International Journal of Current Engineering and Technology
ISSN 2277 - 4106

Research Article

Adsorption of Heavy Metals from Aqueous Solution using Agricultural Wastes

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Accepted 10 October 2013, Available online 19 October 2013, **Vol.3, No.4 (October 2013)**

Abstract

*In this study, removal of lead Pb(II) and zinc Zn(II) from aqueous solutions is investigated using Imperata Cylinderica, a natural plant. During the removal process, batch technique is used to determine the effects of pH(3, 4, 4.5 and 5), plant dose (0.5, 1, 2 and 3 g), metal ion concentration (10 ,20, 50, 70 and 100 mg/L) on adsorption capacity are studied. The maximum uptake of Pb (II) and Zn(II) was 3.772 mg/g and 3.489 mg/g respectively from 50 mg/L of metal solution of 120 minutes contact time at pH 5. The Langmuir and Freundlich adsorption models were used to represent the experimental data and equilibrium data. It is fitted well with both models but the Langmuir isotherm for lead and Zinc was better from Freundlich isotherm. The effect of contact time was studied on the rate of removal of Pb(II) and Zn(II) ions from aqueous solution by Imperata cylinderica was found. The rates of adsorption of lead and zinc were rapid initially within the first 20 minutes and reached a maximum in about 120 minutes***.**

***Key words**: Adsorption, heavy metals, Imperata Cylinderica, Lead, Zinc.*

Introduction

The removal of toxic metal ions and recovery of valuable ions from groundwater, industrial wastewater, marine environments and soil (V. Chairgulprasert *et al*, 2013) have been important in the study of economic and environmental problems. Heavy metals such as lead, zinc, mercury, arsenic, copper and cadmium are highly toxic when adsorbed into the body (L. N. Rao *et al*, 2013). Due to their toxicity and non-biodegradability they can accumulate in food chain posing a severe damage to the living organisms (D. Tirumalaraju *et al*, 2013). Therefore, different methods for the removal of these metals from aqueous solution such as chemical precipitation, ion exchange, filtration, membrane separation, adsorption and reverse osmosis have been reported. These methods are either expensive or inefficient, especially when the concentrations of heavy metal ions are less than 10 mg/l (M. W. Amer *et al*, 2010). The search for new, effective and economical technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption based on metal binding capacities of various biological materials at little or no cost. Biosorption techniques for wastewater treatment have become more popular in recent years with regard to their efficiency in the removal of pollutants, especially heavy metal ions (M.T. Osobamiro *et al*, 2012). Biosorption is a fast and reversible reaction of the heavy metals with biomass. The by-products obtained from biomaterial production are a cheap source of biosorbents (G. O. El-Sayed *et al*, 2011). Several agricultural waste materials have been studied and developed for the effective removal of heavy metals like Spent Leaves of Green and Black Tea (A. Zuorro *et al*, 2010), Bael tree leaf (P. S. Kumat *et al*, 2009), orange peel (F. Gönen *et al*, 2012), rice husk (N. A. Khan *et al*, 2004), banana fiber (K. L. Bakiya *et al*, 2012), Palm Shell (S. Kushwaha *et al*, 2008) and Coconut Husk O. O. Abdulrasaq *et al*, 2010)

The aim of the present study is to examine the ability of Imperata cylinderica as cheep biosorbent for removal of Pb(II) and Zn(II) ions from aqueous solutions. The adsorption equilibrium was determined. Langmuir and Feundlich isotherm equations were employed to quantify the adsorption equilibrium. The effects of solution pH, adsorbent dose, ion metals concentration and contact time on Pb (II), Zn (II) adsorption were examined.

Materials and Methods

Preparation of Imperata cylinderica materials

The grass was collected from Baghdad, Iraq. It was used in the form of a biosorbent powder for the removal of Pb(II) and Zn(II) from aqueous solution. The powder was prepared by washing the grass with distilled water, and then dried. The dried grass was then ground and sieved through a mesh filter to give particles of 150 µm, and stored in an air tight plastic container for further experiments.

Preparation of aqueous solutions

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Single metal solutions of $Pb(NO_3)_2$ and $ZnSO4.7H_2O$ were used to prepare the aqueous test solutions. They were prepared by diluting with deionized water to the desired concentrations. The acidity of each solution was adjusted to give a range of values between pH 3 and 5 by addition of either Hydrochloric acid or Sodium Hydroxide.

Batch Adsorption Studies

All experiments were performed in 100 mL Erlenmeyer flasks at room temperature and the flasks were agitated on a mechanical shaker at 125 rpm throughout the study. Initial testing was carried out with 50 mL samples adjusted to pH 3, at an initial metal concentration of 20 ppm. The biosorbent powder (0.5 g) was then added and the suspension was shaken for 120 min. After shaking, the suspension was filtered and the residual metal ion in the filtrate was analyzed using atomic adsorption spectroscopy.

The metal ion uptake capacity of the biosorbent (qt, mg/g) was calculated from Equation 1.

$$q = \frac{(C_i - C_f)V}{W} \tag{1}$$

where
C_i and C_f (mg/mL) are the initial and final metal ion concentrations in the filtrate.
V (mL) is the volume of the solution.
W (g) is the mass of grass biosorbent used.

Results and Discussion

Effect of Metal concentrations

The effect of Zinc and Lead concentrations on the metal ions uptake were examined as shown in Figure 1. The concentrations used were 10, 20, 50, 70 and 100 g/lit. Experimental results showed that increasing the initial concentrations of Zinc and Lead increases the metal uptake at constant values of adsorbent dose at 0.5 g, pH of the solution at 5 and for contact time of 120 minutes.

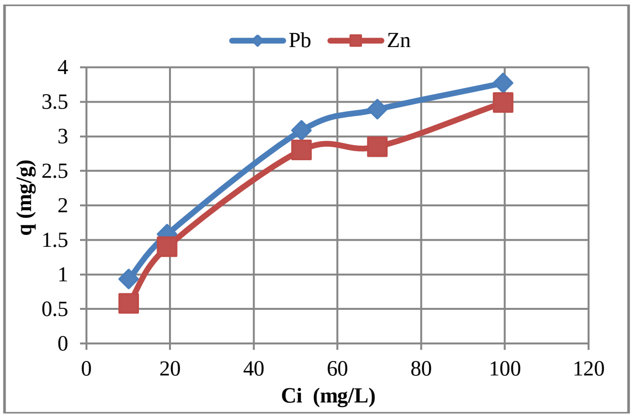

Figure1: The metal uptake versus metal ion concentrations.

The increase of metal uptake was a result of the increase in the driving force, i.e., concentration gradient, with an increase in the initial lead and zinc ion concentrations (from 20 to 100 g/L). This relationship has also been reported by other researcher, who have observed that at high concentrations of the metal ion, affinity towards the active sites of the adsorbent increases (V. Chairgulprasert *et al*, 2013; L. N. Rao *et al*, 2013).

As shown in Fig.1 the metal uptake of lead was greater than that for zinc at the same conditions. This behavior indicate that there is a preferential adsorption pattern that favors Pb(II) than Zn(II). The chemistry of this trend may be attributed to the differences in behavior among these metals or their ions in solution. Whereas, Pb (II) is adsorbed as hydrolyzed species, Zn (II) is not. This behavior is attributed to a number of factors which include (i) the smaller hydrated radius of lead (II) compared to zinc (II); (ii) the higher electro negativity of Pb(II) than Zn(II); (iii) the negative log. of hydrolysis constant for $Pb(OH)_2$ and $Zn(OH)_2$; and (iv) the strength of acidity of these metals Pb(II) is a border line hard Lewis acid while Zn(II) is soft Lewis acid). These factors make Pb(II) to be more preferentially adsorbed through inner-sphere surface complexation reactions than Zn(II) N. Abdus-Salam *et al*, 2005).

Adsorption isotherms

To describe the adsorption process of Pb(II) and Zn(II) onto Imperata cylinderica, the two empirical models of Langmuir and Freundlich isotherms were tested. The adsorption studies were conducted at fixed adsorbent dosage 0.5 g, pH=5 and contact time for 120 min. by varying initial concentrations of heavy metals (20-100 mg/L)
The linear Langmuir equation is represented in Equation 2 I. Langmuir *et al*, 1916):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}\, b} + \frac{C_e}{q_{max}} \tag{2}$$

where C_e is the equilibrium concentration of the remaining metal ion in solution (mg/L),
q_e (mg/g) is the amount of metal ion adsorbed by the adsorbent at equilibrium,
q_{max} is the maximum metal uptake capacity, and K is the equilibrium constant.

The linearized Fraundlich model is represented by Equation 3H. M. Freundlich *et al*, 1906):

$$\log q_e = \log k_F + \left(\frac{1}{n}\right) \log C_e \tag{3}$$

where K_F and 1/n are Freundlich constants indicating the adsorption capacity and intensity, respectively.

The calculated results of the Langmuir and Freundlich isotherm constants are given in Table 1.

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the Imperata cylinderica surface. The plots of specific adsorption (Ce/qe) against the equilibrium concentration (Ce) for Pb(II) and Zn(II) are shown in Figure 2a and 2b respectively and the linear isotherm parameters, q_{max}, b and the coefficient of determinations are presented in Table 1.

Table 1: Langmuir and Freundlich Isotherm Constants and Correlation Coefficients

	Lead	**Zinc**
Langmuir		
q_{max} (mg/g)	3.984	3.69
b (L/mg)	0.211	0.109
R^2	0.996	0.982
Freundlich		
K_f (mg/g)	0.973	0.593
1/n(L/g)	0.332	0.419
R^2	0.982	0.978

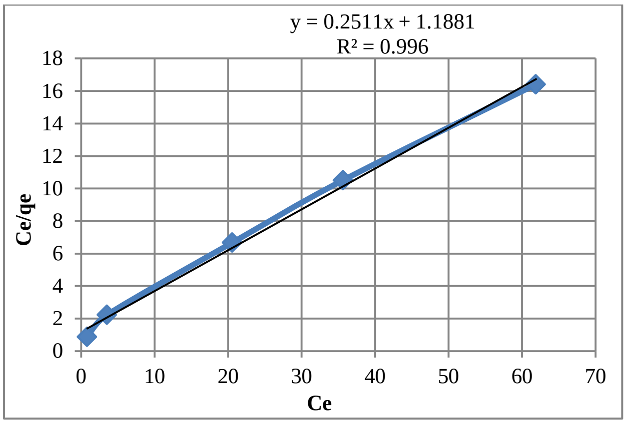

Figure 2a:Equilibrium adsorbtion isotherm for Pb(II) Linearized Langmuir equation.

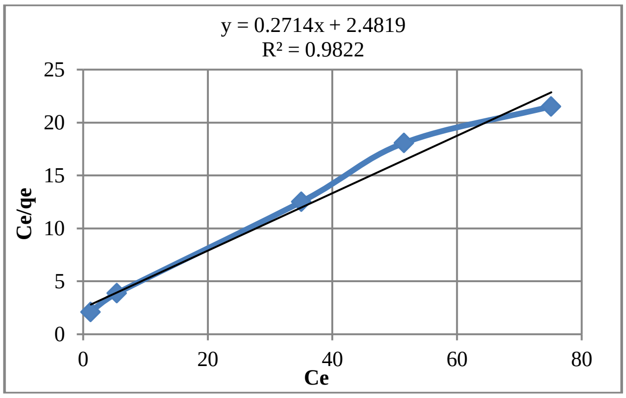

Figure 2b:Equilibrium adsorbtion isotherm for Zn(II) Linearized Langmuir equation.

The adsorption capacity, q_{max}, which was a measure of the maximum adsorption capacity corresponding to complete monolayer coverage showed that the Imperata cylinderica had a mass capacity for Pb2+ (3.984 mg/g) than Zn2+ (3.69 mg/g). The adsorption coefficient, *b* that is related to the apparent energy of adsorption for Pb2+ (0.211 L/g) was greater than that of Zn2+ (0.109 L/g). The data in Table1 further indicated that, the effectiveness of Imperata cylinderica in the adsorption of the two metals from an aqueous solution was Pb(II) > Zn(II). This preferential adsorption behavior could be explained in terms of ionic radii of the metal ions (Pb(II) = 1.19 A°; Zn(II) = 0.70 A°. The element with smaller ionic radius will compete faster for exchange sites than those of larger ionic radius. For each metal the adsorption data fit the langmuir isotherm better from Frendlich isotherm (indicated by a higher value for the regression coefficient, R^2). From Frendlich isotherm, the Pb(II) adsorption exhibited a higher K_f value than the Zn(II) adsorption, demonstrating that the sorbent has a higher capacity for binding Pb(II) than Zn(II) ions K. M. Surchi *et al*, 2011). A 1/n value of <1.0 from Figure 3a and 3b for Pb(II) and Zn(II) respectively.

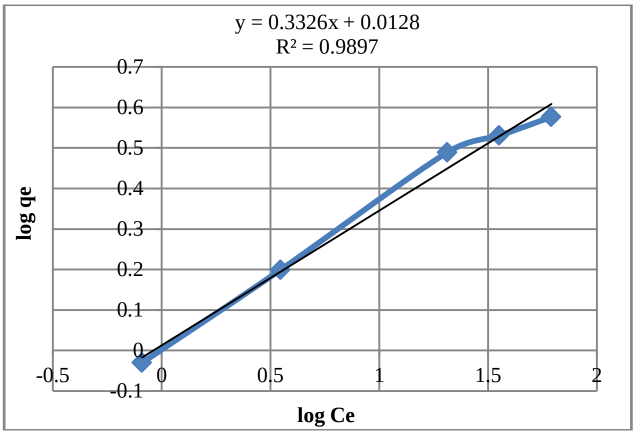

Figure 3a: Equilibrium adsorption isotherm for Pb(II) Linearized Freundlich equation.

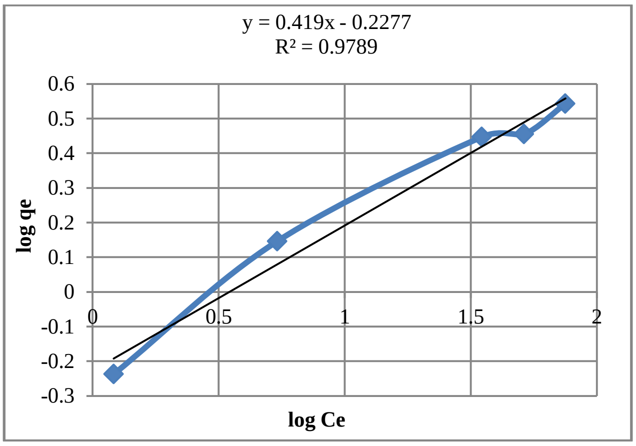

Figure 3b: Equilibrium adsorption isotherm for Zn(II) Linearized Freundlich equation.

Figures above showed that there was also a clear indication that adsorption was most effective at an initial concentration range of 20-100 mg/mL

A comparison between theoretical and experimental studies were shown in figures 4a and 4b for both Pb(II) and Zn(II).

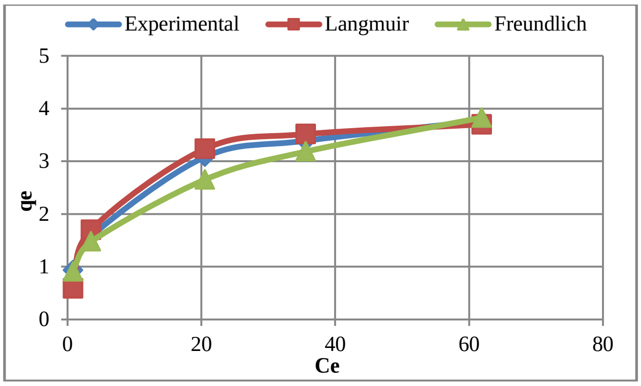

Figure 4a: Experimental and adjusted isotherms for Pb(II).

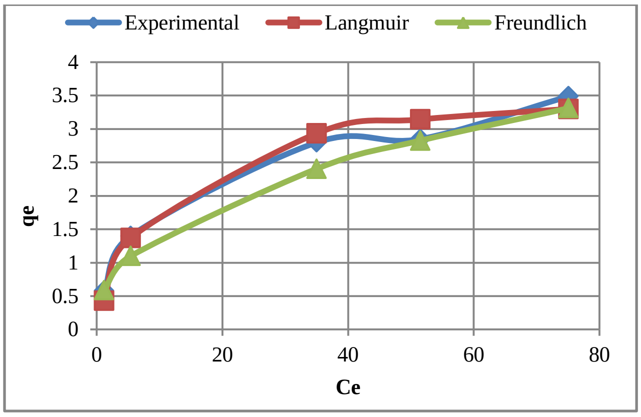

Figure 4b: Experimental and adjusted isotherms for Zn(II).

Effect of Adsorbent Dose

The effect of adsorbent dose on the metal uptake was studied experimentally at constant values of metal concentrations of 50 ppm, pH of the solution at 5 and contact time of 120 minutes. Figure 5 shows that the relationship between metal uptake with adsorbent dose.

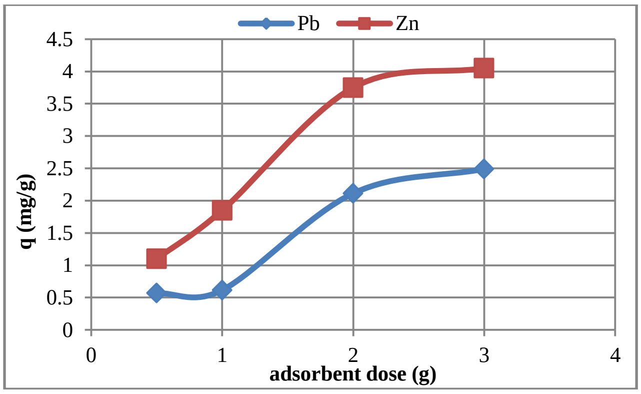

Figure 5: The adsorption uptake versus adsorbent dose.

Adsorbent dose is an important parameter in the adsorption of metal ions from aqueous solution owing to its effect on the amount of metal ions removed per unit mass of the adsorbent O. O. Abdulrasaq *et al*, 2010). Figure 5 showed that increasing the adsorbent dose from 0.5 to 3 g increased the metal uptake for both Pb(II) and Zn(II). This increase in metal uptake due to the greater availability of the exchangeable sites or surface area. Moreover, the metal uptake on adsorbent is determined by the adsorption capacity of the adsorbent for various metal ions (M. Parmar *et al*, 2013). The removal of Zn(II) also followed the same pattern observed for Pb(II) O. O. Abdulrasaq *et al*, 2010).

Effect of pH

The pH of the metal ion solution is an important parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate (G. O. El-Sayed *et al*, 2011). The pH value of solution strongly influences not only the site dissociation of the biomass' surface, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or Inorganic ligands, redox reactions, precipitation, the speciation and the adsorption availability of the heavy metals (M. Parmar *et al*, 2013). To examine the effect of pH on metal ion removal efficiency the pH of Pb(II) and Zn(II) solutions were varied from 3 to 5 at constant metal ion concentrations of 50 ppm, adsorbent dose of 1 g/100ml and contact time of 120 minutes as shown in Fig. 6.

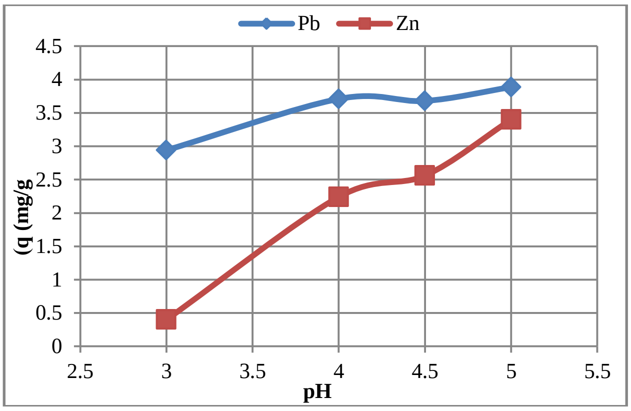

Figure 6: The adsorption uptake versus pH of the solution.

Figure 6 showed that there was an observed increase in adsorption as pH of metal ion solution increased from 3 to 5. However, above pH = 4 the adsorption only increased marginally and reached an optimum value at pH = 5 for both Pb(II) and Zn(II) (Chairgulprasert *et al*, 2013). Generally, metal ions are more soluble at lower pH values and this enhances their adsorption. Removal of metal ions at higher pH values could be attributed to the formation of their hydroxides which results in precipitates. Therefore, removal of metal ions at higher pH values is due to the formation of precipitates rather than adsorption. Adsorption experiments are better performed at low pH to avoid precipitate formation O. O. Abdulrasaq *et al*, 2010).

Effect of Contact time

The contact time effect on the adsorption rate of Pb(II) and Zn(II) was studied at constant values of metal ions concentrations of 50 ppm, pH of the system at 5 and adsorbent dose of 0.5 g. The uptake of Pb(II) and Zn(II) ions as a function of contact time was shown in figure 7.

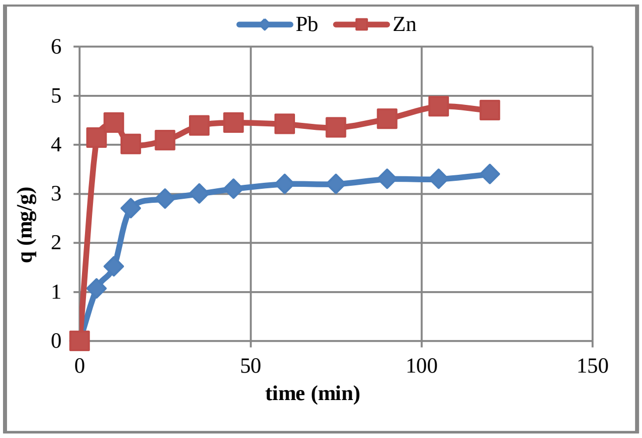

Figure 7: Metals uptake against contact time.

Figure 7 indicate that the adsorption rate for lead increased rapidly over the first 20 minutes and then slowly reaching a maximum adsorption after 120 min. However, the adsorption rate for zinc also increased rapidly over the first 20 min, maximum metal uptake for Zn(II) was achieved after 120 min . For the first 20 min a gradual increase in the rate of adsorption was observed, until a slightly lower adsorption rate at 120 min. Most adsorption studies have indicated that initial adsorption occurs rapidly, but is followed by a slow increase in the rate of adsorption (V. Chairgulprasert *et al*,2013). The optimum time for lead and zinc removal were determined at 5 and 15 min, respectively. As a result of the experimental studies, it is seen that high efficiency for metals adsorption can be obtained at short time periods (S. Veli *et al*, 2007).

The rapid adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The adsorption rapidly occurs and normally controlled by the diffusion process from the bulk to the surface. In the later stage the adsorption is likely an attachment-controlled process due to less available adsorption sites (B. Das *et al*, 2011).

Conclusion

Imperata cylinderica showed a considerable ability for the removal of Pb(II) and Zn(II) from aqueous solutions as a low cost adsorbent. The effect of initial metal ions concentrations, pH, adsorbent dosage and contact time on the adsorption process was discussed. The following conclusions were obtained from the study.

(1) The experimental results showed that increasing the metal ion concentrations increases the metal uptake for both Pb(II) and Zn(II) at the same conditions. The effectiveness of Imperata cylinderica in the adsorption of the metals from aqueous system showed that there is a preferential adsorption pattern that favors Pb(II) than Zn(II). This preferential adsorption behavior could be explained in terms of ionic radii of the metals ions.
(2) The adsorption amount increased with increased adsorbent dose from 0.5 g to 3 g per liter.
(3) There was an observed increase in adsorption as pH of metal ion solution increased from 3 to 5. Above pH = 4 the adsorption only increased marginally and reached an optimum value at pH = 5 for both Pb(II) and Zn(II)
(4) The adsorption rate for metal ions increased rapidly over the first 20 minutes and then slowly reaching a maximum adsorption after 120 min.
(5) As a result of this study, it may be concluded that Imperata cylinderica may be used for removal of heavy metal pollution from wastewater since it is of low-cost, abundant and a locally available adsorbent.
(6) The experimental results were analyzed using Freundlich and Langmuir adsorption models. The data in the linearized forms gave satisfactory correlation factors for the covered concentration range. The metal binding capacity order calculated from Langmuir isotherm was Pb(II) > Zn(II). This preferential adsorption behavior could be explained in terms of ionic radii of the metal ions

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