REMOVAL OF HEAVY METAL IONS FROM CONTAMINATED WATER USING CORNCOB-SULPHONATED PHENOL FORMALDEHYDE CONDENSATE

ABDUL–ALEEM S. ABOUL–MAGD*, SALWA, H. EL–RASHED** and SALMA A. AL–ZAHRANI***

Faculty of Science, Al–Azhar University Department of Chemistry, Cairo, Egypt, Tel.: +2 010 3324796
*** Faculty of Education, Chemistry Department, King Abdul–Aziz Jeddah, K.S.A*
*** Faculty of Science, Chemistry Department, Hail Univ. K.S.A*
E.mail address: dr.aleem@hotmail.com

Abstract

This paper is focused on the use of agricultural by-product as a replacement of the running low cost method for removing heavy toxic and/or radioactive metal ions from water and wastewater. The modification of Egyptian corncobs as a source of low cost plant and recycling material with phenol has been developed in presence of para-formaldedhyde as a cross linking agent. The modification of corncobs was investigated to enhance their natural capacity and could be considered as an added value to the waste plant. In this study, the characterization of the synthesized sulphonated corncob–phenol formaldehyde exchange resin is described and compared with the Dowex $HYRW_2$ –Na polisher cation exchanger. It was found that the synthesized resin is stable in hot water (100ºC), mineral acids (2M), in all most common solvents, and alkali solutions 1:0M withstand temperature up to 100ºC. The modified corncob resin has an exchange capacity of 2.84 m.eq. /g dry resin –H^+ form. The character of copolymer resin adsorption efficiency towards heavy toxic metals has been investigated via different concentrations of Mg (II), Mn (II), Fe (III), Cu (II), Zn (II), Cd (II) and Pb (II) individually in pure aqueous water and aqueous– HCl solutions. Finally a comparison of their removal performance with that of the commercial and the prepared resins was presented in this study where as the last one showed good adsorption efficiency.

Keywords: Corncob – phenol formaldehyde resin, removal of toxic elements by low cost materials, Ion exchange separation.

Introduction

Synthetic ion exchangers are used in a large scale in analytical chemistry and water treatment[1-3]. Treatments processes for removing heavy metal ions from water are needed. Natural materials that are available in large quantities or certain waste products from industrial or agriculture operation may have potential as inexpensive sorbents. Due to their low cost, after these material have been expanded, they disposed off without expensive regeneration, where the cost is an important parameter for comparing the sorbent materials [4].

It has shown that the lignin of different agriculture material via coconut coir, kenaf core, bagasse, kenaf bast and cotton has an ion exchanger character to remove copper, nickel and zinc ions from aqueous–solution depending on the lignin content [5]. An attempt has been made by several authors to prepare less expensive cationic resins from agricultural by-products and rice hush ash respectively [6, 7]. Many lignocelluloses fibers cation exchangers have been prepared by many workers for removing the heavy metal ions from aqueous solution (1-3, 5, 6), while the others deal with the study of the adsorption behavior of bovine serum albumin [8].

Cation exchange processes have been employed with an increased attention in recent years as efficient alternatives for removing toxic elements by different sorbents. In general, a sorbent can be assumed as low cost it requires little processing is abundant in nature, or a by-product or waste material from another industry. This study is aimed to develop a corncobs adsorbent with an open pore structure on its surface in order to enhance the most transport process [6]. Preparation and characterization of the corncob when it is copolymerized with phenol in the presence of para-formaldedhyde as a cross linking agent has been investigated. We have continued this study and herein report sulphonated cationic exchanger has been used for the application in the determination of the partition coefficients of some heavy elements in aqueous solution and in aqueous–hydrochloric acid medium.

Experimental

Corncobs were used as raw materials supported from Egyptian plant byproduct. The corncobs were air dried or in an oven at 60ºC for 4hr, and emery by sandpaper to remove the fluff around the column, crushed and screened in between 641 and 420 mesh size using sieves [ASTM–E 11–61]. The last dust fine and coarse grains were excluded out and not used. The mean values of the raw material were determined according to the following estimation as reported by [9] and the results are given in Table (1).

Table (1) :The mean values of the raw material under several estimations:

	Methods of estimation	Content;%
1	Estimation of solubility material in ethanol	3.6
2	Estimation of solubility material in hot water	5.0
3	Estimation of carbohydrate or holo-cellulose	40.0
4	Estimation of cellulosic content	35.0
5	Estimation of lignin	18.0

6	Estimation of solubility material in 4% NaOH	30.0

Preparation of cationic exchanger based on Sulphonated corncob–phenol–formaldehyde condensate.

The reactions were carried in a three–necked flask, equipped with reflux condenser, thermometer, and the third one is equipped with the mechanical stirrer at 100°C in thermostatic bath.

Procedure:

The synthesis of an ion exchange resin have a three–dimensional cross linking matrix of corncobs with phenolformaldehyde containing fixed ionic sulfonic group. ar can be achieved by the condensation of corncob to phenol in different ratios of 1:1, 1:1.5, 1:2 and 1:2.5 in the presence of the concentrated hydrochloric acid in a ratio twice the total amount of material (Corncob + phenol) at 80°C for 8 hr; the finished yields which was obtained as follows; 45, 55, 62 and 69%, respectively.

Note: The entire yield is soluble in most common organic solvents.

Cross linking

The degree of cross linking can be adjusted by varying the para-formaldedhyde content ratios as; 15%, 25%, 30%, 40% and 50% were added to the above yields with a ratio (2:1), over a period of at least 10 minutes in presence of concentrated HCl (35% by weight)) as a catalyst with a ratio of 1:1 at 30°- 40°C, with stirring thoroughly. The reaction temperature was increased to 80°C for 150 min. The obtained product was a cross linked corncob– phenolformaldehyde [CCPhF] resin, which was found to be insoluble or stable against the common organic solvents at $(CH_2O)_n$ 30% wt/wt and over this ratio. The yields was crushed, washed by 1% NaOH solution and then by 10% HCl solution followed by the de-ionized water at several times, and then finally dried in an oven at 70 - 80°C for 3hr with turning over Table (2)

Table (2): Amount percent of Para-formaldehyde capacities and its characterization after sulfonation

Para-formaldehyde; %.	15*	25*	30	40	60	200
Capacity,meq./g dry resin (H+- form)	3.22	2.5	2.35	1.5	1.1	0.45

Note (*): soluble in most common organic solvents.
Note: Para-formaldehyde it must added to the resin on the warm with strong stirring for complete homogenization before the reaction reached to 80°C.

Sulfonation

The final step is the sulfonation of resin (yield 3); 100g resin with 220 g of concentrated H_2SO_4 (with specific gravity 1.83 gm/cm^3) was added in the presence of Ag_2SO_4 as a catalyst (5 g) at 80° - 90°C for 6 hr. By the completion of the reaction, the yields are cooled, neutralized by adding 3M sodium carbonate solution, washed for several times by water to remove the excess of acid and/ or alkali, and then dried at oven (80°C) for 3hr with turning over. The stability of resin was studied against several reagents. The change in the capacity after the treatments, ranged from 0.42 x 10^{-2} to 3.0%, is illustrated in Table (3).

Table (3) The change in the capacity values of corncob phenol formaldehyde-SO₃Hafter the treatment with various reagents:

Reagents used	Capacity of resin in m. is/g dry resin (H+ -form)
Blank (no reagent)	2.35
NaOH (1N) –24 hr	2.28
Mineral acids (1N) –24 hr	2.30
Common organic solvents	2.34
Boiling water 4 hr	2.35
Thermal treatment in oven at 100°C for 8 hr	2.28

Capacity determination

5g of the resin is converted to the H^+ –form by treatment with a liberal excess of 0.5 – 1.0N HCl in a column or by the repeated batch equilibrium–until the acid remains free of the metal cations. The resin is then washed at several times with de-ionized water to remove the sorbet HCl until the water remains free of Cl$^-$ ions and then dried by air to remove the adherent liquid till it reaches the constant weight. Exact 1.0g of the resin is weighed in a dry 250 ml Erlenmeyer flask. Exactly 200 ml of 0.1N NaOH in 5% wt NaCl solution is added. After standing overnight in the stopper flask, 50 ml aliquots of supernatant NaOH solution is titrated with the standard 0.1M oxalic acid solution using methyl orange indicators [10]. The capacity value can be obtained as follows.

$$Cap. \ m.eq/ \ g \ dry \ resin = \frac{[amount \ of \ NaOH - titrand \ used]xN}{weight \ of \ resin}$$

Infrared analysis

The IR–spectrum of raw material corncob (a) was compared with the copolymer corncob–phenol (b), then with the cross linking of copolymer corncob–phenol in the presence of para-formaldehyde (c) and then finally with the sulfonated products of (d) as shown in Figure (1). A band is appeared at 790cm^{-1} due to the C–O–C in ether bond. This band is disappeared after sulfonation. A stretching enhanced the intensity band at 1650–1600cm^{-1} due to the (C=C). Methylene rocking deformation is appeared at 720cm^{-1}. A band around 1280 to 1200 cm^{-1} is appeared due to the adsorption stretching for methyl group. New bands are appeared at 1340 cm^{-1} and 1160.22 cm^{-1} due to –SO$_2$– and –SO$_3$H, respectively. The broad band which is clearly a characteristic of strongly banded OH group is pointed around 3333 cm^{-1} and 3273 cm^{-1}, (Figure 1) [11].

Preparation of the salt solution

The salt solutions were prepared from their chlorides to obtain exactly 0.01–1.0N solution of Mg (II), Mn (II), Fe (III), Cu (II), Zn (II), Cd (II) and Pb (NO$_3$)$_2$ in aqueous and aqueous –HCl solution .

Determination of various elements

Most of the elements investigated were determined volumetrically using suitable chelatometric with EDTA (di- sodium salt) as the titrant. The indicators used for these titrations were Murexide for Cu (II) at pH=8, Erio-chrome black T for Mg (II), Zn (II) and Cd (II) and for Pb (II) in presence of tartaric acid (powder) at pH=10 together as buffer solution[12]. Dilute nitric acid solution with hexamine indicator at pH=10 for Cd (II) and 5-sulphsalicylic acid indicator for Fe (III).

Determination of K$_d$

The distribution study was carried out in a 100 ml glass–stopper flask containing the dry resin (1g) and in the presence of metal ions concentration ranging from 0.01 to 1.0M in aqueous medium and in presence of hydrochloric acid in different molarities 0.01 to 3.0M at fixed 0.1M metal ions. Batches were equilibrated by shaking for 8hr. All the experiments were carried out at 25ºC ± 0.1ºC. Each solution was analyzed for the metal ions with and without the resin.

The values of partition coefficients (K_d) were calculated using the relation [13–15]:

$$K^d = \frac{\text{m.equi.metal g of dry resin}}{\text{m.equi.metal ml of solution}}$$

Results and Discussion

The present work deals with the synthesis of cation exchange resin based on the condensation of Egyptian corncobs (a) with phenol in the presence of (HCl 35%) as a catalyst with the formation of product (b). The second step is the co-polymerization of product (b) with the Para-formaldehyde yield giving the product of corncob-phenol formaldehyde (product c). In the final procedure [17], is the sulphonation of product (c) gives the corncob-phenol formaldehyde $-SO_3H$ (compound d). Other factors such as the reaction temperature and the reaction time were kept similar to the procedure as previously cited [1 – 3]. It is clear from the yield given in Table (2) that the variation affects of corncob: phenol ratio value (1:2) at 80°C. Table (3) shows an evident at a lower capacity and a higher rigidity at a higher percent of Para-formaldehyde content. In the same time the higher capacity was found with the lower of cross linking agent $(CH_2O)_n$. However it was found that the first two percent of formaldehyde, is not stable against the common organic solvents; i.e., the best one is at 30% wt/wt of $(CH_2O)_n$ to obtain a good capacity and good stability. The aim of such effects is to determine the optimum conditions for such preparation. It is important to note that the weight of the swelling percentages is decreased with the increase of the amount of Para-formaldehyde in the matrix as shown in Table (3). Besides, the lower swelling shows much higher rigid cross linking due to the increase of the amount of $(CH_2O)_n$ in the resin. It was found that the high cross linked resin at 200% $(CH_2O)_n$ is more hardened and leads to a more resistant to the mechanical break down. In general, most of the prepared or the commercial resins in the present are stable in all common solvents except with a temperature up to slightly more than 100°C as shown in Table (4).

The ion exchange partition coefficients of the studied metal ions were investigated on (CCPHF) and on Dowex $HYRW_2$–Na polisher resins as given in Tables (5, 6) and Figures (2, 3). The results indicate the effect of the concentration of the metal ion from 10^{-2} to 10 x 10^{-2} M on the K_d-values of Mg (II), Cu (II), Mn (II), Fe (III), Zn (II), Cd (II) and Pb (II) ions. These elements of the major constituents of

the lithosphere are very toxic elements. The uptake of metal ion per gram dry resin was decreased with the increase of the initial metal concentration. The data showed the maximum partition coefficient values of metal ions on the resin at very dilute metal ion concentration [14]. This behavior is probably due to that the ratio of the number of moles of metal in the aqueous phase to the total number of the exchange capacity is less than the unity and in turn the fractional ion exchanger does not tend to cover all of network in the resin phase [15]. The lowering of the K_d –values is attributed also to the relative amount of ion pairing as shown by the inspection of the activity coefficients of the metal ion–salts [16]. Significant differences were observed in the K_d–values of the studied ions at 1.0M, as it gives zero K_d value for Pb (II) ions only and K_d value of 72.10 for Fe (III) ions. The results agree well with the data given in the presence of the commercial cationic exchanger Dowex HYRW$_2$ Na polisher, refer to Table (6). Those of metal ions are not higher enough at initial metal concentration with the following sequences: Mg (II) > Zn (II) > Cu (II) > Mn (II) > Fe (III) > Pb (II) > Cd (II).

Moreover, an increase in the hydrochloric acid concentrations from 0.01 to 3.0 M HCl lowers the values of partition coefficient. This change becomes more pronounced due to the ability of the metal ions to form an increase in the negatively charged chloro–complexes ions. It is concluded that the Fe (III), Cu (II), Mg (II), Pb (II) and Mn (II) formed much stronger anionic chloride complexes [16] as shown in Tables (6, 7) and Figures (4, 5). The formation of anionic chloro complexes with hydrochloric acid is confirmed by the action of hydrogen ion as governed by the mass reaction equation for a simple exchange and the action of chloride ion by lowering the effective concentration of cation in solution through complex formation [14].

However, the mechanism of desorption is based on the chelating (chloro or nitro negatively charged complexes) between the metal ion and chelating of the acid agents in the resin loading. From the previous concerning, desorption of the chelating agent on the resin is based mainly on both the ion exchange and the partly existing molecular weight. Therefore, the adsorption of metal ions on the resin depends on the HCl concentration in the solution. Moreover, in the process of the adsorption of metal ion, the chelating group must be destroyed to form free metal ions in the solution phase.
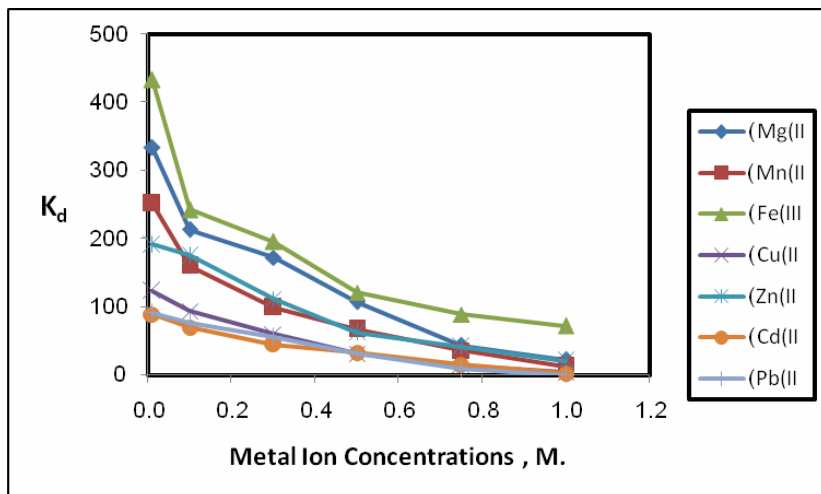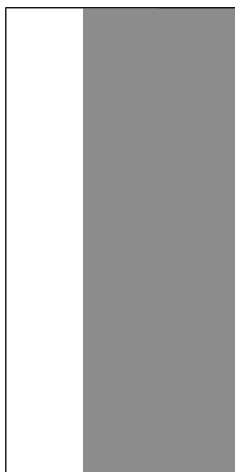
By comparing the results obtained from the presented and the commercial resins, it was found that the synthesized corncob–phenol formaldehyde condensate has several advantages. It can be easy to prepare experimentally and easily, using a continuous counter current operation in much as solid ion exchanger laboratories. In addition, the process of concentration of the active groups in the exchanger phase can adapt to suit the required capacity to give a different capacity. Another important advantage can be seen throughout the usage of the low cost materials in the preparation of exchanger and make such preparation and reformed again by using them in industrial and laboratory at any time over a wide range on extent and scale. Mention may be prepared directly whether cationic and anionic. Further more, these resins could be prepared directly in the cationic or anionic forms

Table (4): Distribution coefficient values in aqueous medium of metal ions of varied molarities on corncob–phenolformaldehyde cation exchanger:

Metal Ions	Metal Ions Concentration, M.					
	0.01	0.1	0.3	0.5	0.75	1.0
K_d – values						
Mg(lI)	333.50	212.91	172.50	107.00	43.00	22.50
Mn(lI)	251.34	160.40	99.50	67.00	35.50	12.20
Fe(lII)	433.15	242.42	195.36	121.00	88.66	72.10
Cu(lI)	123.14	93.70	59.88	31.00	14.40	3.26
Zn(lI)	191.00	175.00	111.20	62.42	41.00	20.60
Cd(lI)	88.89	69.30	44.50	32.5	15.10	2.1
Pb(lI)	91.50	77.00	55.75	30.70	8.14	0.00

Table (5): Distribution coefficient values in aqueous medium of metal ions of varied molarities on Dowex HYRW$_2$–Na polisher cation exchanger:

Metal Ions	Metal Ions Concentration, M.					
	0.01	0.1	0.3	0.5	0.75	1.0
K_d – values						
Mg(lI)	633.35	278.10	173.50	98.23	33.35	12.50
Mn(lI)	395.00	290.13	188.53	166.14	135.10	63.22
Fe(lII)	376.15	341.14	185.19	165.91	130.50	77.00
Cu(lI)	540.12	388.00	250.00	170.00	110.00	91.70

Zn(lI)	550.00	420.00	360.00	220.15	188.07	120.10
Cd(lI)	234.44	216.75	119.21	113.10	98.00	90.00
Pb(lI)	267.00	144.00	81.00	19.31	0.00	0.00

Table (6): Distribution coefficient values in aqueous –HCl solution of varied molarities at 0.1M metal ions on corncob–phenolformaldehyde cation exchanger:

Metal Ions	HCl Concentrations, M.					
	0.01	0.1	0.5	1.0	2.0	3.0
	K_d – values					
Mg(lI)	145.20	114.00	70.50	22.42	9.80	0.00
Mn(lI)	199.00	173.00	100.70	42.42	16.50	1.30
Fe(lII)	370.15	181.81	92.70	66.20	33.50	14.25
Cu(lI)	192.50	165.00	88.00	65.10	25.22	6.13
Zn(lI)	37.77	29.70	12.75	3.50	0.00	0.00
Cd (II)	47.10	43.83	17.50	0.00	0.00	0.00
Pb(lI)	PPT	PPT	PPT	PPT	PPT	PPT

Table (7): Distribution coefficient values in aqueous – HCl solution of varied molarities at 0.1M metal ions on Dowex HYRW$_2$–Na polisher cation exchanger:

Metal Ions	HCl Concentration, M.							
	0.01	0.1	0.3	0.5	0.75	1.0	2.0	3.0
	K_d – values							
Mg(lI)	440.36	260.00	122.00	81.72	13.22	0.00	0.00	0.00
Mn(lI)	245.00	195.00	124.50	88.70	45.50	17.31	8.70	3.31
Fe(lII)	136.17	121.14	98.75	66.32	33.45	16.10	7.50	0.00
Cu(lI)	151.50	122.91	91.50	67.20	26.00	11.01	4.22	1.50
Zn(lI)	180.00	150.00	99.13	33.40	7.20	0.00	0.00	0.00
Cd(lI)	77.78	68.20	51.50	16.50	5.55	0.00	0.00	0.00
Pb(lI)	PPT	PPT	PPT	PPT	PPT	PPT	PPT	PPT

hernolformaldehyde (c) and
γde (d)

**Fig (2): K_d–metal ion concentration in aqueous medium in presence of
synthesized cation exchanger [CCPhF]**
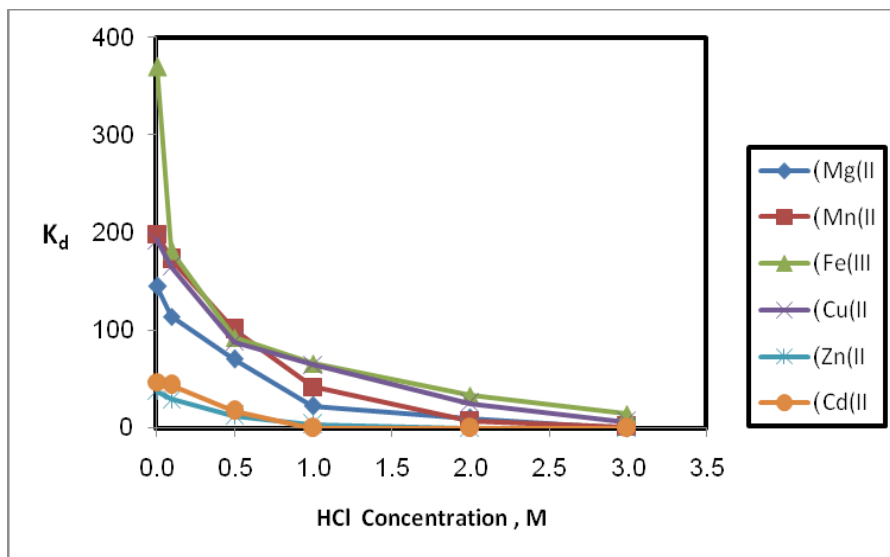
Fig (3): K_d–HCl concentration in aqueous medium in presence of synthesized cation exchanger [CCPhF]
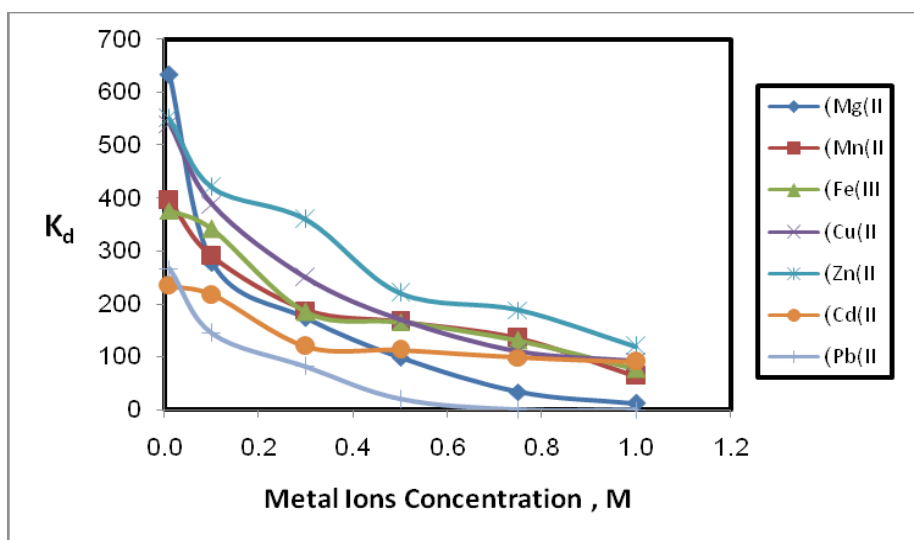

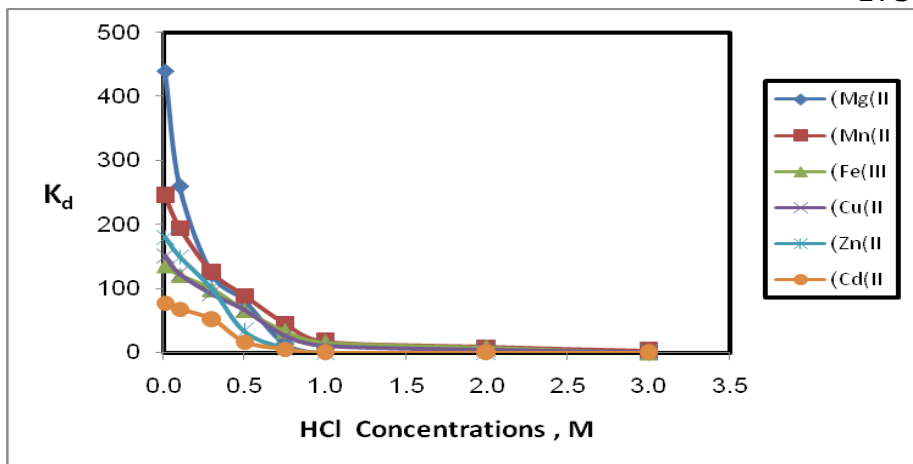**Fig (4) K_d–metal concentration plots in presence of Dowex–Na polisher**

Fig (5) K_d–HCl concentration in presence of Dowex Na–polisher at 0.1M metal ions

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