Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 4, No. 6, p. 19-25, 2014
http://www.innspub.net

RESEARCH PAPER | OPEN ACCESS

# Study of absorption behavior of Pb(II) on impregnated resin containing 1,4-diaminoantraquinone

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Article published on June 05, 2014

**Key words:** Impregnated resin, 1, 4-Diaminoantraquinone, Isotherm models, Kinetic models

**Abstract**

This paper reports the results obtained by studying of adsorption behavior of Pb(II) on Impregnated Resin Containing 1,4-Diaminoantraquinone.For sorption of metal ion on solid adsorbent, the Longmuir, Freundlich and Temkin isotherms are of the most widely used isotherm models. Thus, these three equations were used for analyzing of adsorption behavior. The results show that adsorption of Pb (II) ion on SIR follows from Longmuir model. Furthermore four kinetic models: the pseudo first and second order equations, the Elovich equation and the intra particle diffusion equation were used for investigation of metal sorption kinetic.

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## Introduction

Lead is a cumulative poison that enters the body from lead water pipes, lead-based paints and leaded petrol (Renner, R. 1995). Presence of even traces of Pb (II) in environmental samples leads to environmental pollution and many fatal diseases.

Including dysfunction of renal blood and neurogical systems (Du *et al.*, 2002; Ferreira *et al.*, 1991; Tan L V, Ngoc L, 2011). $Pb^{2+}$easily deposits in blood, kidney, reproductive system, nervous system and brain, and acute lead poisoning can result in colic shock, severe anemia and irreversible brain damage. Lead compounds as anti knocking agents in automobile fuels cause air pollution(Shiri *et al.*, 2011), (Chena *et al.*, 2005), (Jain *et al.*, 2006). Solid phase extraction technique is used in the wide range for pre concentration and separation of ultra trace metal ions. In conventional solid phase methods, a polymeric matrix used to bind the chelating reagents on it through chemical reactions. But its application was limited for not having economic treatment in wide range and need to long time for chemical binding of chelating agent to polymeric support (Jain *et al.,* 2006), (Hennion, 1999), (Reis *et al.,* 2000), (Teixeira *et al.,* 2000), (Teixeira *et al.,* 1998), (Juang and Su, 2004). Alternatively, solvent impregnated resins (SIRs) do not have the problems of conventional adsorbent resins and benefit from advantages of LLE and SPE. Furthermore, high capacity and metal binding strength are the other important characteristics of the SIRs (Prabhakaran and Subramanian, 2004), (Prabhakaran and Subramanian, 2003), (Hosseini and Hosseini-Bandegharari, 2011), (Hosseini *et al.,* 2009), (Hosseini-Bandegharaei *et al.,* 2010), (Hosseini and Hosseini-Bandegharari, 2010).

In the previous work, we studied extraction of Pb(II) metal ion from water samples on amberlit XAD-16 resin containing 1,4-diaminoantraquinone . The results showed that recovery factor upper than 95% was obtained. In this study, we investigate adsorption behavior containing, Longmuir (Langmuir, 1916), Freundlich (Freundlich, 1906) and Temkin isotherms(Ozacar and Sengil, 2005). and kinetic models:

the pseudo first and second order equations( Lagergren,1898 ), (Mc Kay and Ho,1999), the Elovich equation(Chein and Clayton, 1963) and the intra particle diffusion equation(Weber *et al.*, 1980).These are kinetic and thermodynamic studies related to absorption of Pb(II) on resin beads to indicate absorption process is followed from what types of these models. The Langmuir isotherm demonstrates monolayer sorption due to a surface of a finite number of identical sites. Freundlich isotherm can be applied to non-ideal sorption on heterogeneous surface as well as multilayer sorption and The Temkin isotherm equation assumes that the adsorption of adsorbate is uniformly distributed so that the fall in the heat of adsorption is linear rather than logarithmic.

Finally, kinetic models indicate rate and degree of metal ion absorption on SIR.

## Material and apparatus

All the materials used, were of analytical grad and supplied by E.Merk, Darmstadt, Germany. Stock solution of Pb(II) ion was prepared at concentration of $1.0\times10^{-2}$M by dissolving the appropriate amounts of its nitrate salt in 1M HNO3 solution and diluting to the mark(100 mL) with distilled water.

Working solutions were adjusted at the pH 8 and ionic strength of 0. 1 M using ammonium/ammonia buffer solution. These solutions were prepared daily by diluting the stock solution.

A corning 130 model pH-meter was used for pH measurement. A flame atomic absorption spectrometer with Variant AA240 model was used for all absorbance measurements.

*Preparation of SIR*

2.0 g of the chelating agent (DAAQ) was located into a 50 mL stopper flask containing 30 mL 1, 2-dichloroethane and mixed for a few minutes to disperse into the solvent. After that, 3.0 g of the amberlit resin was added to the mixture and shaken for 48 h. After separation of impregnated resin beads with a porous filter, they were rinsed with aliquots of distilled water and 6M HCL until the filtrate solution did not show absorbance against distilled water.

*Adsorption equilibrium procedure*

The adsorption isotherms of Pb(II) ion on SIR was obtained using the batch technique at the optimum pH 8 and room temperature (298 ± 2 K). To study of sorption isotherms, exact 0.05 g of SIR was kept in contact with aliquots of 100ml of buffered solutions containing Pb (II) in the concentration ranges of 5-50ppm . The mixtures were shaken for 35 min. Then, 5 mL of the supernatant was withdrawn and subjected to the determination process.

*Determination of SIR capacity*

To evaluate the adsorption rate procedure of Pb (II), initially sorption capacity of the SIR was monitored in various shaking times. Figure indicates that complete sorption of the metal ion on SIR obtained within 35 min (Fig.1).

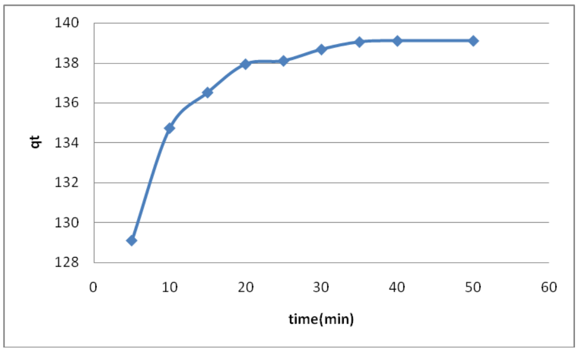


**Fig. 1.** Plot of SIR capacity versus time

*Adsorption rate procedure*

0.05 g of the SIRs were immersed into the vessels containing 100 mL buffered solutions (pH 8) with concentration ($5\times10^{-4}$M) at room temperature. The mixtures were stirred mechanically for pre-determined time intervals (5 min) at a fixed speed (220 rpm). During the stirring, portions of 5-mL of the supernatant was withdrawn from the solutions and subjected to the determination processes.

**Results and discussion**

*Adsorption equilibrium study*

Three isotherm models that widely used for study of metal ions adsorption on solid adsorbents are,The Longmuir, Frendlich and Temkin isotherms.

*Langmuir isotherm*

The Langmuir isotherm demonstrates monolayer sorption due to a surface of a finite number of identical sites and expressed in the linear form as the following equation (1):

$$C_e/q_e= C_e/q_{max}+1/b\ q_{max} \qquad (1)$$

Fig.2 shows the plot of $C_e/q_e$ versus $C_e$ with a high linearity and correlate coefficient for sorption of Pb (II) on SIR.

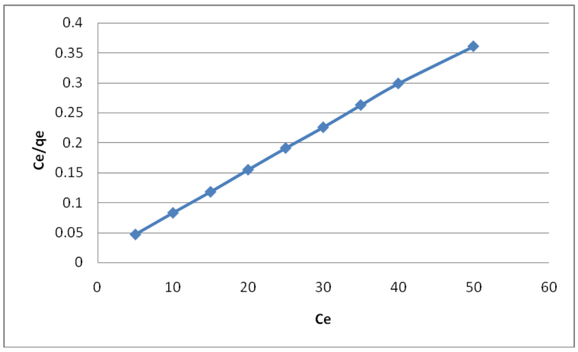


**Fig. 2.** Linearized form of Langmuir sorption isotherm for sorption Pb(II) on SIR(PH 8.0, rpm 200, temperature 298K)

*Freundlich isotherm*

This isotherm can be applied to non-ideal sorption on heterogeneous surface as well as multilayer sorption (35) and is expressed in linear form as:

$$Lnq_e= lnK_f+ 1/nLnC_e \qquad (2)$$

Obviously, the greater values of 1/n denots on favorable sorption.The results from the plot of $Lnq_e$ versus $lnC_e$ are summarized in table1. As it is observed, apoor linearity is obtained according to the Freundlich model.

**Table 1.** Isotherm parameters and equations from isotherm models for the SIR

| | | | |
|---|---|---|---|
| **Langmuir isotherm** | | | |
| **Equation** | **$R^2$** | **$q_{max}$(mg $g^{-1}$)** | **b (Lm$g^{-1}$)** |
| y=0.0072x+0.0107 | 0.9997 | 139.112 | 0.672 |
| **Frendlich isotherm** | | | |
| **Equation** | **$R^2$** | **$K_F(g^{1-(1/n)}L^{1/n}g^{-1})$** | **n(g $L^{-1}$)** |
| y=0.298 x +5.0281 | 0.7195 | 152.67 | 3.35 |
| **Temkin Isotherm** | | | |
| **Equation** | **$R^2$** | **$B_T$ (L$g^{-1}$)** | **$A_T$(mmol$L^{-1}$)** |
| y=0.008x+0.1427 | 0.4243 | 0.008 | 5.576E7 |

*Temkin isotherm*

The Temkin isotherm equation assumes that the adsorption of adsorbate is uniformly distributed so that the fall in the heat of adsorption is linear rather than logarithmic ( 21) and is expressed in linear form as:

$$q_e = B_T \ln A_T + B_T \ln C_e \qquad (3)$$

Table1 shows the results from the plot of $q_e$ versus $lnC_e$ and it is obvious that this isotherm is not a convenient model for adsorption of Pb(II) on SIR.

Adsorption kinetics study.

The kinetic modeling is helpful for the prediction of sorption rate. Also, the desired kinetic model gives important information for designing the sorption process for wastewater treatment. The sorption process of a metal ion into a macro porous impregnated resin, such this SIR, can be divided into three stages: diffusion through the liquid film surrounding the EIR beads (called external mass-transfer, or film diffusion), diffusion through the particle pores (called pore diffusion), and finally a chemical reaction with the functional groups of extractant molecules. Among them, the last step is assumed to be very fast in most cases. But the first and the second steps can be the rate-controlling step, either singly or in combination. Therefore, kinetic modeling was carried out for investigating the appropriate model for explaining the nature of sorption process (Hosseini-Bandegharaei *et al.*, 2011). Kinetics of Pb(II) sorption was modeled by four models, namely the first-order Lagergren model, the pseudo-second-order equation, Elovich model and intraparticle diffusion model, at initial Pb(II) concentration($5\times10^{-4}$M).

The pseudo-first-order Lagergren equation is given as Eq.(4)

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (4)$$

Where qe and qt (mg $g^{-1}$) are the amount of Pb(II) adsorbed at equilibrium and at time t (min), respectively and $k_1$ ($min^{-1}$) is the rate constant of pseudo-first order sorption.

The pseudo-second-order equation is expressed as Eq. (5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (5)$$

Where $K_2$ (g$mg^{-1}$ $min^{-1}$) is the rate constant of pseudo-second order sorption and qe is the sorption capacity at equilibrium (mg $g^{-1}$).

Elovich model [26] is described as Eq. (6):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (6)$$

Where α is initial sorption rate (mg g⁻¹ min⁻¹) and β is the desorption constant (gmg−1).

The intraparticle diffusion [27] equation can be described as Eq. (7):

$$q_t = k_i t^{0.5} + I \qquad (7)$$

$k_i$ can be determined by the slope of the straight-line portion of a plot of $q_t$ versus $t^{0.5}$. Values of $I$ give an idea about the thickness of the boundary layer.

Fig.3-6 displays these four kinetic models respectively. As observe from figures, the best kinetic model for interpreting this phenomenon is Elovich model.

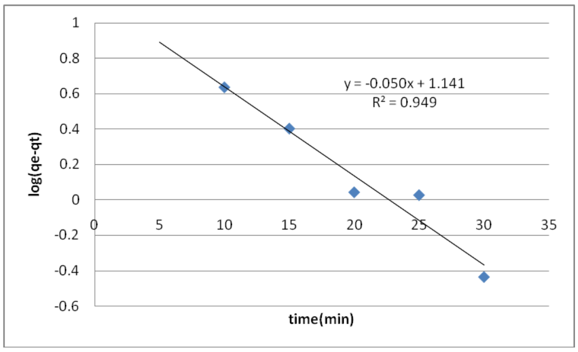


**Fig. 3.** Linear plot of pseudo first order equation

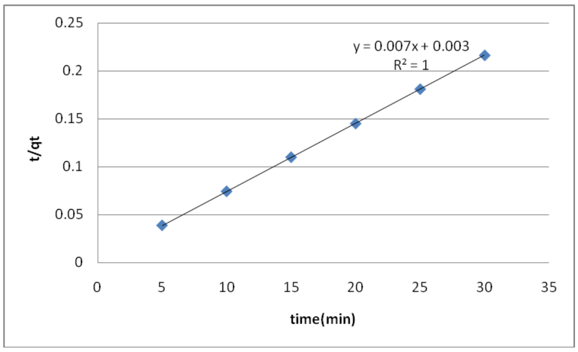


**Fig. 4.** Linear plot of pseudo second order equation

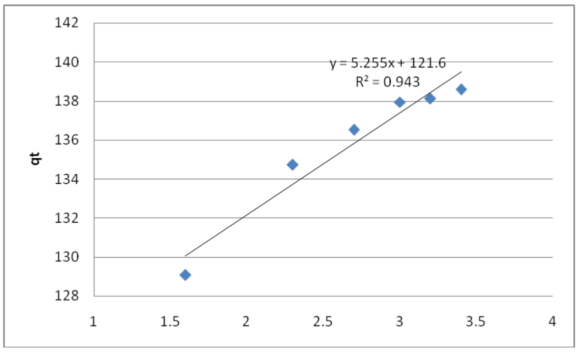


**Fig. 5.** Linear plot of Elovich model

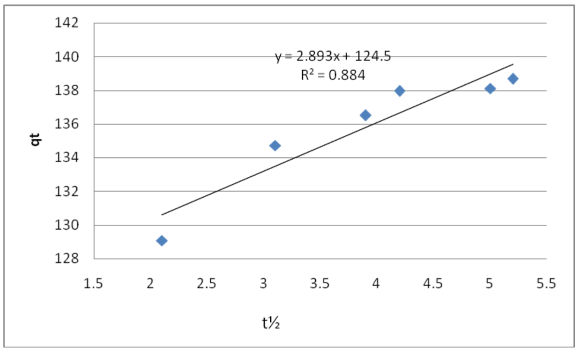


**Fig. 6.** Linear plot of intra particle diffusion

## Conclusion

Amberlit resin XAD-16 impregnated with 1,4-diaminoantraquinone is an adsorbent solid phase for removal of Pb(II) from water samples. It has some advantages such as high capacity and recovery, faster rate of equilibrium and high sorption rate. From these advantages, we can conclude that this SIR is a convenient adsorbent for extraction of metal ions especially Pb(II).

## Acknowledgements

The authors wish to thank the Islamic Azad University-Neyshabur, Iran for financial support of this work.

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