

Selective Removal for Toxic Ions from Aqueous Environment Using Ion Exchange Resin

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ABSTRACT

This study evaluated the performance of a strong-acid cation exchange resin Dowex Marathon C in the removal of Pb(II), Cu(II) and Fe(III) from aqueous solution. Batch sorption studies were carried out to determine the effect of contact time, initial concentration of metal ions, solution acidity, resin dose and temperature on the removal of these metal ions. The equilibrium data fitted well with the Langmuir and Temkin type isotherms. The kinetics of the adsorption data was analyzed using four kinetic models viz. pseudo-first-order, pseudo-second-order and intra-particle diffusion models. The results from the kinetic studies indicated that the rate of adsorption follows a pseudo-first-order and pseudo-second-order with respect to the temperature solution and that in general the order of data for both Pb(II) and Cu(II) fit is pseudo-first-order > pseudo-second-order > intra-particle diffusion model while Fe(III) show different fit order. The results obtained from thermodynamic studies revealed that the adsorption process is endothermic in nature as well as the feasibility and spontaneity of these metal ions removal. The values of ΔH^0 , ΔG^0 and ΔS^0 of the adsorption process were calculated. The low value of ΔH^0 (<40 kJ mol⁻¹) for Pb(II) and Cu(II) indicated that adsorption process occurs mainly through a physical means, whereas Fe(III) show opposite trends.

Key words: Adsorption; Removal; Kinetics; Thermodynamic

Introduction

Water is a vital factor in many industrial processes, including mining. Water is much more than a medium for cooling, creating steam, transport or cleaning; it is often an essential component of the process or product (Kemp *et al.*, 2010). As water shortages increase, so does the need to use unconventional supplies such as seawater or wastewater for industrial processes. The water deficit may also be met by energy intensive water recovery systems such as cooling water systems for industrial processes. With the right treatment technologies, water can be reused over several cycles which help to bridge the gap between water supply and demand. Low-cost process water recovery is one of the most significant issues facing industry today. Ion exchange is considered to be one of the best and most efficient methods for removing anions from water due to its high efficiency, simplicity and low cost.

Environmental health problems associated with metals in developing countries are complex and frequently severe (Bruce *et al.*, 2015, Gunnar *et al.*, 2015). They relate to the mining of mineral deposits in these countries, the smelting of metal-containing ores, and the secondary smelting of batteries and electronic waste products transported into these countries for recycling. Despite efforts in the international community to promote sustainable development, these activities are frequently conducted in developing countries under conditions of limited health and safety regulation due to the limited resources available to implement environmental and occupational health standards in many developing countries. Poor nutrition and a general lack of food are also contributory factors that exacerbate susceptibility to metal toxicity. These issues are further compounded by metal contamination of food crops through the utilization of cadmium-containing phosphate fertilizers, arsenic in irrigation water from contaminated groundwater, and other metals or chemicals from industrial or municipal wastewater sources.

Metal poisoning may or may not be apparent from the clinical features induced. The exposure pattern in terms of time, concentration, and route of exposure is a determinant of the clinical effect. Short-term high-level and long-term low-level exposure by ingestion is seen more often in the domestic environment and inhalation exposure is seen more often in occupational settings. Acute and chronic clinical effects of metal toxicity may involve the gastrointestinal, respiratory, cardiovascular, renal, hemopoietic, and central nervous systems. In the diagnosis of metal poisoning, the presenting features may be nonspecific, with clinical examination giving no indication of the cause of illness (Lars *et al.*, 2015). A full occupational history is required, along with knowledge of the work processes involved, and a detailed history is required where poisoning may occur in the domestic environment, particularly when poisoning results from the long-term absorption of cumulative metals. However, metal accumulation and poisoning may occur in the absence of

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environmental exposure, as, for example, transfusional siderosis in thalassaemias, iron overload in idiopathic hemochromatosis, and copper accumulation in Wilson disease. In addition to history and clinical examination, trace metal analysis in body fluids, tissues, and environmental samples is required, together with biochemical and physiological investigation.

A number of therapeutic agents counteract the effects of an absorbed toxic metal by combining to form a less toxic compound that may be excreted more effectively by displacing it from its receptor site or by promoting translocation into a tissue where it cannot exert its toxic effects. Toxic metal antagonists, i.e. chelating agents, compete for toxic metals with ligands essential for their physiological function by forming a stable complex with the metal in the form of a heterocyclic ring. Chelating agents possess electron donor groups with a high affinity for the metal to be removed, thus causing its release from complexes with proteins or other endogenous ligands in a form that can be readily excreted. Chelation is indicated in the treatment of metal poisoning and metal storage diseases, in blood transfusion in iron overload, and to aid the elimination of metallic nuclides. However, chelation may result in depletion of essential metals or redistribution of toxic metals to other tissues such as the brain. Chelators themselves may also have toxic effects.

For these reasons, several methods, such as biological treatment, membrane processes, adsorption method, ion exchange, ultrafiltration, solvent extraction, chemical precipitation, phytoextraction and reverse osmosis are the common methods of removing metal contamination from aqueous solutions. Among these approaches, the adsorption method seems as one of the most prominent choice because of its low cost and minimized amount of metal contamination. The adsorption or ion exchange process has received much attention, especially for wastewater that contains low concentrations of metals and complex-forming substances.

The main objective of this study was to investigate the equilibrium and kinetic parameters of Dowex Marathon C cation exchange resin. In addition, various parameters such as Pb(II), Cu(II) and Fe(III) ions concentration, solution acidity, amount of resin, temperature, and were studied to optimize the conditions for effective removal of these metal ions from aqueous solution.

Chemicals and reagents.

The following chemicals (Analytical grade) were employed: Lead(II) chloride, Ferric(II) chloride and Copper(II) chloride, hydrochloric acid, sodium hydroxide. Solutions were prepared with redistilled water. All the chemicals were used as purchased, unless otherwise stated.

Resin

A strong-acid cation exchange resin Dowex Marathon C with sulphonic (acid SO₃H) group was used in this work. Prior to use, the resin was immersed into 1 M NaOH solution for 120 min to replace the hydrogen ions by sodium ions, then it was immersed in 1 M HCl for 120 min to replace all sodium ions by hydrogen ions. Finally, resin was washed with deionized water several times until the resulting water become neutral. Finally, the resin was dried at 100–105°C for 24 h.

Batch experiments

Kinetics experiments were carried out in a thermostated shaker at 28 ± 0.5^o C and 100 ± 10 rpm. 0.5 g of Dowex Marathon C resin and 50 ml of PbNO₃, FeCl₃ or CuCl₂ aqueous solution were stirred in the shaker. Furthermore the adsorption studies were also carried out by varying time interval (5.0–240 min) at 4.95 mmol/l concentration of the metal ion to optimize the time required for the removal of these metal ions from its solution. Samples were withdrawn at desired time intervals. Complexometric titration technique was used to determine the Pb(II), Cu(II) and Fe(III) concentration in the supernatants after the adsorption onto the Dowex Marathon C resin.

The amount of metal ion adsorbed per unit of adsorbent (q_e) and removal yield (R%) were calculated by Eqs. (1) and (2), respectively:

$$q_e = \frac{C_0 - C_e}{1000W} \times V \text{ ----- 1}$$

$$\text{Removal yield (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \text{ ----- 2}$$

where q_e is the equilibrium adsorption capacity (mg g⁻¹), C₀ and C_e is the metal ion concentration (mg L⁻¹) at initial and equilibrium state, V is the volume of solution (L) and W is the weight (g) of adsorbent.

Results and discussion

Effect of contact time

The optimization of the equilibrium time is one of the important parameters for the development of an economical wastewater treatment system. The influence of contact time on the Dowex Marathon C capacity for Pb(II), Cu(II) and Fe(III) metal ions removal at 28°C, 0.5g resin and metal ion concentration 4.95 mmol/l is shown in Fig. 1.

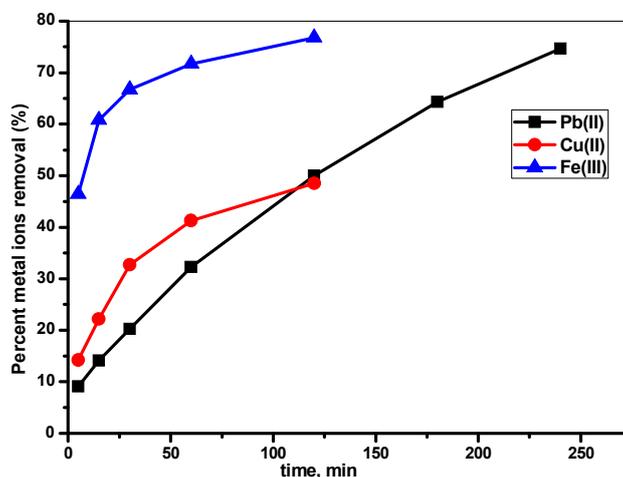


Fig.1 . Effect of contact time on the removal of Pb(II), Cu(II) and Fe(III) at 28°C

The results were expressed as the percentage removal. It is observed that, the maximum removal of Pb(II), Cu(II) and Fe(III) ions from synthetic wastewater on Dowex Marathon C was 86.85, 96.95 and 99.41%, respectively. The optimum equilibrium is reached at this contact time of 240 for Pb(II) and 120 min for both Cu(II) and Fe(III) ions, respectively. The results clearly revealed that, rate of adsorption is higher at the beginning and this is due to availability of a large number of active sites on the resin. As these sites are exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles (Malairajan and Peters, 2013). It has been observed that, the mechanism of metal ions uptake from the aqueous solutions involved four steps: (i) migration of metal ions from the bulk solution to the surface of the adsorbent; (ii) diffusion through boundary layer to the resin surface; (iii) adsorption at a binding site and (iv) intra particle diffusion into the interior of the sorbent surface. The boundary layer resistance will be affected by the rate of sorption and increasing the agitation time will reduce this resistance and increase the mobility of the ions. However, because the process is time dependent, after about 240 or 120 min, the sorption remains constant. The plots of metal ions uptake as a function of time are single, smooth and continuous leading to saturation.

The effect of resin dosage

The adsorbent dosage had a significant effect on the metal ions from aqueous solutions; therefore, the retention of the metals was examined in the relation to amount of the Dowex Marathon C resin. For this reason, the effect of this parameter was investigated at different amounts of the resin were tested in the range of 0.25–2g, in our studies, the effect of resin amount on the sorption of Pb(II), Cu(III) and Fe(III) ions by Dowex Marathon C is represented in Fig. 2. All experiments were carried out at initial concentration of metals, 4.95 mmol/l, volume of sorption medium, 50 ml, temperature, 28±1 °C), and equilibrated for about 2-4 h. It is apparent that the removal efficiency of the resin significantly increased with increasing dose for the three metal ions. It is due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions. An increase in the sorbent amount resulted in a decrease in the contact time required to reach equilibrium. The maximum removal of Fe(III) is ranged from 35.8 to 99.41%, 26.77 to 86.85% for Pb(II) and 13.21 to 96.95% for Cu(II) at the optimum sorbent dose of 0.5 g per 50 mL of synthetic wastewater, as well as for Pb(II) and Fe(III) ions. A similar type of result has also been observed by other researchers (Zhanhua *et al.*, 2012).

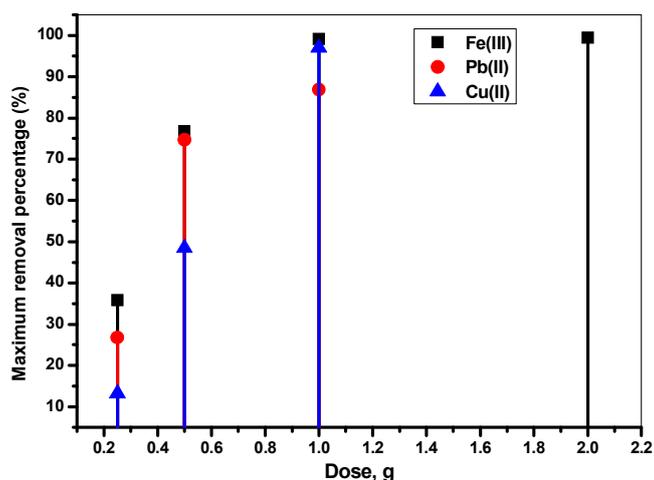


Fig. 2. Effect of amount of resin on the uptake of Pb(II), Cu(II) and Fe(III), 28°C

Although as shown in Fig. 2, the equilibrium adsorption capacity of Dowex Marathon C decreases with increasing in adsorbent dosage of 1 g per 50 mL of synthetic wastewater contaminated with Pb(II) and Fe(III) ions. This reduction can be due to the aggregation of Dowex Marathon C surface area and an increase in diffusion path length (Mohammad and Bimeghdar, 2014). However, for wastewater contaminated with Cu(II) ions, further increase in addition of Dowex Marathon C (> 0.5g) shows no effect on removal of the three metal ions. Accordingly, 0.5 g/50 ml of Dowex Marathon C resin dose was taken as the optimum for experiments.

The effect of metal ion concentrations

One of the most important parameters that influence adsorption process is the initial concentration of adsorbate; therefore, the effect of initial concentration of Pb(II), Cu(II) and Fe(III) was investigated at different ranges of metal ion concentrations (2.45, 4.95, 7.5, 9.85, 25 and 50 mmol/l). The results of this study are shown in Fig. 3. This diagram indicated that the amount of metal ions uptake by constant weight of Dowex Marathon C resin was found to be increased with increase in concentration of the metal ions in synthetic wastewater. In fact the increasing of concentration can provide a driving force to overcome all-mass transfer resistances from aqueous to solid phase. However as shown in Fig. 3 Fe(III) ion increases with increase in its concentration with exception at higher concentration (50 mmol/l), since amount of metal ion uptake show sharp decreases, it is apparent that the adsorbent has a limited number of active sites and these sites were saturated in a certain concentration, so the saturated adsorbent would not be able to uptake more Fe(III) ions. However, the percent removals of the metal ions have opposite trend than that of the amount of metal ions uptake per unit weight. From the results obtained we can observed that the percent removal was significantly decreased from 75.5 to 30.5 % for Pb(II) and 71.5 to 23% for Cu(II), while Fe(III) show higher gradual decreases with percent removal ranged from 83.7 to 23%. The transfer of metal ions by sorption on Dowex Marathon C increases with contact time and attains a maximum value at 180, 120 and 60 min and thereafter remains constant for all metal ions at higher concentration. It is clear from observation that the equilibrium time was independent. In general, the more concentrated the solution is, the better the adsorption is.

In comparison the adsorption capacities of the cation exchange resin towards the metal ions at different concentrations increases in the following order; Fe(III) > Pb(II) > Cu(II) ions. Similar results have been reported by other workers for other adsorbate- adsorbent system (Mohammad and Bimeghdar, 2014, González and Pokrovsky, 2014). The removal metal ion at higher concentration in short equilibrium time has great industrial application as in most of the effluents the higher concentration of metal ions is encountered.

Effect of the solution acidity

The acidity of the liquid samples is an important parameter in the adsorption process, which affects surface charge of the adsorbent and the degree of ionization and specification of adsorbate. Hydrochloric acid was used as complexing agent in a wide range of concentrations namely, 0.01 to 1.0 M. Because the influence of this acid, hydrogen ion is governed by the mass reaction equation for a simple exchange action of the chloride ion by lowering the effective concentration of the cation in solution through complex formation. The effect of

initial HCl concentration on the adsorption process is presented in Fig. 4. It shows that the percentage removal of Pb(II) Cu(II) and Fe(III) ions is dependent on the initial hydrochloric acid concentration of the metal ion solutions because hydrochloric acid concentration influences the metal speciation and changes the charge in the adsorbent. As solution acidity changes from 0.001 to 0.05M.

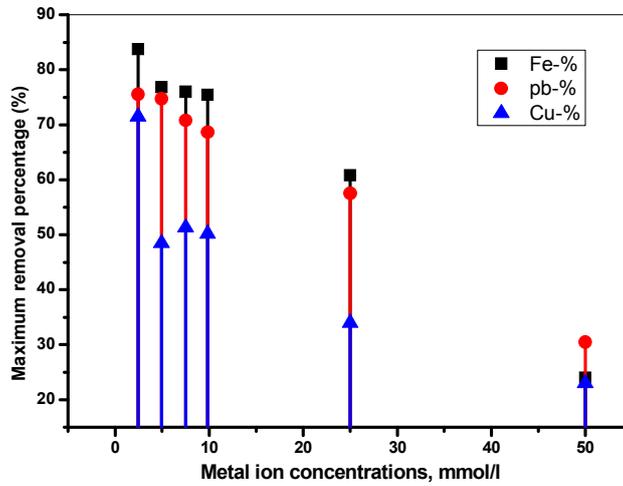


Fig. 3.Effet of metal ion concentratios on the uptake of Pb(II),Cu(II) and Fe(III), 28°C

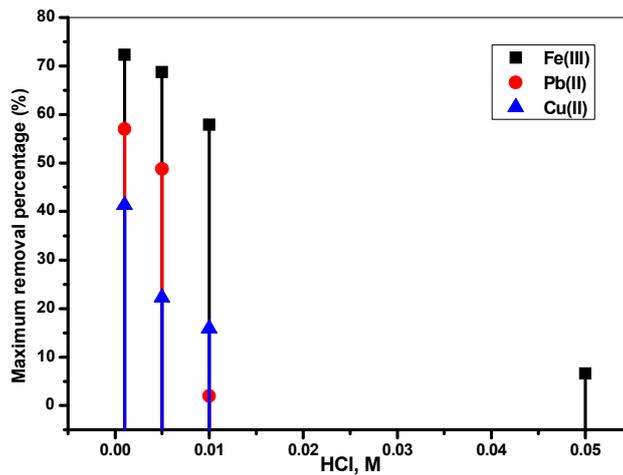


Fig. 4.Effet of HCl concentratios on the removal of Pb(II),Cu(II) and Fe(III), 28°C

Fig. 4 shows that the equilibrium sorption data indicate that: (i) At low acid concentration the metal cations exhibit generally significant uptake and lower affinity with the Dowex Marathon C matrix compared to in pure aqueous medium. In this stage of ion exchange, the sulphonic group of Dowex Marathon C is partially protonated and the percentage removal of the metal ions from the solution decreased. This behavior is a prominent for all sorption processes. However, (ii) At very high solution acidity values, the surface of the resin would be surrounded by the hydronium ions which inhibit the metal ion interaction with binding sites of the resin strongly by greater repulsion forces, however, the overall surface charge on this resin became positive and sorption sharply decreased until on the removal did not occur. (iii) Within the studied acid concentrations range, in general, the percentage removal of cations in majority follows the selectivity order; Fe(III) > Pb(II) > Cu(II). This may be explained in terms of the stability constants of the complexes which the metal ions form with this acid. This acid might form rather stronger complexes with Cu (II) > Pb (II) > Fe (III). Similar trends were observed by other researchers (Mouni *et al.*, 2011, Zhanhua *et al.*, 2012 and Mohammad and Bimeghdar, 2014).

Adsorption isotherms

Equilibrium of the adsorbate sorption on the adsorbent surface at a different temperature is described with empirical models known as adsorption isotherms. Mathematical modeling of adsorption isotherms gives us information about the adsorption mechanism.

The obtained equilibrium data from the adsorption of Pb(II), Cu(II) and Fe(III) onto the Dowex Marathon C resin fitted to the linear equation of Langmuir, Freundlich, Temkin and D-R isotherm models. The linear equation for these isotherm models are expressed as follows:

The model takes the following linear form:

$$C_e/q_e = 1/K_L Q_{max} + C_e/Q_{max} \tag{3}$$

where Q_{max} is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent (mg/g) and q_e is the amount adsorbed on unit mass of the adsorbent (mg/g) when the equilibrium concentration is C_e (mg/l) and K_L (L/mg) is Langmuir constant that is related to the apparent energy of adsorption. As in Eq.(3) shows that a plot of (C_e/q_e) versus C_e should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium.

The slope and the intercept from (Fig. not shown) of this line yield the values of constants Q_{max} and K_L respectively. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L (Altin *et al*, 1998), also known as the adsorption factor, given by Eq. (4):

$$R_L = 1 / (1 + K_L C_o) \tag{4}$$

The value of R_L lies between zero and one for a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L = 0$.

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. The heat of adsorption decreases in magnitude with increasing the extent of adsorption (Koopal *et al*, 1994). The linear Freundlich isotherm is commonly expressed as follows:

$$\log q_e = \log k_F + (1/n) \log C_e \tag{5}$$

where K_F and n are the Freundlich constants characteristics of the system, indicating the relative adsorption capacity of the adsorbent related to the bonding energy and the adsorption intensity, respectively. A plot of $\ln q_e$ versus $\ln C_e$ (Fig. not shown) yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants which are K_F and $1/n$ can be determined from the slope and the intercept respectively according to (Agrawal *et al*, 2004).

Temkin isotherm model assumes that the heat of adsorption of all the molecules in the layer decreases linearly with the coverage of molecules due to the adsorbate-adsorbate repulsions and the adsorption of adsorbate is uniformly distributed and that the fall in the heat of adsorption is linear rather than logarithmic. The linearized Temkin equation is given by Eq. (6):

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{6}$$

where $B_T = RT/b_T$, T is the absolute temperature in K and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The constant b_T is related to the heat of adsorption, A_T is the equilibrium binding constant (L min^{-1}) corresponding to the maximum binding energy. The slope and the intercept from a plot of q_e versus $\ln C_e$ (Fig. not shown) determine the isotherm constants A_T and B_T .

The obtained values of applied adsorption isotherm parameters are reported in Tables 1,a and b. Values of R^2 indicated that Langmuir and Temkin isotherm models for Pb(II), Cu(II) and Fe(III) adsorption was best fitted in comparison with Freundlich and D-R isotherm models. The n values were found to be 2.95, 1.427 and 3.5 for the Pb(II), Cu(II) and Fe(III) adsorption onto the resin from aqueous solution. These values are suggesting that Dowex Marathon C resin is better adsorbent for the separation and removal of Pb(II), Cu(II) and Fe(III) from aqueous solution. The obtained results for the Pb(II), Cu(II) and Fe(III) adsorption are similar to the reported adsorbent by (Özbay, 2009, Monier *et al*, 2010).

Another equation used in the analysis of isotherms was proposed by Dubinin and Radushkevich, 1947, (D-R). It does not assume a homogeneous surface or constant sorption potential, but it applied to estimate the porosity apparent free energy and the characteristic of adsorption and it following form

$$\ln q_e = \ln X_{D-R} - \beta \mathcal{E}^2 \tag{7}$$

Where β is a constant related to the adsorption energy, X_{D-R} the maximum adsorption capacity, \mathcal{E} can be calculated from Eq. (8) where;

$$\mathcal{E} = RT \ln (1 + 1/C_e) \tag{8}$$

From the plot of $\ln q_e$ versus \mathcal{E}^2 of the experimental data for the adsorption of the metal ions by the resin the constants β ($\text{mol}^2 \text{ kJ}^{-2}$) and X_{D-R} (mg g^{-1}) can be calculated from the slope and the intercept, respectively. The mean free energy of sorption, E_{D-R} (kJ/mol) is the free energy change when one mole of ion transferred from infinity in solution to the surface of the sorbent. E_s is calculated from the β value using Eq. (9):

$$E_{D-R} = 1 / \sqrt{-2\beta} \tag{9}$$

The energy of sorption (E_{D-R}) calculated from the D-R model indicates uptake of Pb(II), Cu(II) and Fe(III) on the resin sample can be described by the physisorption/ion exchange or chelation mechanism, as E_{D-R} lies between 8 and 16 kJ mol⁻¹. Uptake of ions followed a physical adsorption mechanism, as E_{D-R} is higher than 8 kJ mol⁻¹ obeyed a ion exchange mode of the metal ions trapping, as the E_{D-R} is between 8 and 16 kJ mol⁻¹ (Burke *et al.*, 2013). Projected chemical equations for physisorption/ion exchange of the metal ions onto the resin surfaces is given in Eqs.10, 11, the uptake via chelation is shown in Eq.10

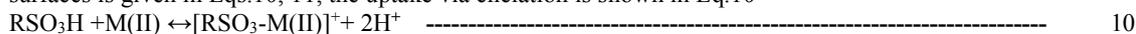


Table 1-a: Adsorption isotherm parameters.

Metal ions	Freundlich			Langmuir			
	n	K_F (mol ⁻¹ L ⁿ /g)	R ²	Q_{max} (mg/g)	K_L L/mg	R_L	R ²
Pb(II)							
	2.948	502.960	0.99763	59.170	0.0169	0.0612	0.99997
Cu(II)							
	1.427	545.378	0.97917	10.455	0.0188	0.2035	0.98326
Fe(III)							
	3.500	69.6480	0.99817	16.744	0.0740	0.0514	0.99983



The values of correlation coefficients are ranged from 0.98 to 0.51 (Table 1b) for the three metal ions studied herein, indicating that the D–R model is less fitting to the experimental data in comparable with other adsorption models.

According to the above discussion, we can conclude that the Langmuir and Temkin models appear to be much applicable for most adsorption processes than Freundlich and D-R isotherm models.

Table 1-b: Adsorption isotherm parameters.

Metal ions	D-R				Temkin		
	B (mol ² /kJ ²)	X_{D-R} (mg/g)	E(kJ/mol)	R ²	K_T (L/min)	B_T (J/mol)	R ²
Pb(II)							
	9.2677x10 ⁻⁴	70.1503	23.227	0.93885	0.000183	25.114	0.98991
Cu(II)							
	7.0389x10 ⁻⁴	13.243	26.65	0.93048	0.001853	12.78933	0.99346
Fe(III)							
	5.6808x10 ⁻⁵	19.387	93.817	0.86703	0.000483	6.10918	0.99952

Adsorption kinetics

The adsorption rate of the metal ion is of the most importance parameters while designing batch adsorption systems. Consequently, it is important to establish the time dependence of such systems under various process conditions. Kinetic studies can be carried out by batch reactions.

The pseudo-first-order and pseudo-second-order also intraparticle diffusion kinetic models were applied to determine the adsorption rate of Pb(II), Cu(II) and Fe(III) onto the Dowex Marathon C resin. The linear equation for pseudo-first-order kinetic model can be expressed as:

$$\log(q_e - q_t) = \log q_e - k_1 t \quad \text{-----} \quad 12$$

Lagergren showed that the rate of adsorption of solute on the adsorbent is based on the adsorption capacity and followed a pseudo-first-order equation (Lagergren *et al.*, 1898 ,Yang and Al-Duri, 2005) which is often used for estimating k_1 considered as mass transfer coefficient in the design calculations.

where q_e and q_t are the amounts of the metal ion adsorbed (mg/g) at equilibrium time and at any instant of time t , respectively, and k_1 (L/min) is the rate constant of the pseudo-first-order adsorption. The plot of $\log(q_e - q_t)$ versus t gives a straight line (Fig. not shown) for the pseudo first-order adsorption kinetics, from the adsorption rate constant, k_1 , is estimated.

Ho developed a pseudo second-order kinetic expression for the adsorption system of divalent metal ions. This model has since been widely applied to a number of metal/sorbent adsorption systems. The adsorption of Pb(II), Cu(II) and Fe(III) onto the Dowex Marathon C resin at a short time scale may involve a chemical sorption which implies the strong electrostatic interaction between the Dowex Marathon C resin functional groups surface and each of Pb(II), Cu(II) and Fe(III). The linear equation for pseudo-second-order kinetic model can be expressed as (McKay and Ho, 1999). The second-order kinetics equation is described as in the following form:

$$t/q_t = (1/k_2 q_e^2) + t/q \quad \text{-----} \quad 13$$

where k_2 (g/mg min) is the second-order rate constant.

Under such circumstances, the plot of t/q_t versus t should give a linear relationship (Fig. not shown), which allows the computation of q_e and k_2 . Where k_2 is the pseudo-second-order rate constant (g mg⁻¹ min⁻¹). The q_{e1} , q_{e2} , k_1 and k_2 values for different temperatures of Pb(II), Cu(II) and Fe(III) solutions were calculated from their respected plots.

The obtained q_{e1} , q_{e2} , k_1 , k_2 and correlation coefficient (R^2) values are tabulated in Table 2. The R^2 values of Fe(III) for pseudo second-order kinetic model are relatively higher than pseudo-first order kinetic model adsorption. However, the experimental q_e values are very close to the calculated q_{e2} values for pseudo-second-order kinetic model.

These results implied that the adsorption of Fe(III), onto the Dowex Marathon C resin obeyed second order model kinetic model (McKay and Ho, 1999, Chen and Li, 2010), while opposite trend was observed for the Pb(II) and Cu(II), where the R^2 values for pseudo first-order kinetic model are relatively higher than pseudo-second order kinetic model adsorption. These results implied that the adsorption of Pb(II) and Cu(II), onto the Dowex Marathon C resin obeyed first-order kinetic model. The diffusion of metal ions cannot be explained on the basis of pseudo-first-order and pseudo-second-order kinetic models only.

Table 2: Kinetic parameters.

Temp, K	Pseudo first-order model			Pseudo second-order model			Intraparticle diffusion model		
	$q_{e,1,cal}$ mg/g	K_1 min ⁻¹	R^2	$q_{e,2,cal}$ mg/g	K_2 (g/mgmin)	R^2	K_{int} (mg/g min) ^{0.5}	C (mg/g)	R^2
Pb(II)									
301	75.45	0.01026	0.97922	100.91	0.000104	0.9059	4.9448	3.75113	0.98530
313	73.255	0.01462	0.99277	99.9	0.000160	0.95971	5.4270	0.15354	0.97218
323	70.1	0.02237	0.98197	102.04	0.000260	0.99502	6.0446	7.01354	0.91314
Cu(II)									
301	12.37	0.02873	0.99584	17.59	0.00289	0.99376	1.2551	2.39676	0.94307
313	14.65	0.06676	0.89062	21.21	0.00390	0.98608	1.2192	6.38413	0.58731
323	19.29	0.06444	0.93505	27.00	0.00240	0.97957	1.6030	6.64159	0.62578
Fe(III)									
301	8.06	0.03068	0.92571	21.91	0.00953	0.99914	0.6738	13.4804	0.76230
313	4.69	0.10296	0.98197	21.71	0.04230	0.99962	0.8647	16.39376	0.95071
323	3.20	0.09410	0.89062	22.56	0.05880	0.99965	0.6175	18.68845	0.97110

Due to this reason, intraparticle diffusion model was applied to estimate the diffusion of Pb(II), Cu(II) and Fe(III) in the Dowex Marathon C resin using Weber–Morris intraparticle diffusion model (Weber *et al.* 1963):

$$q_t = k_{int}t^{1/2} + C \quad \text{-----} \quad 14$$

where k_{int} is the intraparticle diffusion rate coefficient (g mg⁻¹min^{1/2}) and C provides an idea about the thickness of the boundary layer. The plot of q_t vs. $t^{1/2}$ as in (Fig. not shown) shows the three straight-line portions with three different slopes and intercepts values. First portion of curves indicates the boundary layer diffusion while final linear portion is a result of the intra-particle diffusion. Boundary layer is dominant if the intercept values are high as in Ref. (Oubagaranadin *et al.*, 2007).

The intercept values for Pb(II), Cu(II) and for Fe(III) is tabulated in Table 2. The obtained values indicated that adsorption of the three metal ions onto the Dowex Marathon C resin was controlled through a boundary layer effect and intraparticle diffusion rate

Equilibrium distribution coefficient, K_d

Distribution coefficients (K_d) for different metal ions were determined by batch method at different temperatures systems. 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. The distribution coefficients were calculated using the equation.

$$K_d = \frac{\text{amount of metal ion in adsorbent}}{\text{mount of metal ion in solution}} \times \frac{\text{ml of solution}}{\text{g of dry resin}} \quad \text{-----} \quad 15$$

Various portions of (500 mg each) the exchanger in H⁺ form were taken in Erlenmeyer flasks and mixed with 50 mL of different metal ion solutions in the aqueous medium and subsequently shaken for 24 h in temperatures controlled shaker at 28, 40 and 50°C to attain the equilibrium. The amount of metal ion before and after the equilibrium was determined by EDTA titration (AL-Othman and Inamuddin, 2011, Huang *et al.* 2012).

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. Fig. 5 show that the distribution coefficient K_d values increase with the increase in temperatures of metal solutions. The rapid metal sorption has significant practical importance, as this will facilitate with the small amount of resins to ensure efficiency and economy.

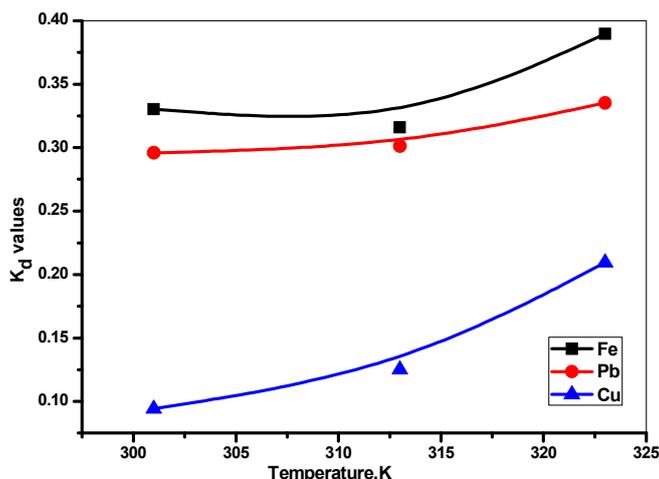


Fig. 5. Distribution coefficients of Pb(II), Cu(II) and Fe(III) at different temperatures

Effect of temperature

The effect of temperature on the sorption of Pb(II) Cu(II) and Fe(III) by the Dowex Marathon C cation exchange resin was studied at three different temperatures as 28, 40, and, 50°C, respectively. The initial concentration of the studied metal ions was 4.95 mmol/l, volume of sorption medium, 50 ml and the amount of resin was 0.5 g. The results indicate that, the percentage removal of metal ions was found to increase with the increase in temperature (Fig. 6).

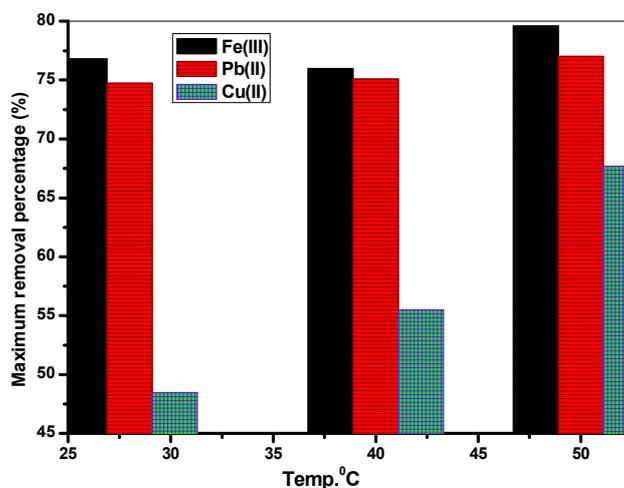


Fig. 6. Effect of temperatures on the removal of Pb(II), Cu(II) and Fe(III)

The increase in adsorption uptake percentage with increase in temperature might be due to the possibility of large number of total pore volume of the adsorbent, an increase of number of active sites for the adsorption as well as an increase in the mobility of the metal ions. However, the effect temperature could also influence desorption of metal ions and consequently affects the adsorption equilibrium (Malairajan and Peters, 2013).

Activation thermodynamic parameters

The magnitude of the heat of adsorption could provide useful information concerning the nature of the resin surface and the adsorbed phase. In order to further explore the adsorption mechanism of the metal ions onto the resin, the adsorption thermodynamic parameters are calculated.

Because the k_2 values have been determined, several thermodynamic parameters including the Arrhenius activation energy (E_a), activation free energy change (ΔG^0), activation enthalpy change (ΔH^0), and activation entropy change (ΔS^0) can be calculated by using the following equations.

$$\begin{aligned} \ln k_2 &= \ln A - E_a/RT && \text{-----} && 16 \\ \ln k_2 &= (k_B T/h)K^* && \text{-----} && 17 \\ \Delta G^0 &= -RT \ln K^* && \text{-----} && 18 \\ \Delta H^0 &= E_a - RT && \text{-----} && 19 \\ \Delta S^0 &= (\Delta H^0 - \Delta G^0)/T && \text{-----} && 20 \end{aligned}$$

where A is the Arrhenius factor, k_B and h are Boltzmann's and Planck's constants, respectively, R is the gas constant ($8.314 \text{ kJ mol}^{-1} \text{ K}^{-1}$), and K^* is the equilibrium constant at temperature, T. A linear plot of $\ln k_2$ versus $1/T$ for the adsorption of Pb(II), Cu(II) and Fe(III) ions onto Dowex Marathon C resin is constructed to generate the E_a value from the slope (Fig. 7). In addition, ΔG^0 , ΔH^0 and ΔS^0 were calculated from Eqs. (16–20) and then the results are given in Table 3.

A linear relationship can be seen with a regression coefficient R^2 in this table. E_a values for Pb(II), Cu(II) and Fe(III) are observed to be 37.92, 6.607 and 76.98 $\text{kJ mol}^{-1} \text{ K}^{-1}$, respectively. These results are indicating that the adsorption has a low potential barrier.

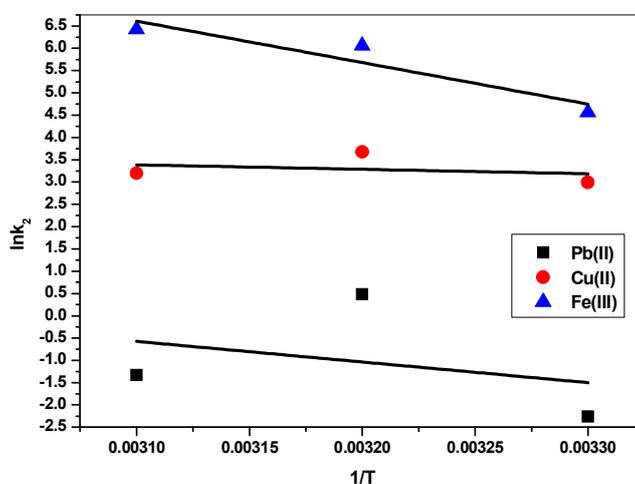


Fig. 7. Arrhenius plot for Pb(II), Cu(II) and Fe(III)

The positive and negative enthalpy change (ΔH^0) values of the adsorption reaction (Table 3) for both lead and copper ions, indicate the endothermic and exothermic nature of the present reactions, respectively. ΔH^0 values obtained from adsorption of Pb(II) onto Dowex Marathon C resin compared with Fe(III) are lower. This result gives clear evidence that the interactions between Pb(II) and the resin surface may be weaker than that of Fe(III). The low value of ΔH^0 ($<40 \text{ kJ mol}^{-1}$) indicated that adsorption process occurs mainly through a physical means, whereas Fe(III) show opposite trends. On the other hand, the positive values of E_a and ΔH^0 indicate the presence of an energy barrier in the adsorption process (Mehmet,2009). The positive values for these parameters are quite common because the activated complex in the transition state is in an excited form. However, the negative values of ΔG^0 increases with increasing temperature indicate the feasibility and spontaneity of the metal ion adsorption process on the resin.

The positive entropy change (ΔS^0) for this reaction (Table 3) has also indicated the increase in number of species at the solid-liquid interface and, hence the randomness in the interface which is presumably due to the release of aqua molecules when the aquated metal ion is adsorbed on the surface of the adsorbent and significant changes occur in the internal structure of the adsorbent through the adsorption of the metal ions onto Dowex Marathon C resin (Sushanta *et al.*, 2014).

Desorption and reusability

Stability of the adsorbent was investigated by regeneration experiments. This procedure is necessary to restore the original adsorption capacity of the adsorbent and it also enables recovering valuable metals from wastewater streams. In this study, Pb(II), Cu(II) and Fe(III) ions, respectively, were desorbed from Dowex Marathon C cation exchange resin using 1.0 M hydrochloric as regenerate presented in Fig. 8 were obtained for

different metals. The regeneration results after adsorption suggest that adsorption efficiency was affected by regeneration.

Table 3: Thermodynamic parameters.

Metal ions	T(K)	ΔS^0	ΔH^0	ΔG^0	Ea	R ²
		J/mol K	kJ/mol	kJ/mol		
Pb(II)	301	359.55	35.418	-72.8	37.92	0.98304
	313	355.44	35.319	-75.9		
	323	352.43	35.235	-78.6		
Cu(II)	301	215.36	-9.11	-73.93	6.607	0.78945
	313	216.96	-9.21	-77.12		
	323	217.17	-9.30	-79.44		
Fe(III)	301	494.96	74.48	-74.5	76.98	0.83065
	313	488.696	74.38	-78.57		
	323	482.26	74.29	-81.47		

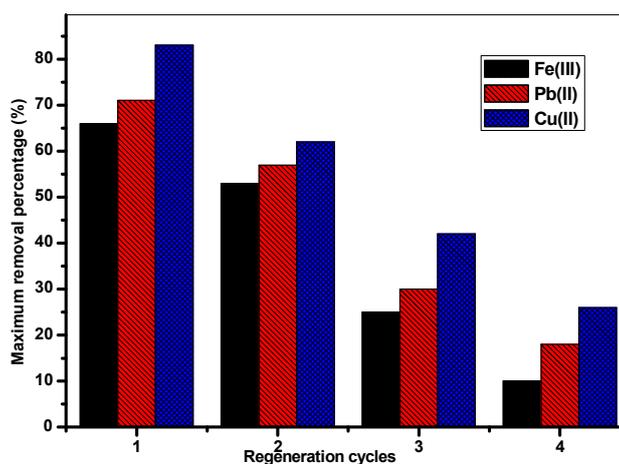


Fig. 8. Desorption cycles of Fe(III), Pb(II) and Cu(II) using 1.0M HCl solution

After the first cycle of regeneration, the adsorption capacities of the adsorbents for Fe(III), Pb(II) and Cu(II) ions decreased 10–26% and after second cycle decreased 25–42%, after third cycle was 53–62% and after fourthly reached at 66–83%. It seems that during the regeneration process the functional groups of the Dowex Marathon C cation exchange resin were intertwined or accumulated causing decrease in adsorption efficiency (Sanna *et al.*, 2013, Arup and Bhattacharya, 2013).

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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References

- Agrawal, A., K.K. Sahu, B.D. Pandey, 2004. Colloids Surface. A: Physicochem. Eng. Aspects., 237: 133-140.
 AL-Othman Z.A., M. N. Inamuddin, 2011. Chemical Engineering Journal 172, 369– 375.
 Altin, O., H.O. Ozbekelge, T. Dogu, 1998. J. Colloid Interface. Science., 198: 130-140.

- Bruce A. F., C. M. Prusiewicz, M. Nordberg, 2015. Metal Toxicology in Developing Countries, Chapter 25; DOI: 10.1016/B978-0-444-59453-2.00025-1, 529–545.
- Arup R., J.Bhattacharya, 2013. Separation and Purification Technology 115, 172–179.
- Burke, M.D.M., M. A. Morris, J.D. Holmes, 2013. Separation. and Purification. Technology., 104:150-159.
- Dubinín, M.M., L.V. Radushkevich, 1947;Chem. Zentr, 1: 875.
- González A.G. and O.S. Pokrovsky, 2014. J. Colloid and Interface. Science. 415, 169–178.
- Gunnar F. N., B. A. Fowler, M. Nordberg, 2015. Toxicology of Metals: Overview, Definitions, Concepts, and Trends, Chapter 1; DOI: 10.1016/B978-0-444-59453-2.00001-9, 1–12.
- Kemp D., C.J. Bond, D.M. Franks, C. Cote; Mining, water and human rights, 2015: making the connection; J. Cleaner Prod. 18, 1553–1562.
- Koopal, L.K., W.H. Van Remsdijk, J.C.M. de Wit, M.F., 1994. J. Colloid and Interface. Science, 166: 51-60.
- Lagergren, S., 1898. Zur theorie der sogenannten adsorption gelöster stoffe, K. Sven.Vetenskapsakad. Handl., 24: 1-39
- Lars G., K. George, 2015. Diagnosis and Treatment of Metal Poisoning: General Aspects; Chapter 23, DOI: 10.1016/B978-0-444-59453-2.00023-8, 487–505.
- Malairajan S., E. Peters, 2013. Journal of Environmental Chemical Engineering 1, 884–890.
- McKay, G., Y.S. Ho, 1999. Process of Biochemistry., 34: 451-465.
- Mehmet U., 2009. Microporous and Mesoporous Materials 119, 276–283.
- Mohammad A. B., S. Bimeghdar, 2014. Chemical Engineering Journal 239, 105–113.
- Monier, M., D.M. Ayad, Y. Wei, A.A. Sarhan, 2010. J. Hazardous. Materials, 177: 962-970.
- Mouni, L., D. Merabet, A. Bouzaza, L. Belkhiri, 2011.Desalination in press.
- Oubagaranadin, J.U.K., N. Sathyamurthy, Z.V.P., 2007. J. Hazardous. Materials, 142: 165-174.
- Özbay, A., 2009. Energy Source A 31: 1271-1279.
- Sanna H., E. Repo, M. Sillanpaa, 2013. Chemical Engineering Journal 223, 40–47.
- Sushanta D., A.Maity, K. Pillay, 2014. Journal of Environmental Chemical Engineering 2, 260–272.
- Yang, X., B. Al-Duri, 2005. J. Colloid and Interface. Science, 287: 25-34.
- Zhanhua H.g, S. Liu, B. Zhang, L. Xu, Xi.Hu, 2012. Carbohydrate Polymers 88, 609– 617.