Sorption of Lead, Zinc and Copper from Simulated Wastewater by Amberlite Ir-120 Resin

By

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Abstract

The presence of heavy metals in the environment is major concern due to their toxicity. In the present study a strong acid cation exchange resin, Amberlite IR 120 was used for the removal of lead, zinc and copper from simulated wastewater. The optimum conditions were determined in a batch system of concentration 100 mg/L, pH range between 1 and 8, contact time between 5 and 120 minutes, and amount of adsorbent was from 0.05 to 0.45 g/100 ml. A constant stirring speed, 180 rpm, was chosen during all of the experiments. The optimum conditions were found to be pH of 4 for copper and lead and pH 6 for zinc, contact time of 60 min and 0.35 g of adsorbent. Three different temperatures (25, 40 and 60°C) were selected to investigate the effect of adsorption temperature on heavy metals adsorption onto Amberlite IR. The equilibrium data were analyzed by the Langmuir and Freundlich isotherms. The thermodynamic parameters such as Gibbs free energy, enthalpy and entropy changes were calculated. Moreover, in order to understand the heavy metal extraction kinetics in the presence of Amberlite IR 120, the ion exchange kinetics was also studied. The ion exchange kinetics data were regressed by the pseudo first-order, second-order models. The results obtained show that the Amberlite IR 120 strong acid cation exchange resin performed well for the removal of lead, zinc and copper.

Keywords: Heavy metals; Simulated wastewater; Sorption; Isotherm; Kinetics; Thermodynamics.

معادن ثقيلة ، فضلات مياه ، امتزاز ، ثبوت درجة الحرارة ، حركيات ، الديناميكا الحرارية.

امتزاز الرصاص والزنك والنحاس من فضلات المياه بواسطة راتنج (Amberlite IR-120)

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:

(Amberlite   .
(   )   IR120)
   100   0.45   0.05   120   5   8   1   /   100
        4   .   180   .
                                  . 0.35   60   6
                                ° 60   40   25
                . Freundlich   Langmuir   .
                                             .

                                        (kinetics)
              .   (Amberlite IR120)   .

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1. Introduction

The release of large quantities of heavy metals into the natural environment has resulted in a number of environmental problems. Toxic metals can be distinguished from other pollutants, since they are not biodegradable and can be accumulated in nature. They also cause various diseases and disorders when exceed specific limits (Gode and Pehlivan, 2003 ; Veli and Alyuz, 2007).

Many separation techniques have been proposed for the identification of metals in various samples, including solvent extraction, ion exchange, co-precipitation, membrane process and sorption (Sule and Ingle, 1996; Adria-Cerezo and LIobat-Estelles, 2000; Leinonen and Lehto,2000). Among the heavy metal removal process, ion exchange process is very effective to remove various heavy metals and can be easily recovered and reused by regeneration operation. Ion exchange resins are a variety of different types of exchange materials, which are distinguished into natural or synthetic resin. Furthermore, it can be as well categorized on the bases of functional groups such as cationic exchange resins, anion exchange resins, and chelating exchange resins (Dofner , 1991).

Certain general rules for cation exchange are: (i) the exchanger prefers ions of high charge, (ii) ions of small hydrated volume are preferred, (iii) ions, which interacts strongly with the functional groups of the exchanger are proffered (Leinonen and Lehto,2000; Greenway et al., 1996; Lin et al., 2000; Seco et al.,1999; Kenaway et al., 2000; Verbych et al., 2004; Badawy et al., 2009).

The aim of the present work was to study the removal of Cu^{+2}, Pb^{+2} and Zn^{+2} from industrial wastewater by ion exchange method using Amberlite IR120 resin. In addition, parameters that influence ion exchange, such as contact time, resin dosage, pH and temperature were investigated. The thermodynamic studies and isotherms models and kinetics parameters were also evaluated from the ion exchange measurements.

2. Experimental
2.1. Materials

Analytical grade reagents were used in experimental studies. Copper Sulfate pent hydrated ($CuSO_4.5H_2O$), Lead Nitrate ($Pb (NO_3)_2$) and Zinc Chloride ($ZnCl_2$) from (E. MERK, Denmark) were used for preparing synthetic solutions. pH adjustments were carried out by using 0.1N HCl and 0.1N NaOH.

Amberlite IR120 strong acid cation exchange resin from (Rohm and Hass) was used its physical and chemical properties are given in Table 1.

2.2. Apparatus

GBC 933 plus Atomic Absorption Spectrometer AAS was used to measure concentrations of soluble copper, zinc and lead. Batch experiments were carried out in SI-600R Lab. Companion shaker. wtw series ion lab pH-meter used for pH measurements.

2.3. Equilibrium studies

The batch ion exchange experiments were carried out in the Laboratory of higher studies/ Department of Environmental Engineering/ College of Engineering/University of Baghdad. These experiments were performed in a wide variety of conditions including different pH, various resin dosages and agitation periods. Effects of each factor were determined keeping other variables constant. In the experiments 100 ml of synthetic solutions containing 100 mg/L of one of heavy metal were added into flasks with different amount of resin varying between 0.05 and 0.45g. pH adjustments were made by using 0.1N hydrochloric acid and 0.1N sodium hydroxide. Solutions were shaked at 180 rpm for a predetermined period. At the end of agitation time resins were filtered and metal contents of solution were analyzed by AAS.

3. Results And Discussion
3.1. Effect of pH

Hydrogen ion concentration is an important parameter affecting the ion exchange process. In order to investigate the effect of the pH on removal of heavy metal by Amberlite IR120, 100 ml of 100 mg/l metal solutions were used. Experiments were

performed in the pH range 1-8. Constant resin amount was added to all reaction bottles and solutions were agitated for 2h at 180 rpm speed. Effect of pH on removal efficiency is shown in Figure. 1.

The removal of metals was increased with increasing pH values. At lower values, the metal ion uptake was inhibited in the acidic medium and this can be attributed to the presence of H^+ ions competing with the metal ions for the sorption sites (Rao et al., 2006). The uptake continuously increases with the increase in pH value and the highest uptake was observed at pH equal to 4 for Cu and Pb and pH equal to 6 for Zn.

The removal of lead is greater than copper and zinc at pH of 4; removal efficiency of lead is 99.833, copper is 99.39, and zinc is 98.14 (Pb > Cu >Zn).

3.2. Effect of resin amount

The resin amount is also one of the important parameters to obtain quantitative uptake of metal ion. The dependence of metal sorption on resin input amount was studied by varying the amount of Amberlite IR120 (0.05-0.45g), while the other parameters such as pH 6, initial metal concentration 100 mg/l, agitating time 2h and stirring speed 180 rpm remained constant.

It was apparent that the adsorption percentage of metal ions increased with higher resin dosages. The higher removal efficiency was achieved by using 0.35 g/100 ml resin dosages (Figure 2). This result proved that increasing the amount of adsorbent provides higher removal due to formation of greater adsorption sites.

3.3. Effect of contact time

The effect of contact time on the ion exchange of metal ions by Amberlite IR120 resin was studied by taking 0.35g resin with 100ml of a metal solution in different flasks. The flasks were shaked for different time intervals. Figure 3 shows the effect of contact time on the removal efficiency. The results show that the percentage of metal ion adsorbed increased with increasing time till reaching the equilibrium and it reached the plateau value at 60 minutes.

3.4. Effect of temperature

To investigate the effect of adsorption temperature on the metal adsorption onto the Amberlite IR120, experiments were carried out at three different temperatures (25, 40 and 60°C) with initial concentrations of lead (II), copper (II) and zinc(II) 100mg/L at 60 minutes contact time and 0.35g resin amount and pH 1 and 6 and a constant stirring speed 180 rpm. The results show an increase in metal removal is observed by increasing the temperature of the system. The results are given in Figures 4 and 5.

As seen from the figure the removal efficiency of lead increased from 94.974 to 98, zinc from 90 to 94.65, and copper from 82.23 to 91.5 with increasing temperature from 25 to 60°C at pH=1and the removal efficiency of lead increased from 99.476 to 99.95, zinc from 99 to 99.91, and copper from 99.816 to 99.911 with increasing temperature from 25 to 60°C.

3.5. Thermodynamic studies

The amounts of sorption of single metal ions by Amberlite IR120 are measured in temperature 298, 313 and 333 °K. Thermodynamic parameters were calculated for the system by using the equation (Gode and Pehlivan, 2003):

$$\ln K_D = \left(\frac{\Delta S^o}{R} \right) - \left(\frac{\Delta H^o}{RT} \right) \qquad (1)$$

where K_D is the distribution coefficient; ΔH, ΔS, and T the enthalpy, entropy, and temperature in Kelvin, respectively; R is the gas constant. The values of enthalpy and entropy were obtained from the slope and intercept of $\ln K_D$ versus $1/T$ plots (Figures 6 and 7).

Gibbs free energy (ΔG) was calculated using the following equation:

$$\Delta G = \Delta H - T\Delta S \qquad (2)$$

Table 2 summarizes the distribution coefficients from a series of batch experiments at different temperatures. The distribution coefficient values for Zn^{+2}, Pb^{+2} and Cu^{+2} were very high and they increased with temperature and the reaction products are favored at high temperatures. This is due to the endothermic ion exchange reactions of divalent cations.

The values of the thermodynamic parameters for the sorption of metal ions on Amberlite IR120 are given in Table 3. The positive values of enthalpy changes show that the adsorption of metal ions is endothermic. Entropy values were

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Found to be positive due to the exchange of the metal ions with more mobile ions present on Amberlite, which would cause increase in the entropy during the sorption process.

3.6. Adsorption isotherms

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. The Langmuir and Freundlich isotherm models are widely used to investigate the adsorption process.

3.6.1 Langmuir Isotherm Model

Langmuir sorption isotherm models the monolayer coverage of sorption surfaces and assumes that sorption occurs on a structurally homogenous adsorbent and all the sorption sites are energetically identical. The saturated monolayer curve can be represented by the expression (Rao et al., 2006 ; Prasad et al., 2000):

$$Q_e = \frac{X}{m} = \frac{Q_0 b C_e}{1 + b C_e} \quad \text{(non-linear)} \quad (3)$$

A linear form of this equation is:

$$\frac{C_e}{Q_e} = \frac{1}{b Q_0} + \frac{C_e}{Q_0} \quad \text{(linear)} \quad (4)$$

where X is the initial concentration of solute minus the final concentration of solute in solution at equilibrium (mg/l), m is the concentration of adsorbent (mg/l), C_e is the equilibrium concentration of metal in solution (mg/l), Q_e is the amount of metal ion sorbed onto resin (mg/g), b, Q_0 is Langmuir constants representing the equilibrium

3.7. Kinetics of adsorption

Adsorption kinetics provides valuable information about the mechanism of adsorption (Veli and Ozturk, 2005). Rate of adsorption uptake, which is required for selecting optimum operating condition for the full-scale batch process, can be described with adsorption kinetics (Gupta and Sharma, 2003).

Constant for the adsorbate-adsorbent equilibrium and the monolayer capacity. b and Q_0 were determined from the slope, intercept of the Langmuir plot (Figure 8).

3.6.2 Freundlich Isotherm Model

Freundlich equation is derived to model the multilayer sorption and for the sorption on heterogeneous surfaces. The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations (Rao et al., 2006; Prasad et al., 2000).
The Freundlich equation is:

$$Q_e = K_f C_e^{1/n} \quad \text{(non- linear)} \quad (5)$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{(linear)} \quad (6)$$

where Q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/l), K_f is a constant indicative of the relative adsorption capacity of the adsorbent (mg/g), 1/n is a constant indicative of the intensity of the adsorption.

Both K_f and n are constants, being indicative of the extent of adsorption and the degree of non-linearity between solution and concentration, respectively.

The linear Freundlich plots are obtained by plotting log Q_e versus log C_e from which the adsorption coefficients could be evaluated (Figure 9).
All constants determined from Langmuir and Freundlich isotherms are given in Table 4.

Kinetic studies for zinc, copper and lead were performed by using 100 mg/l concentration, pH was adjusted to 6, resin mass was 0.35g/100 ml. Samples were taken with different time intervals ranging between 5 and 120 minutes.

3.7.1. Pseudo-first order reaction kinetic

Simple linear equation for Pseudo-first order reaction kinetic is (Sharma and Bhattacharyya, 2004):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

where k_1 is the rate constant of the first-order adsorption, q_t is the amount of heavy metal adsorbed at time t (mg/g) and q_e is the amount of heavy metal adsorbed at saturation (mg/g). Plot of $\ln(q_e - q_t)$ versus t allows calculation of the rate constant k_1 and q_e (Figure 10).

3.7.2. Pseudo-second order reaction kinetic

Pseudo-second order reaction kinetic can be expressed as (Ho and Mckay, 1998):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

where k_2 is the pseudo-second order rate constant (g/mg h), q_e is the amount adsorbed at equilibrium and q_t is the amount of metal adsorbed at time t.

Calculated rate constants (k_1 and k_2), adsorbed amounts of heavy metals per unit resin mass (q_e) and linear regression correlation coefficients (R^2) for pseudo-first and –second-order reaction kinetics are summarized in Table 5. In pseudo-second-order reaction kinetic, calculated values of q_e are closer to experimental values for zinc, copper and lead. Furthermore as seen from Table 5, correlation

Similar to pseudo-first order reaction kinetic, q_e and k_2 can be determined from the slope and intercepts of plot t/q_t versus t (Figure 11).

coefficients are higher for second order kinetic studies.

4. Conclusion

In this paper optimal removal conditions were determined with batch experiments. Ion exchange processes was pH-dependent and optimal removal efficiencies for zinc at pH 6, copper and lead at pH 4. Adsorption of the three metal ions reaches equilibrium within 60 minutes and 0.35g/100 ml of resin.

The thermodynamic parameters of ion exchange process were calculated. Ion exchange equilibrium at temperatures 298 , 313 and 333°K of Zn, Cu, and Pb are found to be endothermic processes.

Experimental results were evaluated with Langmuir and Freundlich; the results show Freundlich isotherm fit the ion exchange equilibrium data better than the Langmuir.

Pseudo-second-order reaction kinetic has provided a realistic description of removal of Zn, Cu, and Pb with closer experimental and calculated values of q_e. Also correlation coefficients are higher in pseudo-second-order kinetics.

Experimental and theoretical results of this study demonstrate that the Amberlite IR120 cation exchange resin is suitable for adsorption of zinc, copper, and lead from aqueous solutions.

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Table 1: Characteristics of Amberlite IR120.

Matrix	Styrene
Functional group	Sulfunic acid
Particle size (mm)	0.3-1.2
Maximum temperature (°C)	120
pH range	0-14
Total capacity (equiv/l)	1.8

Table 2: Distribution coefficients of heavy metal at different temperatures.

pH=1				
Metal	k_d			R^2
	298°K	*313°K*	*333°K*	
Zn	2.5714	3.7959	5.0547	0.9809
Pb	5.3990	11.1429	14.0000	0.8869
Cu	1.3221	2.3117	3.0756	0.9456
pH=6				
Metal	k_d			R^2
	298°K	*313°K*	*333°K*	
Zn	66.7834	158.4444	317.1746	0.9871
Pb	54.2399	123.9379	571.1429	0.9858
Cu	23.8456	50.7347	320.7416	0.9656

Table 3: Thermodynamic parameters for the adsorption of metal ions on Amberlite IR 120.

pH=1					
Metal	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)		
			298°K	*313°K*	*333°K*
Cu	19.6609	68.8216	-20.4892	-21.5215	-22.8979
Zn	15.8191	61.1819	-18.2164	-19.1341	-20.3578
Pb	22.0604	88.9182	-26.4756	-27.8093	-29.5877
pH=6					
Metal	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)		
			298°K	*313°K*	*333°K*
Cu	61.8595	232.6598	-69.2708	-72.7607	-77.4139
Zn	36.5134	157.9244	-47.0249	-49.3938	-52.5523
Pb	55.8360	219.8222	-65.4512	-68.7485	-73.1449

Table 4: Isotherm parameters calculated for zinc, copper and lead removal by Amberlite IR120.

Metals	Langmuir isotherm			Freundlich isotherm		
	b	Q_e	R^2	n	K_f	R^2
Zn	0.092486	312.5000	0.6156	1.517451	29.76457	0.9648
Pb	0.415493	169.4915	0.9776	2.504383	44.09608	0.9847
Cu	0.095238	178.5714	0.7994	2.159827	24.37250	0.9463

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Table 5: Comparison of adsorption rate constants, experimental and calculated q_e values for the pseudo-first-
and –second-order reaction kinetics of removal of zinc, copper and lead by Amberlite IR120.

Metals	$q_{e\ experimental}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		K_1 (1/min)	$q_{e\ calculated}$ (mg/g)	R^2	K_2 (g/mg min)	$q_{e\ calculated}$	R^2
Zn	28.4286	0.0785	13.4180	0.9374	0.0222	28.8184	0.9999
Cu	28.3971	0.0760	17.9179	0.9607	0.0114	29.2398	0.9998
Pb	28.5237	0.0991	16.3988	0.9565	0.0173	29.1545	0.9997
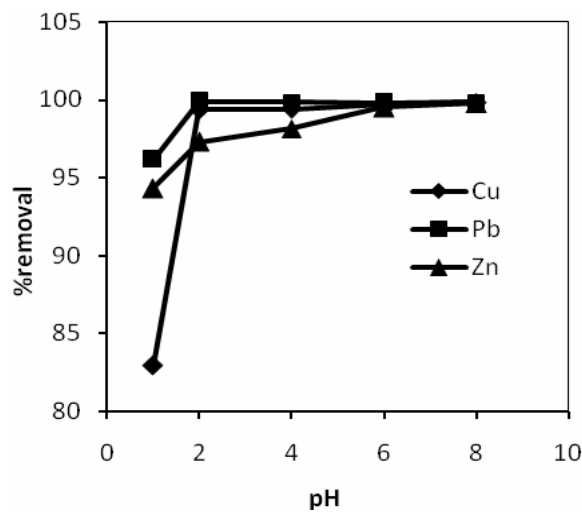
Fig. 1: Effect of pH on removal of zinc, lead, and copper by Amberlite IR120
(initial metal conc. 100 mg/L, resin dosage 0.35 g/100 mL, agitation period 2 h).
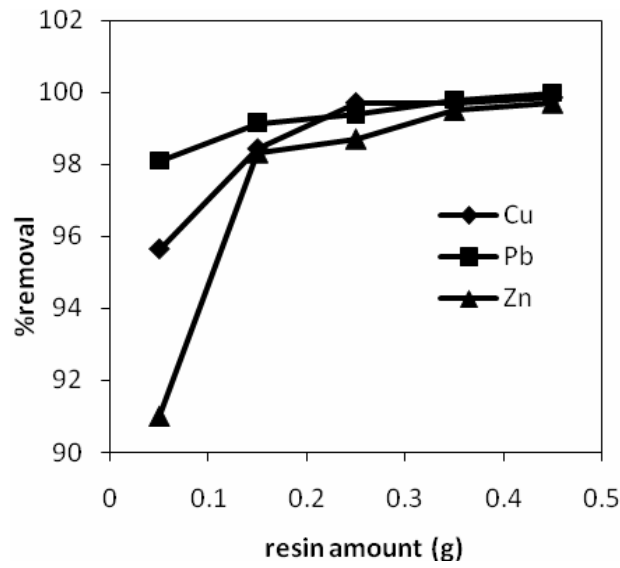
Fig. 2: Effect of resin amount on removal of zinc, lead, and copper by Amberlite
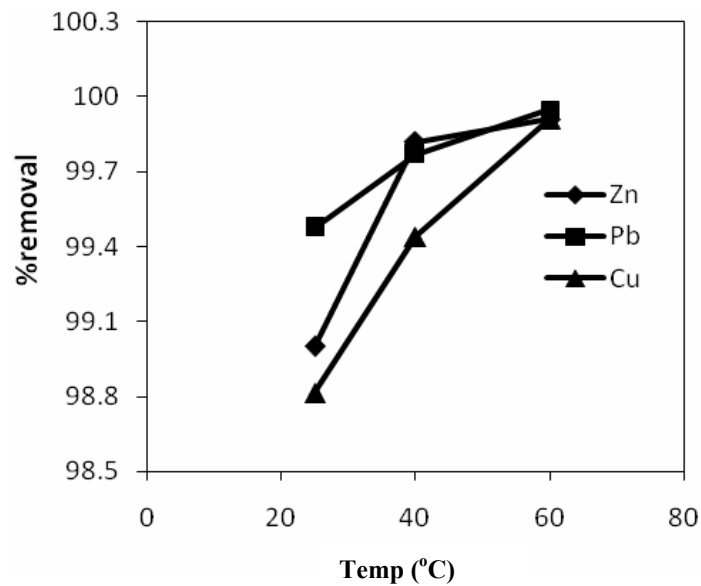IR120 (initial metal conc. 100 mg/L, pH 6, agitation period 2 h)
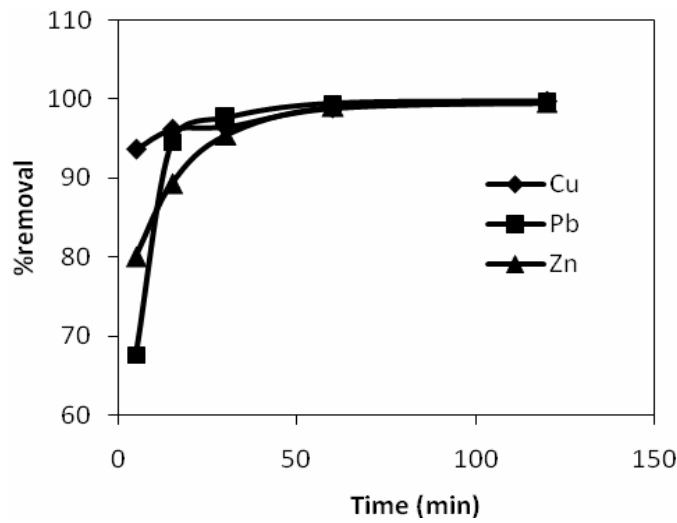
Fig. 3: Effect of contact time on removal of zinc, lead, and copper by Amberlite
IR120 (initial metal conc. 100 mg/L, pH 6, resin amount 0.35 g/ 100 ml).

1050
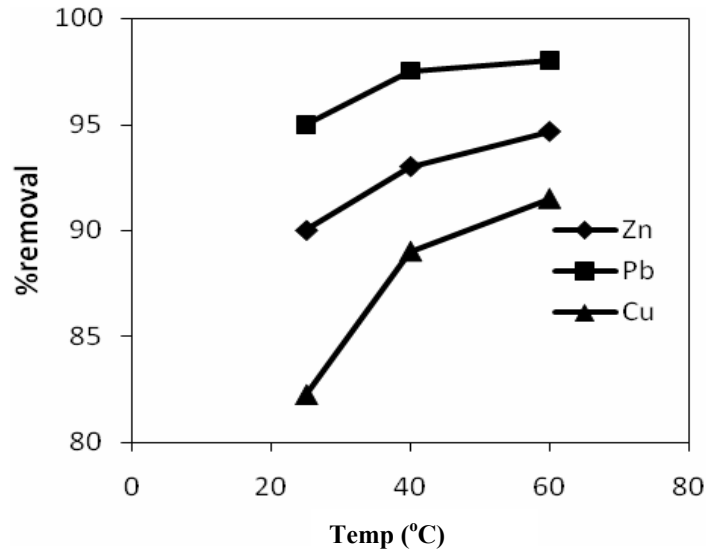
Fig. 4: Effect of temperature on removal of zinc, lead, and copper by Amberlite IR120 (initial metal conc. 100 mg/L, pH 1, resin amount 0.35 g/ 100 mL, contact time 60 min).

Fig. 5: Effect of temperature on removal of zinc, lead, and copper by Amberlite IR120 (initial metal conc. 100 mg/L, pH 6, resin amount 0.35 g/ 100 mL, contact time 60 min).
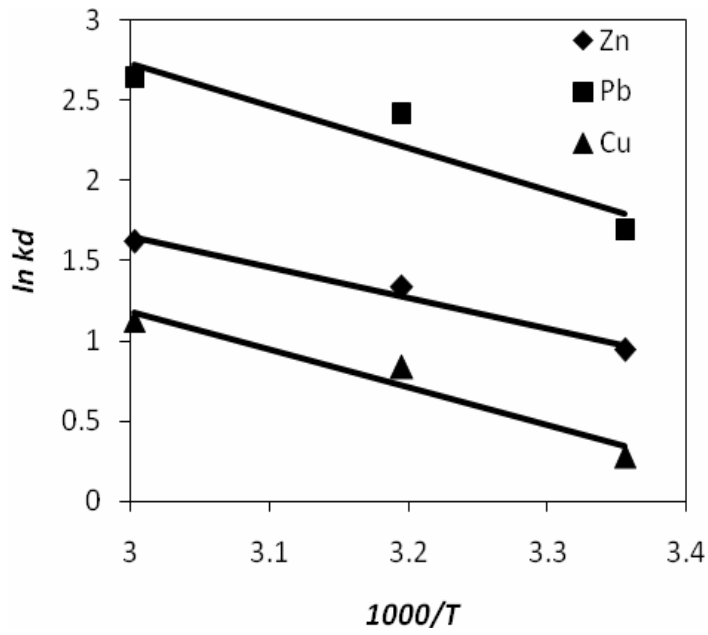
Fig. 6: The distribution coefficient versus 1/temperature at pH 1.
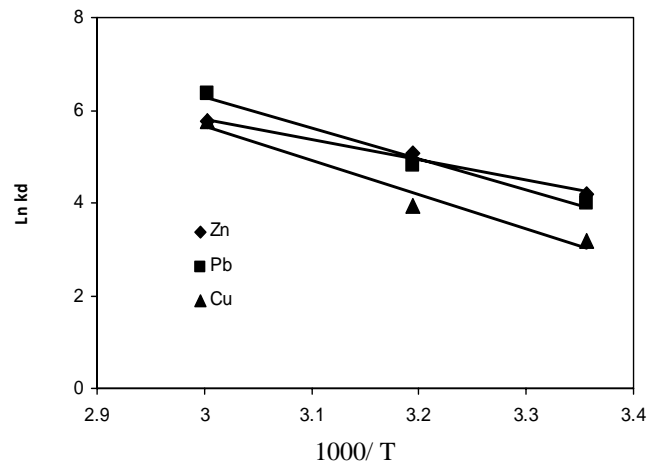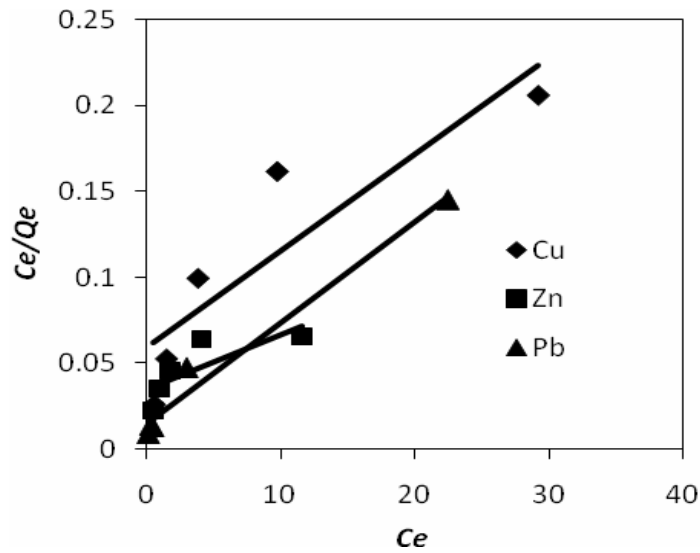

Fig. 7: The distribution coefficient versus 1/temperature at pH 6.

Fig. 8: Langmuir adsorption isotherm for removal of zinc, copper and lead
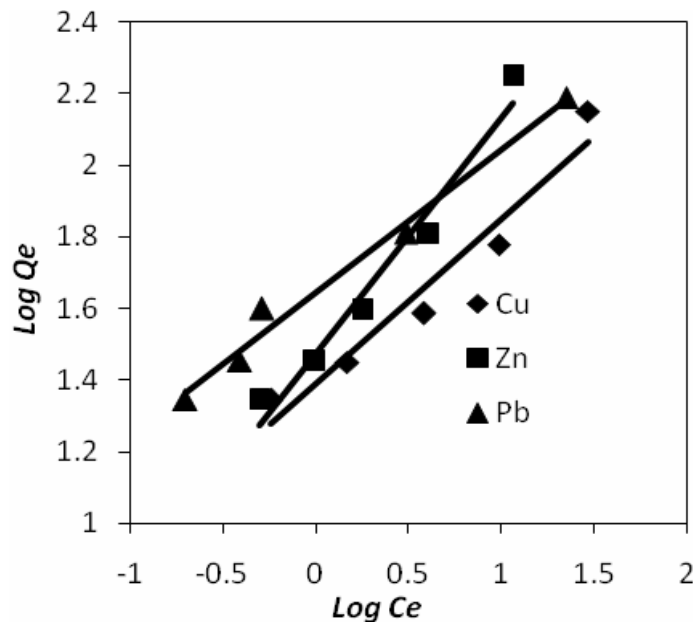by Amberlite IR120.

Fig. 9: Freundlich adsorption isotherm for removal of zinc, copper and lead
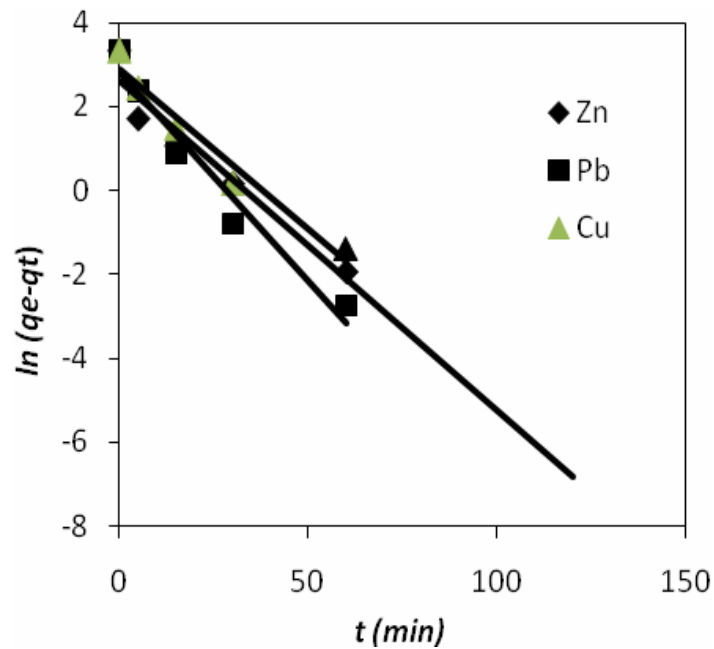by Amberlite IR120.

Fig.10: Pseudo-first-order reaction kinetics for the adsorption of zinc, copper and lead.
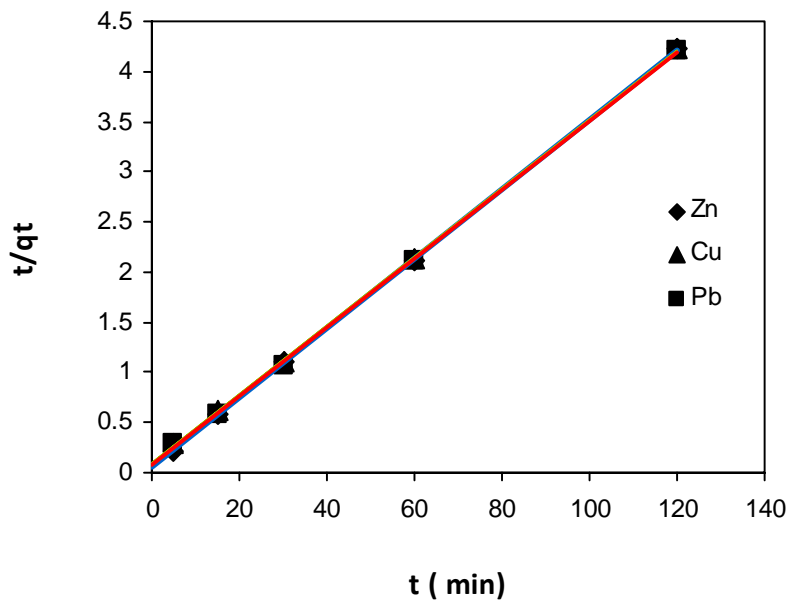

Fig. 11: Pseudo-second-order reaction kinetics for the adsorption of zinc, copper and lead.