fe^{3+}$  because it has maximum charge.

The Langmuir model effectively described the sorption data with all correlation coefficients values  $> 0.95$ , according to the sorption energy  $b$  (L/g) parameter. Sorption on cation exchange resin purolite C100 produced the following sequence:



The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. The isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich sorption isotherms were also applied to the adsorption of  $Ce^{4+}$ ,  $Fe^{3+}$  and  $Pb^{2+}$  metal ions on cation exchange resin purolite C100 as shown in Fig. 4:

$$\log C_{ads} = \log K + \frac{1}{n \log C_{eq}} \quad (5)$$

where  $C_{eq}$  is the equilibrium concentration in mg/L and  $C_{ads}$  shows that the sorption seems to follow the Freundlich isotherm model as well as the Langmuir isotherm. The constants  $K$  and  $n$  were calculated for each cation as shown in Table 4.  $K$  is a parameter related to the temperature and  $n$  is a characteristic constant for the sorption system under study. A value of  $n$  between 2 and 10 shows good sorption. The numerical value of  $1/n < 1$  indicates that sorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the sorbent by the sorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface [20,22].

**Table 3**  
Characteristic parameters and correlation coefficients of the experimental data according to Langmuir equation.

Sorption parameter	Metal ions		
	$Ce^{4+}$	$Fe^{3+}$	$Pb^{2+}$
Ionic radius (Å)	1.010	0.640	1.200
$Q$ (mg/g)	13.95	11.55	9.64
$b$ (L/g)	0.028	0.020	0.016
Correlation coefficients	0.999	0.989	0.952

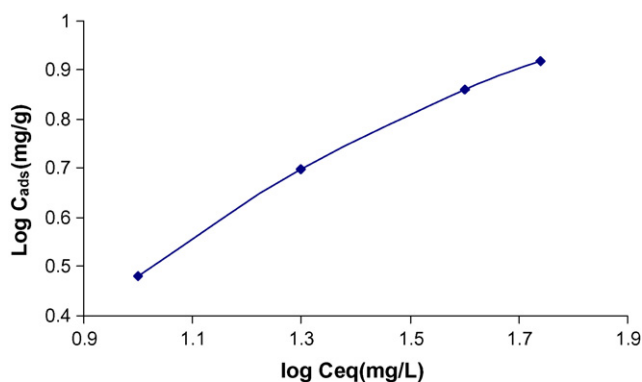


Fig. 4. Freundlich plots for  $\text{Ce}^{4+}$  ions adsorption on cation exchange resin purolite C100 ( $\text{H}^+$  form) at  $25 \pm 0.1$  °C.

The DKR has been used to describe the sorption of metal ions. The DKR equation has the form:

$$\ln C_{ads} = \ln X_m - \beta \varepsilon^2 \quad (6)$$

where  $C_{ads}$  is the number of metal ions adsorbed per unit weight of adsorbent (mg/kg),  $X_m$  is the maximum sorption capacity,  $\beta$  is the activity coefficient related to mean sorption energy, and  $\varepsilon$  is the Polanyi potential, which is equal to:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_{eq}} \right) \quad (7)$$

where  $R$  is the gas constant ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ) and  $T$  is the temperature (K). The saturation limit  $X_m$  may represent the total specific micropore volume of the sorbent. The sorption potential is independent of the temperature but varies according to the nature of sorbent and sorbate [24]. The slope of the plot of  $\ln C_{ads}$  versus  $\varepsilon$  gives  $\beta$  ( $\text{mol}^2/\text{J}^2$ ) and the intercept yields the sorption capacity,  $X_m$  (mg/g). The sorption space in the vicinity of a solid surface is characterized by a series of equipotential surfaces having the same sorption potential. This sorption potential is independent of the temperature but varies according to the nature of sorbent and sorbate. The sorption energy

Table 4

Freundlich adsorption constants  $\log K$  and  $n$  for metal ions on cation exchange resin purolite C100 ( $\text{H}^+$  form) at  $25 \pm 0.1$  °C.

Adsorption parameters	Metal ions		
	$\text{Ce}^{4+}$	$\text{Fe}^{3+}$	$\text{Pb}^{2+}$
$\log K$ (mg/g)	0.098	0.144	0.343
$1/n$	0.594	0.527	0.570
Correlation coefficient	0.995	0.973	0.950

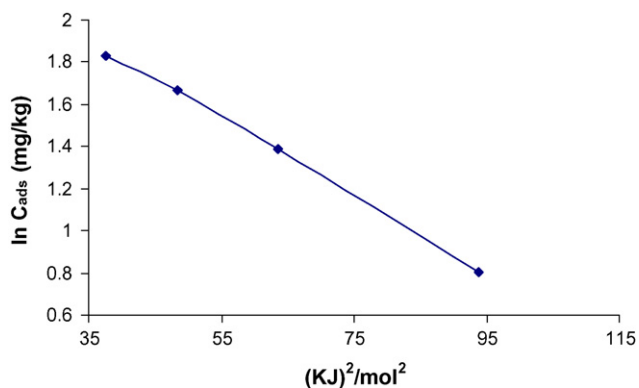


Fig. 5. DRK plots of  $\text{Pb}^{2+}$  ions on cation exchange resin purolite C100 ( $\text{H}^+$  form) at  $25 \pm 0.1$  °C.

Table 5

Parameters calculated from DKR equation for metal ions adsorption on cation exchange resin purolite C100 ( $\text{H}^+$  form) at  $25 \pm 0.1$  °C.

DKR	Metal ions		
	$\text{Ce}^{4+}$	$\text{Fe}^{3+}$	$\text{Pb}^{2+}$
$X_m$ (mg/g)	16.71	12.82	10.43
$\beta$ ( $\text{mol}^2/\text{J}^2$ )	-0.013	-0.0146	-0.0158
Sorption energy, $E$ (kJ/mol)	6.18	5.86	5.62
Correlation coefficient	0.999	0.985	0.971

can also be worked out using the following relationship:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (8)$$

The plot of  $\ln C_{ads}$  against  $\varepsilon^2$  for metal ions sorption on cation exchange resin purolite C100 is shown in Fig. 5. The DKR parameters are calculated from the slope of the line in Fig. 5 and listed in Table 5. As shown in this table, the  $E$  values are nearly 6.00 kJ/mol for all metal ions. This value lies in the range of physical adsorption mechanism [22]. The sorption capacity  $X_m$  in the DKR equation is found to be 16.71, 12.82 and 10.43 mg/g for  $\text{Ce}^{4+}$ ,  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  metal ions, respectively.

#### 4. Conclusions

The adsorption percent (%) of the cation exchange resin purolite C100 was evaluated by measuring the extent of adsorption of various metals ions in water under equilibrium conditions at 25 °C. Distribution coefficient ( $K_d$ ) was calculated at different concentrations of metal ions in aqueous medium, the results show that the distribution coefficient  $K_d$  values decrease with the increase in the concentration of metal ions.

A detailed isotherm analysis of experimental data was carried out to determine the best isotherm models for the sets of equilibrium data for  $\text{Ce}^{4+}$ ,  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  metal ions on cation exchange resin purolite C100. It was noted that ionic radius has an influence in the magnitude of metal loading on the adsorbent. The experimental results were analyzed using three two-parameter adsorption isotherm models—the Langmuir, Freundlich, and Dubinin–Radushkevich isotherms. Evaluating the correlation coefficients from the three isotherm equations showed that the Dubinin–Radushkevich isotherms and Langmuir isotherms described the data appreciable than Freundlich sorption capacity increases with increase in smaller ionic radius metal ion. We conclude that ion exchange resin purolite C100 could be exploited for the adsorption of some heavy metals.

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