

# The study of various parameters affecting the ion exchange of $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Cd}^{2+}$ , and $\text{Pb}^{2+}$ from aqueous solution on Dowex 50W synthetic resin

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## Abstract

A gel resin containing sulfonate groups (Dowex 50W) was investigated for its sorption properties towards copper, zinc, nickel, cadmium and lead metal ions. The use of selective ion exchange to recover metals from aqueous solution has been studied. The ion exchange behavior of five metals on Dowex 50W, depending on pH, temperature, and contact time and adsorbate amount was studied. Experimental measurements have been made on the batch sorption of toxic metals from aqueous solutions using cation exchanger Dowex 50W. The maximum recoveries (about 97%)  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$  and (about 80%)  $\text{Pb}^{2+}$  were found at pH ranges 8–9. The amount of sorbed metal ion was calculated as 4.1, 4.6, 4.7, 4.8, and 4.7 mequiv./gram dry resin for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$ , respectively. The precision of the method was examined at under optimum conditions. Selectivity increased in the series:  $\text{Pb} > \text{Cd} > \text{Cu} > \text{Zn} > \text{Ni}$ . It has been observed that, selectivity of the  $-\text{SO}_3\text{H}$  group of the resin increases with atomic number, valance, degree of ionization of the exchanged metals. The equilibrium ion exchange capacity of resin for metal ions was measured and explored by using Freundlich and Langmuir isotherms. Langmuir type sorption isotherm was suitable for equilibrium studies.

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## 1. Introduction

The treatment of wastewater containing low concentrations of heavy metals is a problem for industries. In this case, one of the common methods for removing metals is ion exchange technique. Ion exchange onto low cost media such as synthetic resins offers an attractive and inexpensive option for the removal of dissolved metals. There has been growing concern over the effect of heavy metals on humans and aquatic ecosystems. There are many different applications of ion exchangers in industry. Recoveries of inorganic substances on heavy metal cations from wastewater are examples of their application. Modern ion exchange materials are prepared from synthetic polymers such as styrene–divinylbenzene copolymers, which have been sulfonated to form strongly acidic cation exchangers. A selective elimination is possible by means of heavy metal-selective ion

exchangers, which exhibit a sufficiently high affinity for heavy metals. However, the method is not extensively adapted to metals removal in industrial wastewater treatment. Ion exchange offers a good solution for cleaning waste streams [1–8]. Many separation techniques have been proposed for the identification of metals in various environmental samples, including solvent extraction, ion exchange, co-precipitation, membrane processes and sorption [9–11]. Among these methods, ion exchange is highly popular and has been widely practiced in industrial wastewater treatment processes [12,13].

An effective way of separating solute particles and capable of extracting positively charged ions is ion exchange technique. Ion exchange technique is widely used method for the separation and pre-concentration of inorganic ions. In ion exchange, ions of positive charge and negative charge ions from an aqueous solution replace dissimilar ions of the same charge initially in the solid. The ion exchanger contains permanently bound functional groups of opposite charge-type. Cation-exchange resins generally contain bound sulfonic acid groups; less commonly, these groups are carboxylic, phosphonic, phosphinic,

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and so on. Certain general rules for cation exchange are: (i) the exchanger prefers ions of high charge, (ii) ions of small hydrated volume are preferred and (iii) ions, which interacts strongly with the functional groups of the exchangers are preferred [14–19].

Dowex-type ion exchangers are durable, insoluble and compatible. The structural polymeric backbone of the resin is styrene cross-linked with divinyl benzene functionalized with a sulfonic acid functional group as the ion exchange site. They were supplied in the sodium form. This form is very stable and has an excellent shelf life. This resin traps metals from aqueous solution in an efficient way [14–16,20–24]. Ion exchange resins have been developed as a major option for treating wastewaters over the past few decades [25–27]. Selective resins reduce the residual concentration of heavy metal to below the maximum limits [28–33]. The influence of complex formation on ion exchange sorption equilibrium and on the distribution of metal ions between the liquid and resin phases has been extensively studied [34–37]. In order to evaluate the performance of ion exchange process, predictions of the adsorbate partitioning between an aqueous solution and ion exchanger surface are required. For this purpose, batch sorption techniques are performed to obtain the distribution function of a solute between the solid and solution phase at equilibrium.

The aim of this work was to study selective ion exchange material, Dowex 50W for effective and economical applications for the elimination of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$  in aqueous solutions. Then, the batch method was used to determine the equilibrium data of the selected sorbents. The results obtained with Dowex 50W was compared with commercial Amberlite AR-120 resin.

## 2. Experimental

### 2.1. Materials

Analytical grade reagents were used. Solutions of certain molarities of test metals were prepared by dilution of sulphate, chloride and nitrate salts of metals ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  and  $\text{Pb}(\text{NO}_3)_2$  from Sigma Co.) with double distilled water. The pH buffer solutions were obtained from Aldrich Company.

Synthetic Dowex 50W and Amberlite IR-120 in hydrogen form (16–45 mesh size) were obtained from Fluka Co. The properties of the resins are given in Table 1. Both acidic and salt forms of the resin are stable at temperatures up to 120 °C.

### 2.2. Apparatus

Unicam 929 Model Atomic Absorption Spectrometer (AAS) operating with an air–acetylene flame was used to analyse the concentration of metals in solutions. The pH measurements were performed with Jenway 3010 Model pH meter. A thermo stated shaker (Gallenkamp Incubator) of Orbital model was used for ion exchange experiments.

Table 1  
Characteristic data of tested Dowex 50W

Type	Strong acid cation exchanger Dowex 50W-X8
Active group	Sulfonic acid
Matrix	Gel(microporous)-styrene divinylbenzene
Ionic forms as shipped	$\text{H}^+$
Physical form	Spherical beads
Standard mesh sizes (wet)	20–50
Mean particle size ( $\mu\text{m}$ )	560
Effective pH range	0–14
Total exchange capacity mequiv./g dry resin	$\text{H}^+$ form 4.8

### 2.3. Procedures

#### 2.3.1. Water washing of ion-exchangers

The resins were washed with diluted HCl and, then, the hydrogen form of the resin was washed with double distilled water to remove all the excess acid. The dried material at 378 K was used for further experimental work.

#### 2.3.2. Equilibrium studies

In batch operation, resins and solution dumped into a vessel and after mixing, the solution and the resin allowed for equilibrium for 4 h in the shaker. The Dowex 50W resin and solution were separated by filtration through a membrane filter (0.45 mm). Sorption of the metal by the filter medium was controlled by washing it twice with diluted HCl and the filtrate was analyzed for the remaining metal ion concentration by AAS. The same measurements were repeated three times and average values have been taken as the remaining metal amount in the solution phase. The batch ion exchange experiments were performed in a wide variety of conditions including various concentrations, different pH and temperature ranges. Equilibrium data for copper, zinc, nickel, cadmium and lead were determined by contacting different amount of resin with equal volumes of a solution containing  $5 \times 10^{-3}$  M of the metal at constant temperature. Preliminary runs showed that about 2 h were needed to reach equilibrium. After equilibrium, the resin and solution were separated by filtration, the metal content of the solution was determined by AAS. The metal concentration in resin was obtained by a material balance.

#### 2.3.3. Analysis

The metal ion concentration in the original solution and the metal ions left in bulk solution were determined by the AAS technique.

## 3. Results and discussion

In this study, ion exchange properties of copper, zinc, nickel, cadmium and lead on Dowex 50W resin has been studied by using batch technique and the results were compared with Amberlite IR-120 resin. The equilibrium ion exchange level as a function of the solution pH, temperature, and contact time and sorbate concentration was determined by AAS technique. The

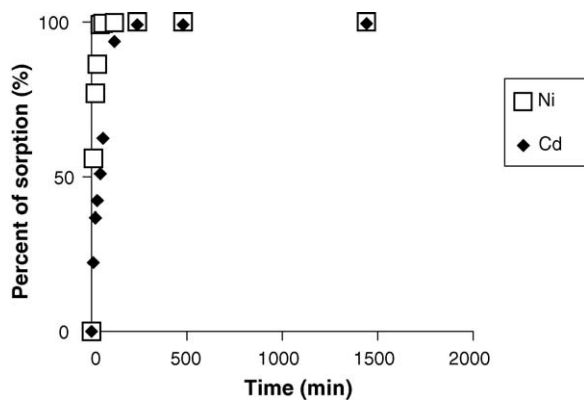


Fig. 1. Effect of contact time on the sorption of  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  by Dowex 50W (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1^\circ\text{C}$ ; stirring rate, 180 rpm; pH 8).

resins have good thermal stability, and very good resistance to attrition and the action of solvents.

### 3.1. Effect of contact time

The effect of contact time on the ion exchange of metal ions by the Dowex 50W resin was studied by taking 0.1 g resin with 20.0 ml of a metal solution in different stoppered flasks. The flasks were shaken for different time intervals in a temperature-controlled shaker. Fig. 1 shows the effect of contact time on ion exchange of  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  using Dowex 50W. Fig. 2 shows the effect of contact time on ion exchange of  $\text{Pb}^{2+}$  using Dowex 50W. Fig. 3 shows the effect of contact time on ion exchange of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  using Dowex 50W resin. The results show that the percentage of metal ion adsorbed increased with increasing time of equilibration and it reached the plateau value at 70 min for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and 60 min for  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ .

### 3.2. Effect of resin amount

The resin amount is also important parameters to obtain the quantitative uptake of metal ion. The retention of the metals was examined in the relation to the amount of the resin. For this reason, amount of the resin were tested in the range of 0.01–0.13 g

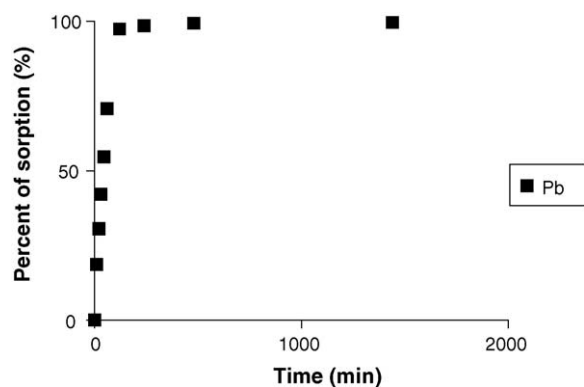


Fig. 2. Effect of contact time on the sorption of  $\text{Pb}^{2+}$  by Dowex 50W (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1^\circ\text{C}$ ; stirring rate, 180 rpm; pH 8).

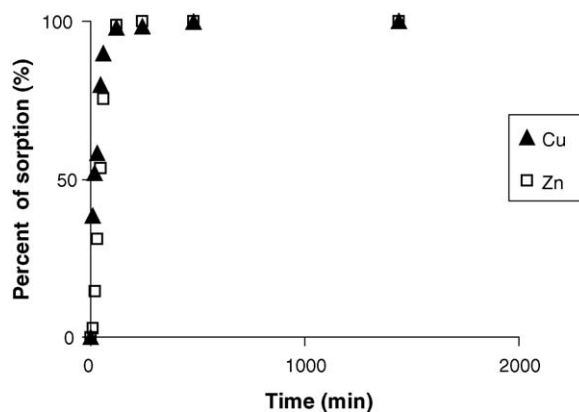


Fig. 3. Effect of contact time on the sorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  by Dowex 50W (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1^\circ\text{C}$ ; stirring rate, 180 rpm; initial pH, 8).

and equilibrated for 2 h at an initial chromium concentration of 100 ppm, 20 ml solution. All experiments were carried out at the same stirring speed, 180 rpm. The results are given in Figs. 4 and 5. It is apparent that by increasing the resin amount, the sorption density, and the amount adsorbed metal ion per unit mass increases. It was found that the retention of metals increased with increasing amount of the resin up to 0.10 g. This value was taken as the optimum amount for other trials. Since the fraction of metal removed from the aqueous phase increases as the sorbent dosage is increased in the batch vessel with a fixed initial metal concentration, the curves in Figs. 4 and 5 approach asymptotic values from 0.1 to 0.12 g resin. An increase in the sorbent amount resulted in a decrease in the contact time required to reach equilibrium.

Sorption of metal ion was increased as the resin amount rises. This result was expected because for a fixed initial metal concentration, increasing adsorbent amount provides greater surface area and sorption sites [25]. It is readily understood that the number of available sorption sites increases by increasing the resin amount.

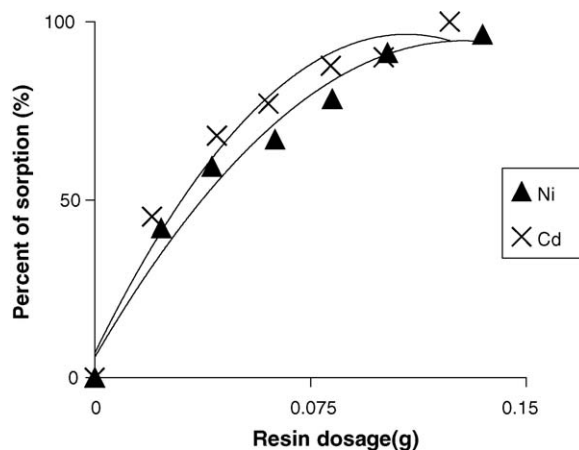


Fig. 4. Effect of resin dosage on the ion exchange of  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  on Dowex 50W resin (initial concentration of metals, 100 ppm; amount of resin, 0.01–0.13 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1^\circ\text{C}$ ; stirring rate, 180 rpm; pH 7).

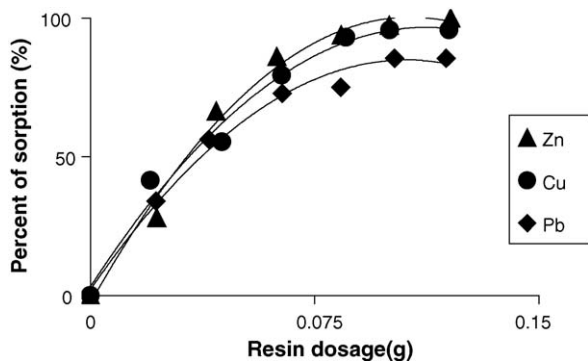


Fig. 5. Effect of resin dosage on the ion exchange of  $Zn^{2+}$ ,  $Cu^{2+}$  and  $Pb^{2+}$  on Dowex 50W resin (initial concentration of metals, 100 ppm; amount of resin, 0.01–0.13 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1$  °C; stirring rate, 180 rpm; pH 7).

### 3.3. Effect of pH

The effect of the pH of the sample solutions on the sorption of metal ion on the Dowex 50W and Amberlite IR-120 resins was evaluated by adjusting the pH in a range of 2–10. The retention of metals on the resin was studied as a function of hydronium ions. Hydronium ion concentration (pH effect) is an important parameter affecting the ion-exchange process. Buffer solutions of potassium hydrogen phthalate–HCl and potassium dihydrogen phosphate–NaOH were used for pH adjustment. The maximum recoveries for strong electric field are present and electrostatic effects may become the dominant factor, such that small ions, which have a higher charge density are bound more strongly [35]. The maximum recoveries (about 97%) for  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$  and (about 80%) for  $Pb^{2+}$  were found at pH ranges 8–9, as shown in Fig. 6. It is clear that all the metals were poorly adsorbed at  $pH < 4$ . Similar results obtained with previous study with Amberlite IR-120 [36].

Although, in general, the experimental conditions, such as metal concentration and pH, have a strong effect on the distribution coefficient,  $K_d$  and it can be used as a comparative measure

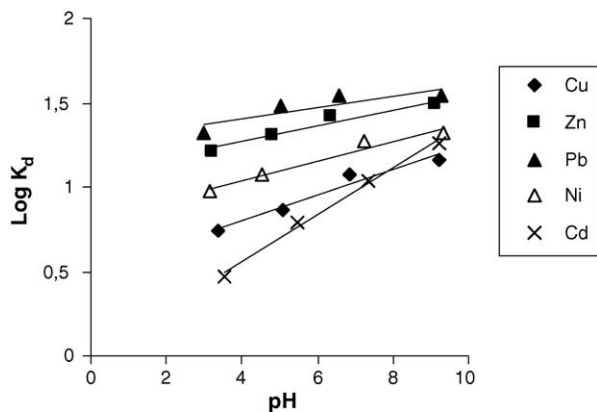


Fig. 6. The Distribution coefficients of  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Ni^{2+}$  ions on the Dowex 50W as a function of pH (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml; temperature,  $25 \pm 1$  °C; stirring rate, 180 rpm).

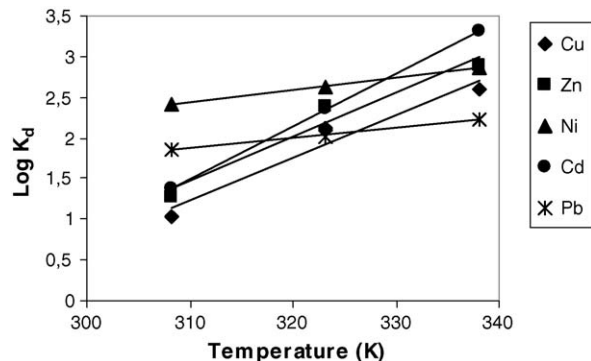


Fig. 7. The distribution coefficients of  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Ni^{2+}$  ions on the Dowex 50W as a function of temperature (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1$  °C; stirring rate, 180 rpm).

of the efficiencies of various exchangers. The results show that pH value is very significant for the performance of exchangers, thus pH adjustment may be a feasible alternative to prepare effluent for ion exchange.

### 3.4. Effect of temperature

Fig. 7 shows the effect of temperature on the distribution coefficient ( $K_d$ ) for the ion exchange of metal ions onto resins. The distribution coefficient is defined as the ratio of metal ion concentration on the resin to that in the aqueous solution. The  $K_d$  values for  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ , and  $Cd^{2+}$  metal ions was very high and it increased with temperature and the reaction products are favored at high temperatures, as seen in Fig. 7. This is due to the endothermic ion exchange reactions of divalent cations. The equilibrium constants for such reaction increase with temperature and the reaction products are favored at high temperatures [18,19]. The working capacity of an ion exchanger depends on metal concentrations and temperatures. The surface energy of the Dowex 50W increases with temperature. Similar results obtained with the sorption studies completed with the Amberlite IR-120 [36].

### 3.5. Ion exchange studies

#### 3.5.1. Batch sorption

The metal binding could be quantitatively determined experimentally under varying conditions. The effect of metal concentration, pH values, and temperatures has been studied in batch systems. The ion exchange isotherms were plotted between the amount of metal ion adsorbed per gram of resin ( $mmol\ g^{-1}$ ) and the amount of metal ions left in equilibrium solution,  $C_e$ ,  $mmol\ l^{-1}$ . The results for the copper, zinc, nickel, cadmium, and lead ions were determined at room temperature by using Dowex 50W as shown in Figs. 8–10. These results show that ion exchange of  $Cd^{2+}$  and  $Pb^{2+}$  was higher than that of the other metal ions studied. The ion exchange studies done by Amberlite IR-120 resin showed that recovery of  $Ni^{2+}$  and  $Zn^{2+}$  metals were higher than recovery of other metals [36]. The amount of sorbed metal ion per gram dry were calculated as 4.1, 4.6,

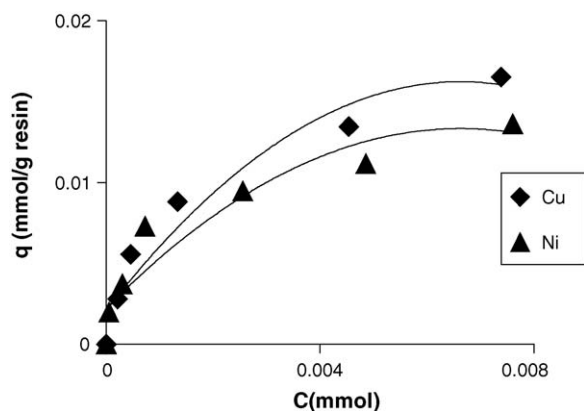


Fig. 8. Ion exchange isotherms of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions on Dowex 50W (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1^\circ\text{C}$ ; stirring rate, 180 rpm; initial pH, 8).

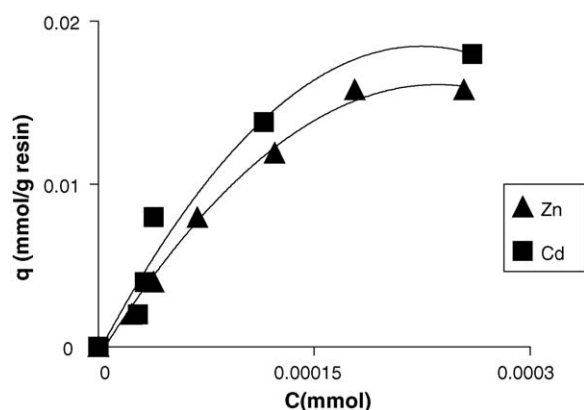


Fig. 9. Ion exchange isotherms of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions on Dowex 50W (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1^\circ\text{C}$ ; stirring rate, 180 rpm; initial pH, 8).

4.7, 4.8, and 4.7 mequiv./gram dry resin for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$ , respectively. The precision of the method was examined at under optimum conditions. The mean recovery was  $97.02 \pm 0.06\%$  ( $n = 8$ ,  $p = 0.96$ ) and the R.S.D. was  $\sim 3.8\%$ .

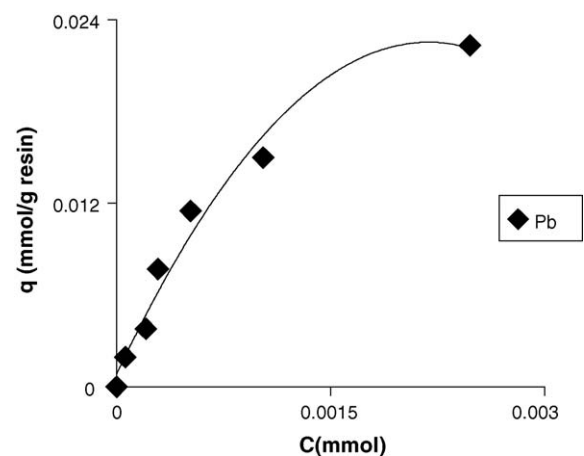


Fig. 10. Ion exchange isotherms of  $\text{Pb}^{2+}$  ions on Dowex 50W (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1^\circ\text{C}$ ; stirring rate, 180 rpm; initial pH, 8).

The  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$  extraction rate is high for the Dowex 50W resin for the first 40 min of the process. This could be explained by the easy access of sulfonic functional groups for ion exchanging. It is natural that a high degree of swelling, as well as a cross-linking agent concentration, leads to the polymer chain extension that makes the functional groups of resin efficiently involved in the exchange process. Ion exchange of the  $-\text{SO}_3\text{H}$  groups increases with atomic number, valence and degree of ionization of the exchange metal ion. The ionic radius changes of these ions are  $\text{Ni}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+}$  [19,36]. Small ions, which have a higher charge density are bound more strongly [26]. As ionic radius increases due to charge density decreases, the ion exchange capacity of the Dowex 50W resin increases, as for  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ .

### 3.5.2. Isotherms' models

The determination of substances in trace amounts involves extremely time-consuming procedures. In general, a sorption process could be preceded by the following mechanisms: (1) ion-exchange reaction, (2) physical sorption, (3) molecular sorption of electrolytes, (4) complex formation between the counter ion and the functional group, and (5) hydrate formation at the surface or in the pores of the ion exchanger [36].

The ion exchange process is not a surface phenomenon; more exchange can be found in the interior of the bead. Comparison of the changes in the rate and isotherms of exchange, associated with the change in the concentration of the solution, showed that there is a definite relation between them. Reaction rates are variable as the size range of metal that may diffuse into and out of the resin structure. Ion exchange resins, generally, have greater selectivity for ions with increasing valence or charge. Among ions with the same charge, higher affinities are seen for ions with a higher atomic number. The rate of exchange, or kinetics, of ion exchange reactions depends on several factors. The solution being treated, the size of the ions being exchanged and the ionic mobility influence the kinetic rate. Temperature and the ionic form of the exchange sites also influence the rate of reaction. The comparison of the rate and isotherms of exchange, associated with the change in the concentration of the solution showed that there is a definite relation between them. At the same concentration, the rate of exchange is higher the greater the selectivity of the ion-exchange resin with respect to the entering ion.

Table 2 shows the selectivity factors, which are the measure of the affinity of Dowex 50W for a particular metal ion as compared to that for  $\text{Cu}^{2+}$ . We immersed the exchanger in a solution containing two metals ions, which their relative con-

Table 2  
Selectivity of Dowex 50W resin relative to its affinity for  $\text{Cu}^{2+}$

Metal ions	Selectivity
$\text{Ni}^{2+}$	0.97
$\text{Zn}^{2+}$	1.00
$\text{Cd}^{2+}$	1.20
$\text{Cu}^{2+}$	1.00
$\text{Pb}^{2+}$	1.30

centration in the exchanger equal. If one of the ions is favored by the Dowex 50W, then the isotherm for its uptake appeared above the others. The deviation from the other indicated the relative affinity of the exchanger for the ion. The actual selectivity value depends on the pH, the ionic strength, and the presence of other complex-forming agents. Selectivity increased in the series:  $Pb > Cd > Cu > Zn > Ni$ . Selectivity decreases with increasing ionic radius of the hydrated ion. Due to electrostatic effects, the metal binding strength increases with decrease of the radius of hydrated metal ion and increase of charge of the metal ion. If a strong electric field is present, electrostatic effects may become the dominant factor, such that from the isotherm of metal ions it could be assumed that the stronger binding sites are occupied first; and then the binding strengths are decreased with increasing degree of site occupation [34]. Since the selectivity changes in the conformity with the change in the concentration, the rate of mass exchange is influenced simultaneously.

The most common shape of the graph of amount adsorbed for unit weight of adsorbent versus the concentration in the fluid in equilibrium is Freundlich or Langmuir sorption isotherms. The Freundlich and Langmuir sorption isotherms were used to analyze the results as these isotherms have been shown to be useful in describing ion exchange behavior of metals on resins [23,24]. The shape of the resulting curve indicated the feasibility of the separation media. Equilibrium isotherms for metals  $q=f(C)$  were plotted in Figs. 8–10. Freundlich isotherm was generated by plotting  $q$  versus  $C$ .

Freundlich equation:

$$q = K_f C^n \quad (1)$$

where,  $K_f$  and  $n$  are coefficient,  $q$  the weight adsorbed per unit weight of adsorbent and  $C$  is the equilibrium metal concentration in fluid. Taking logs and rearranging the Eq. (1):

$$\log q = \log K_f + n \log C \quad (2)$$

The coefficients  $K_f$  and  $n$  can be estimated from the slopes. The experimental results were used for the calibration of parameters of the Freundlich sorption isotherm and are presented in Table 3. The isotherms are nonlinear and each can be described by Freundlich isotherm.

Langmuir equation:

$$C/q = 1/K_b A_s + C/A_s \quad (3)$$

where,  $A_s$  and  $K_b$  are coefficient,  $q$  the weight adsorbed per unit weight of adsorbent and  $C$  is the metal concentration in

bulk solution. Since the correlation coefficients were high for each metal-sorbent equilibrium as seen from the Table 3, the Langmuir-type sorption isotherm was suitable for equilibrium studies.

### 3.5.3. Ion exchange kinetics

Experiments were also performed in order to understand the kinetics of metal removal by these resins. For the equilibrium rate study, to determine the time required for the separation to reach equilibrium,  $10^{-3}$  M solution of metals was treated with the resin and mixed. With time, small aliquots of the solution are periodically removed and the solution separated from the media was analyzed with AAS. It is a well-established fact that the ion exchange of ions in aqueous system follows reversible first-order kinetics, when a single species is considered on a heterogeneous surface. It must be remembered that the two important physicochemical aspects for parameter evaluation of the sorption process as a unit operation are the kinetics and the equilibrium. Kinetics of sorption describing the solute uptake rate, which in turn governs the residence time of sorption reaction, is one of the important characteristics defining the efficiency of sorption. Hence, in the present study, the kinetics of metal removal has been carried out to understand the behavior of this resin.

The sorption of metals onto the resins followed reversible first-order rate kinetics. The sorption of metal from liquid to solid phase may be expressed as [25]:



where  $k_1$  is the forward reaction rate constant,  $k_2$  the backward reaction rate constant.

Using the kinetic equations numbered (2)–(17) in Ref. [25], the overall rate constant, the forward and backward rate constants were calculated. For instance, by plotting  $\ln(1-U_t)$  versus  $t$  (Figs. 11–15), the overall rate constant  $k$  for given concentration of metal was calculated by considering the slope of straight lines by using Eqs. (7) and (9) in Ref. [25], the equilibrium constant  $K_C$ , forward and backward rate constants  $k_1$  and  $k_2$  were calculated and shown in Table 4. From the Table 4, it is seen that the forward rate constants for the removal of metal were much higher than the backward rate constants namely, the desorption process. This suggests that the rate of ion exchange is clearly dominant. Both resins have about the same order of magnitude for the ion exchange rates even if they are characterized

Table 3  
Parameters of Langmuir and Freundlich isotherms for sorption of metals on Dowex 50W resin

Metal	Langmuir isotherm method			Freundlich isotherm method		
	$A_s^a$	$K_b$ (l/mol)	Correlation coefficient	$K^a$	$n$	Correlation coefficient
$Cu^{2+}$	0.3500	952.38	0.986	2.6903	2.3641	0.9281
$Zn^{2+}$	0.3012	4742.93	0.949	50.4890	1.4660	0.9625
$Ni^{2+}$	0.1282	1471.76	0.988	0.9881	1.4771	0.9442
$Cd^{2+}$	0.2460	8130.08	0.789	32.0630	1.6280	0.7858
$Pb^{2+}$	0.2280	1329.08	0.974	11.7460	1.5202	0.9343

<sup>a</sup> mmol/g dry resin.

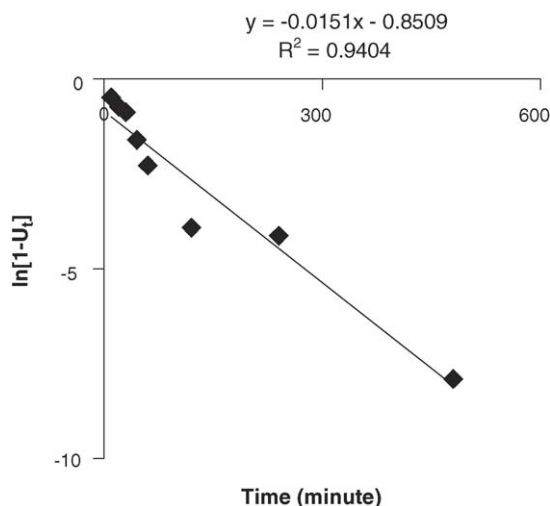


Fig. 11. Kinetic fits for the ion exchange of  $\text{Cu}^{2+}$  on Dowex 50W (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1^\circ\text{C}$ ; stirring rate, 180 rpm; initial pH, 8).

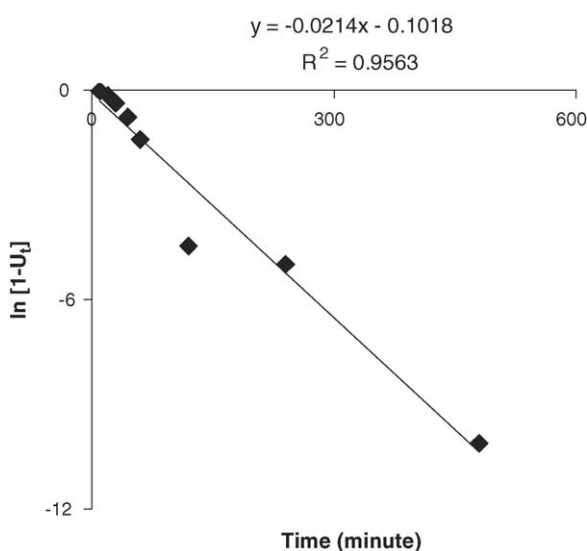


Fig. 12. Kinetic fits for the ion exchange of  $\text{Zn}^{2+}$  on Dowex 50W (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1^\circ\text{C}$ ; stirring rate, 180 rpm; initial pH, 8).

by different values of the exchange capacities. The exchange reaction is diffusion so the rate of diffusion of ion has effect of the ion exchange reaction. A characteristic feature of the systems considered is that the rate of mass exchange in the case of exter-

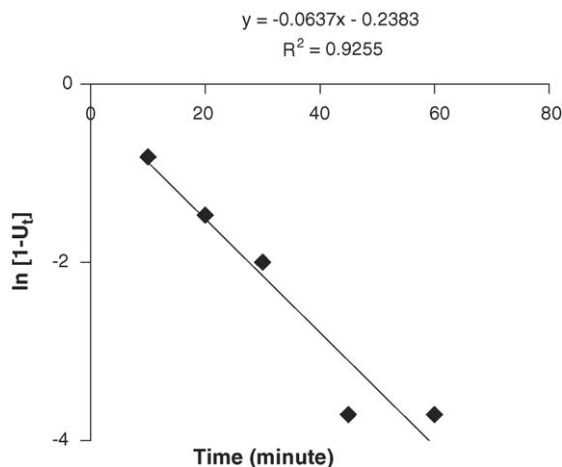


Fig. 13. Kinetic fits for the ion exchange of  $\text{Ni}^{2+}$  on Dowex 50W (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1^\circ\text{C}$ ; stirring rate, 180 rpm; initial pH, 8).

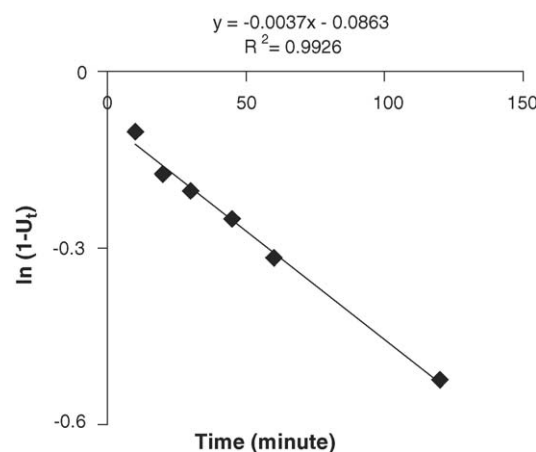


Fig. 14. Kinetic fits for the ion exchange of  $\text{Cd}^{2+}$  on Dowex 50W (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1^\circ\text{C}$ ; stirring rate, 180 rpm; initial pH, 8).

nal and internal diffusion kinetics depends on the concentration of the solution and the selectivity of the exchange and the separation of the regions where a particular mechanism operates is, therefore, extremely complex. The internal diffusion kinetics is favored by a convex sorption isotherm, a high concentration and a large resin grain diameter. Thus, sections through resin treated with metal solutions in Figs. 8–10 showed gradually rising curves, which is evidence in support of the internal diffusion transport mechanism.

Table 4

Rate constants for removal of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$  with Dowex 50W system

Metal	Metal amount (mmol)	Overall rate constant $k = k_1 + k_2$ ( $\text{h}^{-1}$ )	Forward rate constant $k_1$ ( $\text{h}^{-1}$ )	Backward rate constant $k_2$ ( $\text{h}^{-1}$ )
$\text{Cu}^{2+}$	0.05	0.015	0.015	0.00025
$\text{Zn}^{2+}$	0.05	0.021	0.021	0.00024
$\text{Ni}^{2+}$	0.05	0.064	0.064	0.00005
$\text{Cd}^{2+}$	0.05	0.004	0.004	0.00002
$\text{Pb}^{2+}$	0.05	0.006	0.006	0.00002

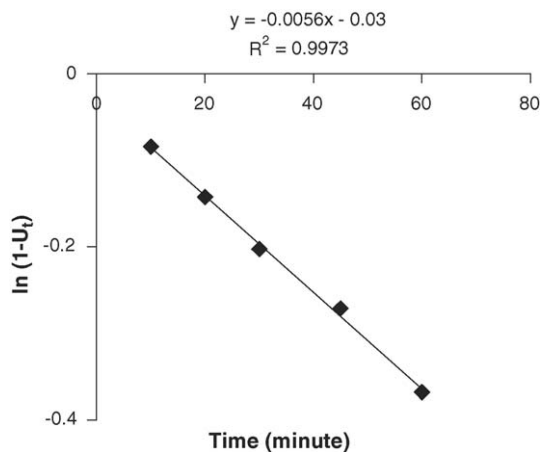


Fig. 15. Kinetic fits for the ion exchange of  $\text{Pb}^{2+}$  on Dowex 50W (initial concentration of metals, 100 ppm; amount of resin, 0.1 g; volume of sorption medium, 20 ml, temperature,  $25 \pm 1$  °C; stirring rate, 180 rpm; initial pH, 8).

#### 4. Conclusion

The aim of this work was investigation the sorption properties of Dowex 50W resin towards copper, zinc, nickel, cadmium and lead metal ions in aqueous solutions. The selection of the most suitable resin for a particular situation requires a careful balance of physical and chemical properties of the resins as well as of the solution, which is to be treated. The Dowex 50W resin was several times more efficient than the conventional resins and natural adsorbents in removing toxic and harmful transition metals from aqueous solutions. The strong acid cation exchanger (Dowex 50W) has fast kinetics in the uptake of transition metals and their operation cost is cheaper compared with the other synthetic resins. Weakly acidic resins and inorganic ion exchangers are known to have relatively slow kinetics for metal-ion exchange. Regeneration of Dowex 50W resin is possible with appropriate diluted acids or salts but natural adsorbents such as activated carbon and coal cannot be regenerated.

The experimental measurements have been carried out by the batch sorption of toxic metals from the aqueous solutions. The selectivity of  $-\text{SO}_3\text{H}$  group of the resin showed an increase with atomic number, valance, and degree of ionization of the exchanged ions. The ion exchange behaviors of five metal ions on Dowex 50W, depending on pH, temperature and adsorbate amount were studied. The maximum ion exchange capacities of sorbent for metal ions were calculated as 4.1, 4.6, 4.7, 4.8, and 4.7 mequiv./gram dry resin for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$ , respectively. The resulting  $K_d$  values were used as comparative measure of the efficiencies of Dowex 50W exchanger in the treatment of wastewater systems. For a given metal-bearing wastewater, it is possible to design a batch treatment system to remove  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Ni}^{2+}$  ion at any pH within the range 2–9. A batch contractor requires about 1 h con-

tact time to achieve 80–97% removal percentages from aqueous solution.

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