

# Anion Exchange Behavior of Some Elements in Acetic Acid-Hydrochloric Acid Media

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**Abstract:** The heavy metals contamination of soil and water has stimulated the search for soft technologies to remove these pollutants. The objective of this study is to develop a rapid and quantitative sequential separation methods of Cd(II), Zn(II), Mn(II) and Ni(II) with a strong base anion exchange resin prolite A-400 in both chloride form-RCl and acetate form-RAc. The adsorbabilities of metal ions have been studied in the presence of different acetic acid concentrations. The  $K_d$  data of metal ions were the following selectivity sequence: Cd(II) > Zn(II) > Mn(II) > Ni(II). The adsorbabilities of metal ions were slightly higher over the whole molarity range of acetic acid (0–18 M) for RCl-resin form than RAc-resin form. The addition of HCl acid to acetic acid medium markedly enhanced the sorption of many heavy metal ions on purolite A-400. Several binary separations of metal ions were achieved on the basis of their  $\kappa_d$  values. Furthermore, Langmuir and Freundlich isotherme have been described. [Journal of American Science. 2010; 6(10): 97-108]. (ISSN: 1545-1003).

**Keywords:** Adsorption; Heavy Metals; Ion Exchange; Separation; Langmuir and Freundlich Isotherme

## 1. Introduction

The increase of environmental contamination as a consequence of industrial development is a challenge that society must face [1]. The heavy metals are among the most important pollutants in natural and treated water and are becoming a severe public health problem [2]. The removal of such toxic metal ions from industrial wastewaters has received much attention in recent years because they cause health hazards in human being and animals. Various methods, such as ion exchange, adsorption, reduction, precipitation, reverse osmosis and electro dialysis techniques have been developed for the removal and recovery of heavy metal ions from sewage and industrial wastewater [3].

Several technologies were proposed for the purification of drinking water (ground water) contaminated with heavy metals. Among them, ion exchange processes are attractive for heavy metal removal because repeated use of ion exchangers is possible. Commercially available anion exchange resins, which are cross linked polystyrene with chemically fixed quaternary ammonium groups, having high selectivity to heavy metals [4,5].

In this work the adsorbabilities of some metal ions by the strong base anion exchange resin Purolite A-400 in the chloride form (RCl) and in the acetate form (RAc) were studied. This was done in the presence of different concentrations of aqueous acetic acid.

The distribution coefficients of Cd(II), Zn(II), Mn(II) and Ni(II) in RCl form and RAC form were determined in the presence of acetic acid as a function of the hydrochloric acid concentration and separation metal ions have been discussed. Furthermore Langmuir and Freundlich Isotherme have been described.

## 2. Material and Methods

### 2.1. Adsorbent

Purolite A-400 is a clear gel type I strong-base anion exchanger with high operating capacity [6,7]. The active sites for anion exchange in this resin and in all other strongly basic anion exchange resins are quaternary ammonium groups Fig.(1). Purolite A-400 was procured from purolite International Limited, Hounslow, UK. A short list of characteristics of purolite A-400 is presented in Table (1).

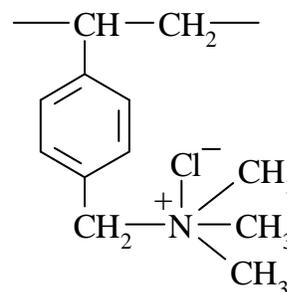


Fig. (1): Active structural unit of Purolite A-400

**Table (1): Physical and chemical characteristics of the anion exchange resin purolite A-400.**

|   |   |
|---|---|
| Polymer matrix structure                                    | Polystyrene cross-linked with divinyl benzene |
| Physical form and appearance                                | Clear golden spherical beads                  |
| Functional groups   | Type I quaternary ammonium                    |
| Ionic form, as shipped                                      | Cl <sup>-</sup> (Chloride)                    |
| Reverible swelling<br>Cl <sup>-</sup> → OH <sup>-</sup>     | 20% max.                                      |
| pH range, stability, OH-form                                | 0 – 13  |
| Total exchange capacity, Cl <sup>-</sup> form, dry, weight. | 3.7 eq/kg min.                                |

### 2.1.1. Treatment of used resin for the experiments

#### 2.1.1.1. Resin in the chloride form

The basic anion exchange resin Purolite A-400 was converted to the chloride form by packing the resin into column through which sufficient amount of (2 M) hydrochloric acid was passed for long time enough to be sure that all the resin was converted to the chloride form. The resin was washed with aqueous solvent 70% ethyl alcohol until the effluent was free of acid. The resin was then dried under vacuum at 25°C.

#### 2.1.1.2. Resin in the acetate form

The anion exchange resin was converted to the acetate form by packing the resin into a column through which sufficient amount of acetic anhydride was passed for long time enough to be sure that all the resin was converted to the acetate form. The resin was washed with deionized water until the effluent was free of acid, this was confirmed by M.O. as indicator. The resin was then dried under vacuum at 25°C.

#### 2.1.1.3. Determination of the capacity by applying an anion exchange resin (Column Method)

In the general method used, 5g of the treated anion exchanger (Cl<sup>-</sup> form), was packed into a micro column, leached with exactly 1 liter of 1 % (w/v) ammonium hydroxide solution. Further the resin was leached with exactly 1 liter of 4 % sodium sulphate solution. The effluent was collected in a separating flask. The chloride ions contents of 100 ml aliquots from each of leachate were determined by titration against standard 0.05 N silver nitrate, in the presence of potassium chromate as an indicator. The exchange

capacity, mequiv./g dry Cl form resin, was calculated from the following equation [8]:

$$\text{Capacity} = \frac{ml (AgNO_3) \times N (AgNO_3) \times 10}{\text{weight of sample}} \quad (1)$$

The result of calculated capacity of Purolite A-400 in chloride form anion exchanger = 3.5 mequiv./g dry resin.

### 2.2. Chemicals

All chemical used were BDH of analytical grade.

#### 2.2.1. Preparation of different solutions

A stock solution  $5 \times 10^{-3}$  M of Mn(II) chloride and Cd(II), Zn(II) and Ni(II) acetate salts were prepared. Different concentrations of these metal ions ( $2 \times 10^{-4}$  and  $2 \times 10^{-5}$  M) were prepared by diluting from the stock solution. All the solution samples were determined by plasma optical emission mass spectrometer (ICP-Ms). Different concentrations of acetic acid and HCl were prepared.

### 2.3. Apparatus

2.3.1. Plasma optical emission mass spectrometer (POEMS 3) USA. Inductivity coupled plasma (ICP)1999.

#### 2.4. Determination of the distribution coefficients $K_d$

Distribution coefficients were determined by a batch technique. Weighed amount of resin were added to known volumes of the complex and gently stirred until equilibrium was attained. Aliquots taken

before the addition of the resin and at equilibrium and titrated to determine metal concentration in solution in each case.

The distribution coefficient  $K_d$  was calculated using the following equation [9]:

$$K_d = \frac{\text{amount of metal ion in adsorbent}}{\text{amount of metal ion in solution}} \times \frac{v}{m} \text{ ml/g} \quad (2)$$

Where  $v$  is the volume of the solution (ml) and  $m$  is the weight of adsorbent (g).

### 2.5. Column operations

The column operations for the individual separation methods were performed in a standard manner. Purolite A-400 (2g of the corresponding form) was transferred to the ion exchange column (1.2 cm diameter  $\times$  25cm) and the resin bed was washed with a solution (50 ml) of the same composition as that employed as a sorption solution. After passage of the sorption solution, the resin was usually treated with (50 ml) of a "wash solution", also of the same composition but containing  $2 \times 10^{-5}$  M of two elements. The mixture was passed through the column as a flow rate of 0.3 ml/min. This quantitatively eluted the non adsorbed element. Thereafter, the adsorbed element was eluted by (250 ml) of (1M) hydrochloric acid which passed through the column as the same flow rate [10,11].

## 3. Results and Discussion:

3.1. The adsorbabilities of some metal ions from aqueous acetic acid solutions on Purolite A-400 in the chloride form-RCl

The adsorbabilities were expressed as weight distribution coefficients,  $K_d$  (amount of ion per g of dry resin/amount of ion per ml of solution), which were determined by batch equilibration techniques [12,13].

The distribution coefficients of Ni(II) at  $2 \times 10^{-5}$ M and  $2 \times 10^{-4}$ M concentration showed no measurable change in the presence of acetic acid concentrations ranging from 0.0 to 16.4M. In addition  $K_d$  was less than unity ( $<1$ ) [14]. Ni(II) is not adsorbed on RCl resin until 16 M acetic acid, indicating the tendency of Ni(II) to either form less stable anionic complexes or not to form such complexes (Fig. 2).

Mn(II) shows the slight tendency to form anionic complexes at 16 M acetic acid with  $K_d$  value (158.0) at  $2 \times 10^{-5}$  M and (125.0) at  $2 \times 10^{-4}$ M. Zn(II) showed a maximum  $K_d$  of 316.0 at  $2 \times 10^{-5}$ M and 400.0 at  $2 \times 10^{-4}$  M at 16M acetic acid, while the  $K_d$  of Cd(II) is 1258 at  $2 \times 10^{-5}$  M and 1000.0 at  $2 \times 10^{-4}$  M. Thus, Zn(II) and Cd(II) were shown to form quite stable complexes.

Cd(II) shows highest  $K_d$  values at all concentrations of acetic acid from (0) to (16) M. Thus Cd(II) complexes were the most preferred complex species for Purolite A-400. Zn(II) was more preferred by this resin as compared to Ni(II) and Mn(II). The  $K_d$  data of the metal ions suggest the following selectivity sequence:



The results indicated that it is possible to interpret qualitatively the adsorption of bivalent metals on the chloride form of a strong base anion exchanger Purolite A-400 in acetic acid-water mixtures.

At low water content, the dielectric constant of the solvent phase is supposed to remain low enough to exclude ionic dissociation of any component of the mixture.

At very low concentration of acetic acid, the increasing dielectric constant of the acetic acid-water mixture will lead to ionic dissociation and the formed complex will not be favoured [15].

3.2. The adsorbabilities of some metal ions from aqueous acetic acid solutions on Purolite A-400 in the acetate form-RAc

A rather broad investigation on adsorbabilities of the metal ions with concentrations  $2 \times 10^{-5}$  M and  $2 \times 10^{-4}$  M on Purolite A-400 in acetate form in acetic acid solutions was studied. It should be noted that "no adsorption" means that the  $K_d$  value is smaller than or equal to unity. The adsorbability of Ni(II) at  $2 \times 10^{-5}$  M and  $2 \times 10^{-4}$  M is found to be negligible below 16 M acetic acid. However, it is adsorbed at very high acetic acid concentrations ( $>16$  M) and shows an extremely steep adsorption curve, (Fig. 3).

In addition, the adsorbability of Mn(II) shows similar behaviour to nickel it is adsorbed in the presence of acetic acid concentration  $> 14$  M and  $K_d$  rapidly increases with acid concentration. The distribution coefficient of Mn(II) at  $2 \times 10^{-4}$  M equals 100 in the presence of 16 M acetic acid. Also Cd(II) and Zn(II) as shown in Fig.(3) show linearly increasing adsorption relations. The adsorption of these metal ions is continuously enhanced by increasing the concentration of acetic acid. The adsorption appears to be the highest for Cd(II), intermediate for Zn(II) lowest for Mn(II) and Ni(II).

A qualitative interpretation for the behaviour of the metal ions can be given on the basis of two effects. First, acetic acid enhances the

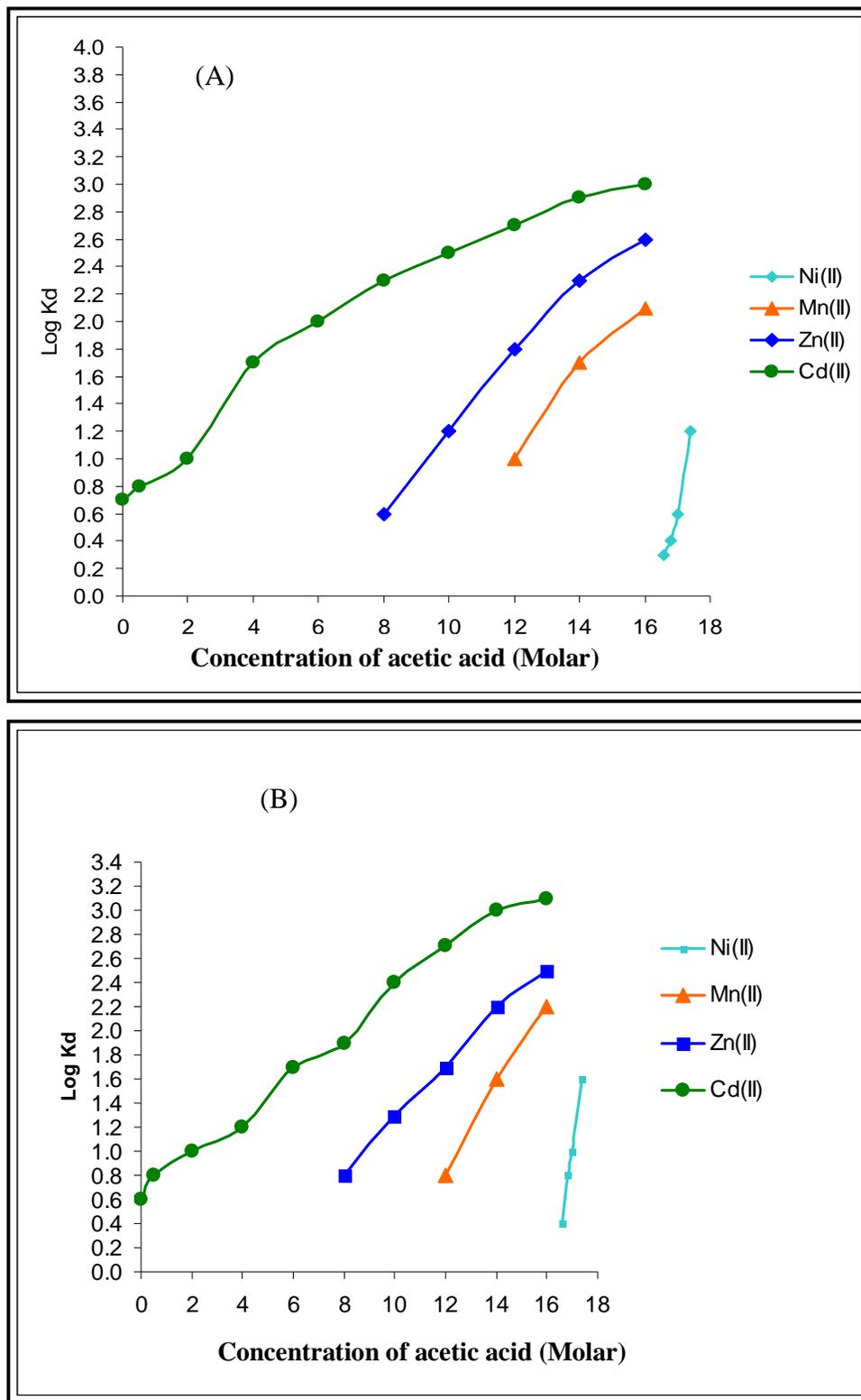
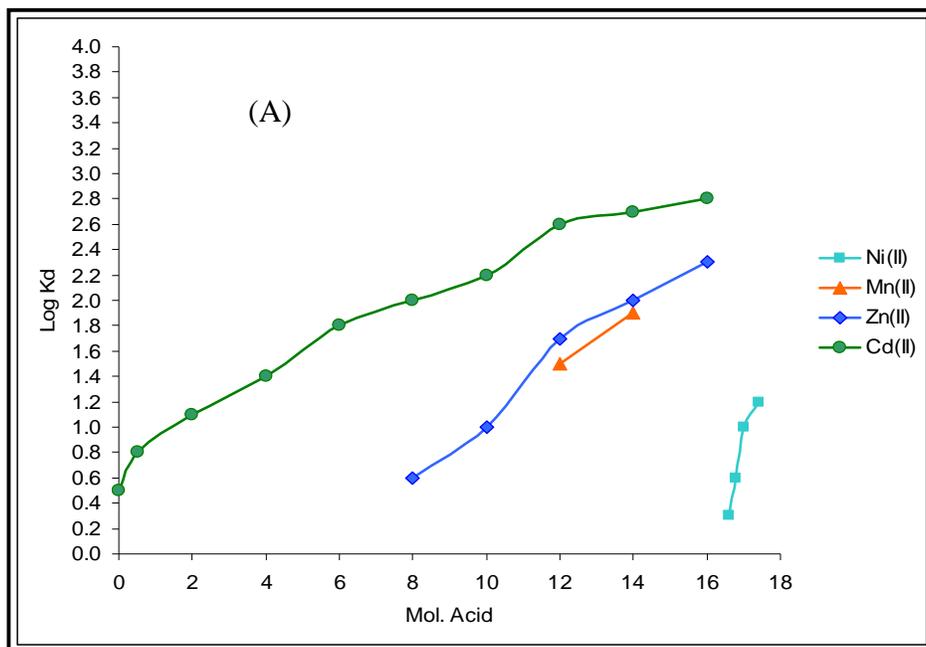
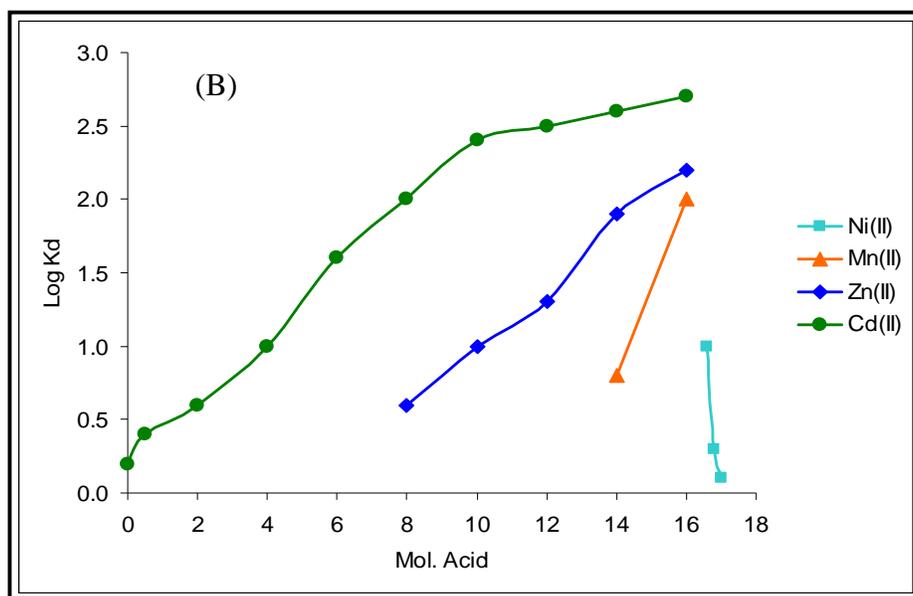


Fig. (2): Variation of the distribution coefficients for studied metal ions  $2 \times 10^{-5}$  M (A) and  $2 \times 10^{-4}$  M (B) treated with acetic acid using Purolite A-400 anion exchange resin in chloride form at 25 °C.



Concentration of acetic acid (Molar)



Concentration of acetic acid (Molar)

Fig. (3): Variation of the distribution coefficients for studied metal ions  $2 \times 10^{-5}$  M (A) and  $2 \times 10^{-4}$  M (B) treated with acetic acid using Purolite A-400 anion exchange resin in acetate form at 25 °C.

formation and stabilization of acetate complexes to a greater extent, causing many metals to be adsorbed on the Purolite A-400. This is due to lower the dielectric constant of the medium. Second The adsorption of the metal ions increases inversely with the dielectric constant of the solvent employed [16]. This may be explained by the lower dielectric constant of acetic acid ( $\epsilon_{\text{HAc}} = 6.20$ ) as compared with water ( $\epsilon_{\text{H}_2\text{O}}=80.36$ ) [17]. Thereby increasing the attraction between ions. Therefore ion association and complex formation are favoured.

The metal ions tending to be retained in the solution, may play an important role, especially at high acetic acid concentrations. This is because solvation of the metal acetate complex by the solution outside the resin competes with the process by which the metal complex is taken into the resin phase. Ordinary uptake by the resin predominates, but an unusually strong solvating effect may cause the metal complex to remain mostly in the solution phase outside the resin. Apparently the latter occurs with Mn(II) and Ni(II) when acetic acid is present. The strongly adsorbed metal ion Cd(II) is (in all probability) present as anionic species [17].

### 3.3. Comparative study of RCl- and RAc-resin form

The influence of the exchangeable anionic groups of the resin on the adsorbability of the metal ions Cd(II), Zn(II), Mn(II) and Ni(II) were examined by comparing the  $K_d$  value for the systems: aqueous acetic acid/RCl and aqueous acetic acid/RAc.

From the foregoing results, Figs. (2,3), some striking conclusions can be drawn. Over the molarity range of acetic acid (0-8M) Ni(II), Mn(II) and Zn(II) show a negligible adsorption for RCl-resin and RAc-resin but these metal ions are strongly adsorbed from high concentrations of acetic acid in RCl-resin and RAc-resin. The  $K_d$  values of Ni(II) and Mn(II) sharply increased with acetic acid concentrations > 16.4 M for Ni(II) and > 14 M for Mn(II) in both RCl-resin and RAc-resin as shown in Figs.(2,3). Cd(II) shows adsorption over the whole acetic acid molarity range (0-16 M) in the two resin forms.

The  $K_d$  values for the system of aqueous acetic acid/RCl and aqueous acetic acid/RAc for Cd(II), Zn(II), Mn(II) and Ni(II) show similar behaviour but the adsorbabilities of these elements are slightly higher over the whole molarity range of acetic acid (0-18 M) for RCl-resin form than RAc-resin form.

These results are quite logical, since in an earlier qualitative physicochemical interpretation of the adsorption behaviour of the elements from acetic acid solutions on RCl-resin[12], it was suggested that the formation of metal acetate complexes was responsible for the high  $K_d$  values in concentrated

acetic acid solutions (with a low dielectric constant: ( $\epsilon_{\text{H}_2\text{O}}=80.36$ ,  $\epsilon_{\text{HAc}} = 6.20$ ). However, the results show that the chloride ions introduced in the system from the RCl-resin, are required for high adsorption. Consequently, it can be stated that the increasing affinity of these elements for the RCl-resin in highly concentrated acetic acid solutions is due to the enhanced formation and adsorption of metal chloride or metal-acetate-chloride complexes [18].

### 3.4. Anion exchange behaviour of Cd(II), Zn(II), Mn(II) and Ni(II) in acetic acid – hydrochloric acid medium

The distribution coefficient of Cd(II) and Zn(II), Mn(II) and Ni (II) on Purolite A-400 on chloride form-RCl and acetate form-RAc were determined as a function of the hydrochloric acid concentration in the presence of aqueous acetic acid solution. Because of its ability to form negatively charged complexes with many metal ions, aqueous hydrochloric acid is one of the most frequently used and thoroughly investigated mineral acids in the field of anion exchange. This negatively charged chloride complexes show varying adsorption behaviour under different conditions of acidity [19,20].

The hydrochloric acid concentrations were ( $2.0 \times 10^{-4}$ ,  $2.0 \times 10^{-3}$ ,  $2.0 \times 10^{-2}$ ,  $1.2 \times 10^{-1}$ ,  $2.0 \times 10^{-1}$  and  $6.0 \times 10^{-1}$  M). The metal ion concentrations were  $1.0 \times 10^{-5}$  and  $2.0 \times 10^{-5}$  M for Cd(II);  $2.0 \times 10^{-5}$  M for Zn(II);  $1.0 \times 10^{-8}$  and  $2.0 \times 10^{-5}$  M for Mn(II);  $5.0 \times 10^{-6}$  and  $2.0 \times 10^{-5}$  M for Ni(II). The experiments were carried out for different acetic acid concentrations: 7.9 and 16 M for Cd(II); 16 M for Zn(II); 16 and 17.2 M for Mn(II); 16.5 and 17.2 M for Ni(II). The results are plotted as  $K_d$  versus mequiv.Cl<sup>-</sup>/g dry resin in RCl and RAc.

The adsorption function, Fig.(4) in 16 M acetic acid for RCl resin and RAc-resin for Zn(II) at  $2 \times 10^{-5}$  M shows a rather sharp increase upto 3.64 mequiv.Cl<sup>-</sup>/g of dry resin which is about the capacity of RCl (3.5 mequiv.Cl<sup>-</sup>/g dry resin). At higher chloride content, the values of  $K_d$  decreased. The values of  $K_d$  for RCl-resin were considerably higher than that of RAc-resin. The same behaviour was obtained with Cd(II), Mn(II) and Ni(II) on RCl-resin form and RAc-resin form in aqueous acetic-hydrochloric acid solutions.

From the results obtained, it can be concluded that the addition of HCl acid to the acetic acid media markedly enhances the adsorption of many metals on Purolite A-400.

In general the adsorbability decreases with increasing concentration of hydrochloric acid [21].

This effect is different from ion to another, depending perhaps on the stability of the dominant chloro-complex species in the conditions concerned. Such an effect generally means that chloride competes more effectively for ion-exchange sites as the hydrochloric acid concentration increases, which has been shown in the strongly basic anion-exchange resin-hydrochloric acid system. The high concentration of acetic acid makes the formation of chloro-acetate complexes easier even at low chloride concentrations, because acetic acid lowers the dielectric constant of the medium ( $\epsilon_{\text{H}_2\text{O}}=80.36$ ,  $\epsilon_{\text{HAc}}= 6.20$ ), thereby increasing the attraction between ions. Therefore, ion association and complex formation are favoured.

There are agreement of the  $K_d$  of RCl-resin and RAc-resin, because the chloride anions introduced by the RCl-resin are responsible for the high adsorbability of the elements on RCl-resin from concentrated acetic acid solutions. While as in the acetic acid-resin-metal ion system, it is unimportant whether the complex-forming chloride anions are introduced by the resin or by the solvent. In a qualitative way, this can be explained by the very strong affinity of the chloride ions for the RAc-resin, with the results that in the presence of an equivalent amount of chloride anions in the solvent, the RAc-resin is almost quantitatively converted to the chloride form, thus behaving like a RCl-resin [18].

Negatively charged ions are proper targets for sorption on strongly basic anion exchange resins of the quaternary ammonium polystyrene-divinylbenzene type (e.g. Purolite A-400). However, due to the high selectivity of the resin for certain anions, the targeted element may be efficiently sorbed even if it has only a relatively small fraction in the negatively charged complexes in equilibrium with other species [22].

### 3.5. Quantitative separation of metal ions in a binary system

The distribution coefficients obtained from the equilibrium studies can be used to predict the behaviour of species in a column separation. For column separations, it is desirable to have widely divergent distribution coefficients for the metal ions to be separated. The ion to be eluted from the column should have a low distribution coefficient in order to be eluted from the column in a reasonable volume. The ion to be retained on the resin should have a large distribution coefficient in order to minimize the possibility of contamination [23].

Because of its high selectivity and wide applicability, ion exchange chromatography has been

extensively utilized for the separation of elements. The method involved the adsorption of a mixture of ions on ion exchange resins followed by selective elution [24].

The separation of metals as acetate complexes from aqueous acetic acid solutions using anion exchange columns is now a well established and valuable analytical procedures [25]. In this method, metals that form anionic acetate complexes are taken up from strong acetic acid solutions, other metals pass through the column. Then the metals on the column are eluted one or two at a time using aqueous solutions of hydrochloric acid that are progressively more dilute [26].

Based on the results of measurements of distribution coefficients of metal ions Cd(II), Zn(II), Mn(II) and Ni(II) in various concentrations of acetic acid, the most suitable conditions were selected for the quantitative separation of the metal ions.

From the distribution coefficient that obtained, the separation factors were calculated using the simple relationship [10].

$$\text{separation Factor} = \frac{K_d \text{ of metal ions}}{K_d \text{ of Cd(II)}} \quad (3)$$

The reason why the  $K_d$  of Cd(II) was selected as the basis for these calculations due to it strongly retained by the resin and to its high distribution coefficient in these media comparing with other metal ions.

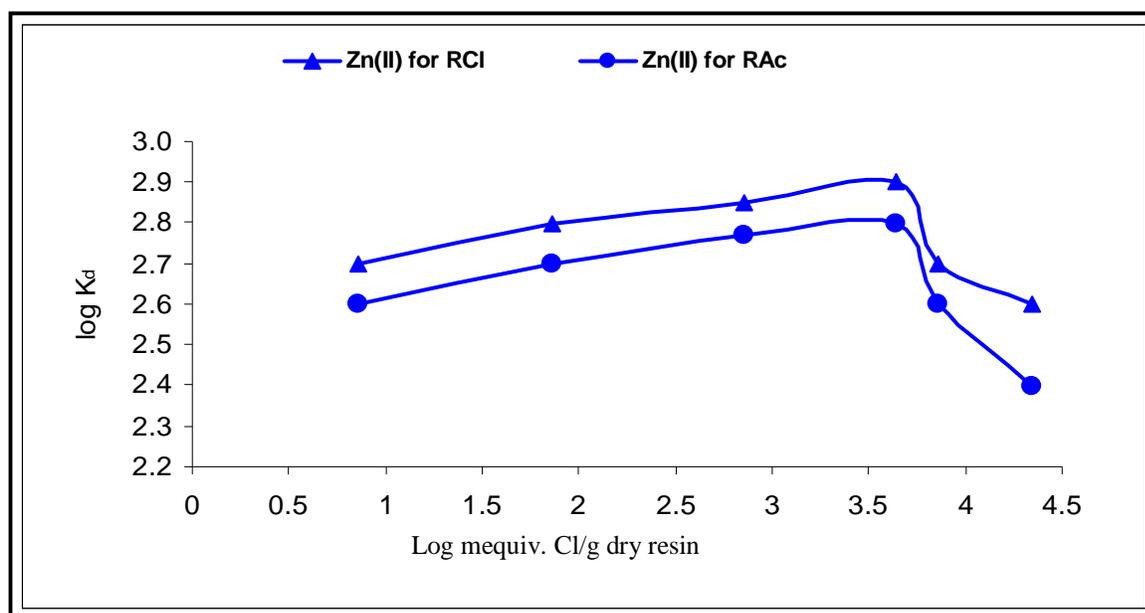
Table (2) shows that, a medium consisting of 6 M acetic acid and the resin in the chloride form could be used effectively to separate Cd(II) from Zn(II), and a medium consisting of 8 M acetic acid and the resin in the acetate form could be used effectively to separate Cd(II) from Zn(II).

Table (2): also shows a medium consisting of 10 M acetic acid and the resin in the chloride form could be used to separate Cd(II) from Mn(II), and a medium consisting of 12 M acetic acid and the resin in the acetate form could be used effectively to separate Ni(II) from Mn(II), Zn(II) and Cd(II).

For the medium consisting of 14M acetic acid and the resin in the chloride form Cd(II) and Ni(II) can be separated from each other, finally Mn(II) and Zn(II) could be separated by using 16 M acetic acid and resin in the chloride form. A separation based on this technique of separating one

**Table (2): Distribution coefficients of metals in  $2 \times 10^{-5}$  M in different acetic acid concentrations.**

| Concentration of acetic acid (M) | $K_d$  |     |        |     |        |      |        |       |
|----------------------------------|--------|-----|--------|-----|--------|------|--------|-------|
|                                  | Cd(II) |     | Ni(II) |     | Mn(II) |      | Zn(II) |       |
|                                  | RCl    | RAc | RCl    | RAc | RCl    | RAc  | RCl    | RAc   |
| 6                                | 60.0   | 63  | < 1    | < 1 | < 1    | < 1  | < 1    | < 1   |
| 8                                | 79.0   | 100 | < 1    | < 1 | < 1    | < 1  | 6.3    | 3.9   |
| 10                               | 251.0  | 157 | < 1    | < 1 | < 1    | < 1  | 20.0   | 10.0  |
| 12                               | 501.0  | 315 | < 1    | < 1 | 6.3    | 31.0 | 50.0   | 30.0  |
| 14                               | 1000.0 | 500 | < 1    | < 1 | 39.0   | 79.0 | 158.0  | 100.0 |
| 16                               | 1258.0 | 630 | < 1    | < 1 | 158.0  | < 1  | 316.0  | 200.0 |

**Fig.(4): Log  $K_d$  values of Zn(II) in RCl and RAc forms for 16 M acetic acid as a function of hydrochloric acid concentrations at 25°C.**

or more adsorbed elements from each other merely by changing the solvents was shown in Figs. (5, 6).

### 3.6. Equilibrium studies

The equilibrium adsorption isotherm is fundamental importance in the design of adsorption system [27-29]. Equilibrium data, commonly known as sorption isotherms, are basic requirement for the design of sorption system. These data provide information on the capacity of the sorbent. The sorption of Cd(II), Zn(II), Mn(II) and Ni(II) from aqueous solutions on a strongly basic anion exchange resin Purolite A-400 as a function of their concentrations was studied at 25°C. The sorption data have been subjected to different sorption isotherms,

namely Langmuir and Freundlich Models. These equations are widely used the former assumes that maximum adsorption occurs when the surface is covered by the functional groups and the latter being purely empirical [30].

#### 3.6.1. Langmuir isotherm

The Langmuir adsorption isotherm model is valid for monolayer sorption on to a surface with a finite number of identical sites. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent [31]. It is then assumed that once a metal ion occupies a site, no further adsorption can take place at that site. Moreover, the Langmuir equation is based

on the assumption of a structurally homogeneous adsorbent where all adsorption sites are identical and energetically equivalent. The saturated or monolayer capacity can be represented by the expression [30,32].

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (4)$$

Where  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  the amount adsorbed at equilibrium (mg/g), and  $Q_0$  and  $b$  are the Langmuir constants related to the capacity and the energy of adsorption respectively. The Langmuir adsorption isotherm model can be rearranged to a linear expression as follows:

$$C_e/q_e = 1/Q_0 b + 1/Q_0 C_e \quad (5)$$

The Langmuir adsorption isotherm plot ( $q_e$  vs.  $C_e$ ) and the linear plot of  $C_e/q_e$  vs.  $C_e$ , indicate the applicability of Langmuir adsorption isotherm. The values of  $Q_0$  and  $b$  were calculated from the slope and the intercept of the linear plots  $C_e/q_e$  vs.  $C_e$ .

The sorption data were analysed according to the linear form equation of the Langmuir isotherm. The isotherms of all four metal ions were found to be linear over the whole concentration range studied and the correlation coefficients were extremely high as

shown in Table (3). These values of the correlation coefficients strongly support the fact that the metal ions (specially Zn(II), Mn(II) and Ni(II) in RAc-resin and Zn(II), Ni(II) in RCl-resin) closely follow the Langmuir model of sorption.

### 3.6.2. Freundlich isotherm

The Freundlich model, which is an indicative of surface heterogeneity of the sorbent, is given by [30,32].

$$q_e = K_f C_e^{(1/n)} \quad (6)$$

The Freundlich equation can be linearized by logarithmic transfer:

$$\log q_e = \log K_f + 1/n \log C_e \quad (7)$$

where  $K_f$  and  $1/n$  are Freundlich constants related to adsorption capacity and adsorption energy. Freundlich constants,  $K_f$ ,  $n$  and the correlation coefficient,  $R^2$  for the different concentrations of metal ions were calculated from the linear plots of  $\log q_e$  vs  $\log C_e$  are presented in Table (3). The results showed that the adsorption also followed Freundlich isotherm, but the resin showed better fit for Freundlich isotherm than Langmuir isotherm for Cd(II)-RCl, Zn(II)-RCl.

**Table (3): The values of the parameters of Langmuir and Freundlich isotherm for sorption of metal ions on Purolite A-400 at 25°C.**

| Metal Ions          | Langmuir Method |         |       | Freundlich Method |      |       |
|---------------------|-----------------|---------|-------|-------------------|------|-------|
|                     | $Q_0$ (mg/g)    | B (L/g) | $R^2$ | $K_f$ (mg/g)      | n    | $R^2$ |
| <b>Cd(II) - RCl</b> | 0.310           | 0.900   | 0.988 | 0.160             | 3.50 | 0.989 |
| <b>Zn(II) - RCl</b> | 0.135           | 0.098   | 0.979 | 0.014             | 1.40 | 0.985 |
| <b>Zn(II) - RAc</b> | 0.020           | 0.410   | 0.991 | 0.008             | 1.78 | 0.977 |
| <b>Mn(II) - RCl</b> | 0.0002          | -45.4   | 0.996 | 0.350             | 0.97 | 0.997 |
| <b>Mn(II) - RAc</b> | 0.020           | 38.0    | 0.991 | 0.020             | 6.20 | 0.976 |
| <b>Ni(II) - RCl</b> | 0.050           | 0.18    | 0.987 | 0.008             | 1.35 | 0.974 |
| <b>Ni(II) - RAc</b> | 0.180           | 4.13    | 0.999 | 0.140             | 5.98 | 0.917 |

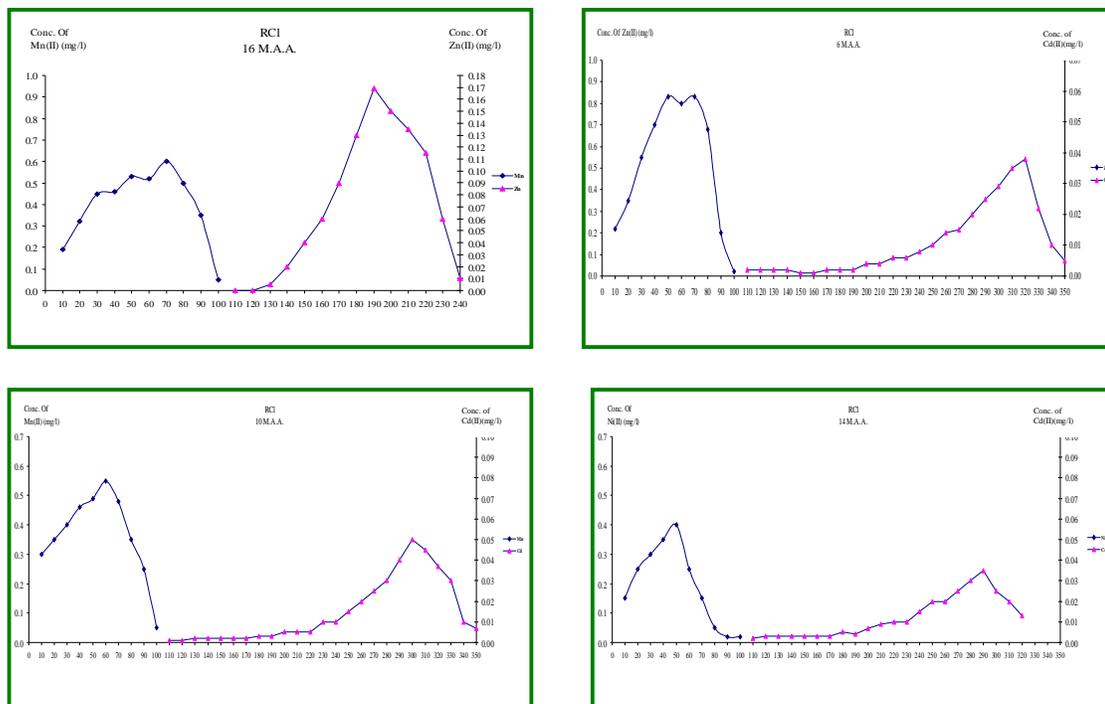


Fig. (5): Separation of some metal ions on Purolite A-400 in the chloride form at 25°C.

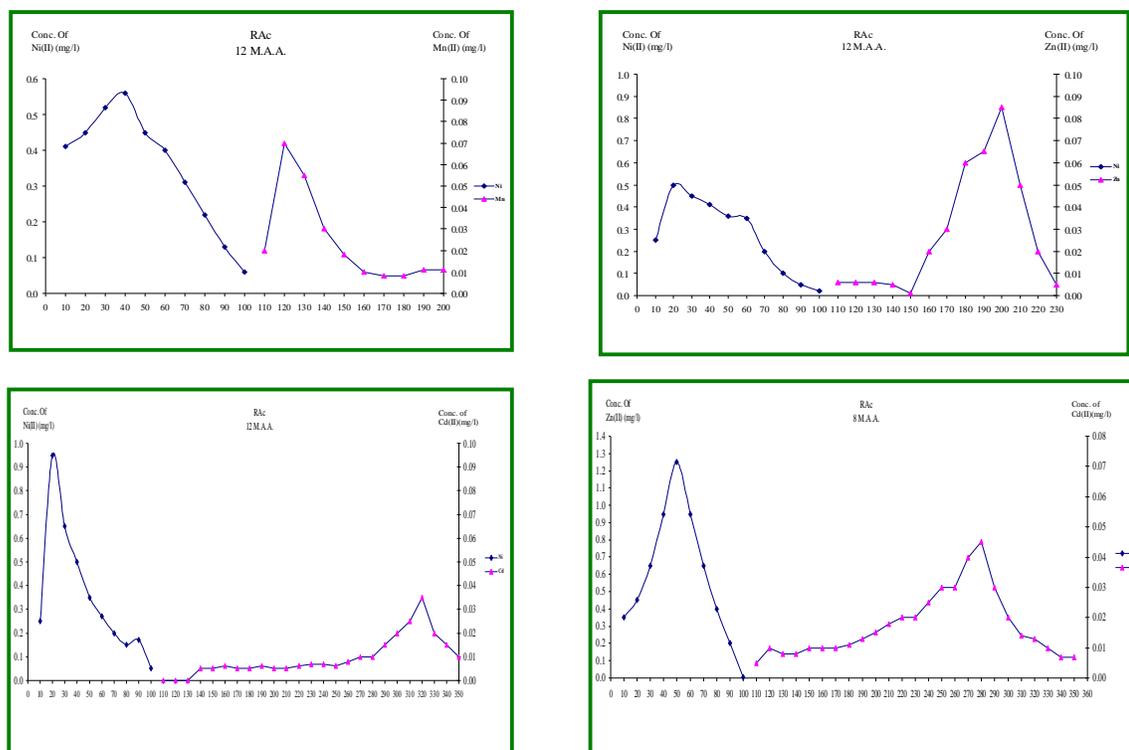


Fig. (6): Separation of some metal ions on Purolite A-400 in the acetate form at 25°C.

#### 4. Conclusion

The present investigation shows that, anion exchange resin purolite A-400 can be employed for the separation of some metal ions from their mixtures. The adsorbabilities of the metal ions from aqueous acetic acid solutions on purolite A-400 resin in chloride form (RCl) was slightly higher than the acetate form (RAc), and addition of HCl acid to acetic acid medium markedly enhances the sorption of many metals on purolite A-400. The sorption data of Cd(II), Zn(II), Mn (II) and Ni(II) have been subjected to different sorption isotherms, namely, Langmuir and Freundlich. These data provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. The described methods provide a simple, fast and economic means for separating of metal cations from wastewater.

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