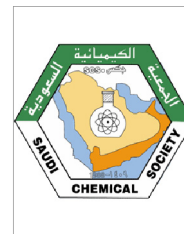




King Saud University
Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



REVIEW

Batch adsorptive removal of Fe(III), Cu(II) and Zn(II) ions in aqueous and aqueous organic–HCl media by Dowex HYRW₂-Na Polisher resin as adsorbents



Abdul-Aleem Soliman Aboul-Magd ^{a,*}, Salwa Al-Rashed Al-Husain ^b,
Salma Ahmed Al-Zahrani ^c

^a Faculty of Science, Al-Azhar University, Department of Chemistry, Cairo, Egypt

^b Faculty of Education, Chemistry Department, King Abdul-Aziz, Jeddah, Saudi Arabia

^c Faculty of Science, Chemistry Department, Hail University, Saudi Arabia

Received 17 March 2011; accepted 10 April 2011

Available online 15 April 2011

KEYWORDS

Removal of toxic metal;
Ion exchange partition;
Separation processes

Abstract Of the metal ions in tap, Nile, waste and sea water samples and some ores were carried out. Removal of heavy metal ions such as Fe(III), Cd(II), Zn(II), Cu(II), Mn(II), Mg(II), and Pb(II) from water and wastewater is obligatory in order to avoid water pollution. Batch shaking adsorption experiments to evaluate the performance of nitric and hydrochloric acid solutions in the removal of metal ions by cation exchange resin at the same conditions for both, such as the effect of initial metal ion concentration, different proportions of some organic solvents, H⁺-ion concentrations and reaction temperature on the partition coefficients. The metal adsorption for the cation exchanger was found to be significant in different media for both nitric and hydrochloric acids, i.e., the adsorption up take of metal ions presented in this work is very significant depending on the characteristics of ions and on the external concentrations of solute. The presence of low ionic strength or low concentration of acids does have a significant adsorption of metal ions on ion-exchange resin. The results show that the ion exchanger could be employed for the preconcentration, separation and the determination.

© 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

* Corresponding author. Tel.: +20 10 33 24 796.

E-mail address: dr.aleem@hotmail.com (A.-A.S. Aboul-Magd).

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

Contents

1.	Introduction	S2
2.	Experimental.	S2
2.1.	Materials and methods	S2
2.2.	Determination of various elements	S2
2.3.	Determination of partition coefficients	S3
2.4.	Column operation.	S3
3.	Results and discussion	S3
3.1.	Effect of metal ion concentrations	S3
3.2.	Effect of acid concentrations	S3
3.3.	Effect of organic solvents	S4
3.3.1.	In HNO ₃ –THF media.	S4
3.3.2.	In case of THF–HCl media.	S5
3.3.3.	In case of DMSO–HNO ₃ media	S6
3.3.4.	In case of isopropyl alcohol–HNO ₃ media	S6
3.3.5.	In case of acetone–HNO ₃ media	S7
3.3.6.	In case of acetone–HCl media	S7
4.	Separation techniques	S7
5.	Conclusion	S8
	References	S8

1. Introduction

Heavy metal ions are very toxic elements present in waste waters from different industrial sources (Phillips et al., 2007; Wan Ngah and Hanafiah, 2008; O'Connell et al., 2008; Srivastava et al., 2009; Gode and Pehlivan, 2006). Increasing presence of heavy metals in water stream, tap water and ground water is a very dangerous environmental concern (Vaughan et al., 2004; Lin and Juong, 2000; Karthikeyan et al., 2005; Kendü- zler et al., 2006; Apiratkul and Pavasant, 2008). For this purpose, there is a persistence need to remove heavy elements from industrial sewage and other pollution sources (Erdem et al., 2004). Many investigations obtained various technologies for eliminating of pollutants, via, adsorption on activated carbon, chemical precipitation, coagulation and ion exchange resin. Among of these methods, ion exchange resin which is found to be the best for removal of metal ions because of its relative simplicity of application, non-corrosive, simple regenerations and could be used several times.

This is a continuous research into specially absorbents using synthetic ion exchange resin that facilitate cheap and effective chemical regeneration process (Lakshmi and Srinivasan, 2004; Wang and Joing, 2007).

The aim of this work is to investigate the performance of Dowex HYRW₂-Na Polisher cation exchange resin as solid-phase extractor in removing of Cu(II), Zn(II), Mg(II), Fe(III), Mn(II), Cd(II) and Pb(II) from aqueous medium. Tests were conducted to determine the adsorption coefficient of these metal ions from other different media. The parameters that influenced the adsorption coefficient, such as initial metal ion concentration, acid concentration and different organic solvents in different proportions were investigated. The organic solvents that have been used are: THF, DMSO, isopropyl alcohol and acetone, to enhance the sorption capacity of adsorbent toward heavy metal ions. Also, competitive adsorption of coexisting binary-metals onto the resin was studied

based on the adsorption coefficient data for possible separation using column chromatography techniques.

2. Experimental

2.1. Materials and methods

All reagents were of analytical grade and all solutions were prepared using distilled-water. The laboratory glassware was kept overnight in a chromic acid solution. It was rinsed thoroughly with water several times (tap water) and followed with distilled water and then, dried. Stock solutions of metal ions of different concentrations in aqueous and aqueous-acid-organic solvent were also prepared. In general nitric (55%) and hydrochloric acids (35%) were obtained from Merck. Dowex HYRW₂-Na Polisher (Chemical Process Co., Red-Wouk City, USA) was washed with ethanol, 0.5 M/l HCl solution and distilled water respectively to be neutralized, dried for 4 h at 40–50 °C. The exchange capacity of the resin was 3.92 mequiv./g dry resin H⁺-form as determined by weight titration with standardized NaOH (Vogel, 1966).

2.2. Determination of various elements

The elements investigated were determined by volume using EDTA-di-sodium salt as the titrant. The solutions were diluted as required to obtain standard solutions containing 0.01–1.0 mol of metal ions. About 100 ml of metal solution in the presence of desired acid concentrations and organic solvents was taken in reagent bottles of 100 ml capacity, known amounts of 1.0 g resin was added separately in 50 ml of the above solutions. The solutions were then agitated for a predetermined period at 25 °C in a shaking incubator (Model Jeio Tech SI-900R). The resin was separated and the filtrate was analyzed by titration with EDTA. Adsorption studies were carried out with different concentrations of metal ions or

HNO₃ and/or HCl solutions in the presence of solvents while maintaining the dry resin dosage at 1.0 g in order to correct any adsorption of metal ions on the container surface, control experiments were carried out without resin. It was found that there was no adsorption by the container walls. In addition, all mixing containers were kept sealed throughout the duration of each test to minimize dissolution of gaseous species in the atmosphere.

One millilitre solution of the metal ions was taken and diluted with cooled de-ionized water on the basis of analysis of chemical composition. Murexide indicator was used for Cu(II) at pH 8. Eriochrom Black T for Mg(II) and Zn(II) ions; while for Mn(II) and Pb(II) ions were analyzed in the presence of triethylamine indicator with two granules of NaOH and tartaric acid solution with hexamine indicator at pH 10. Dilute HNO₃ solution with hexamine indicator for Cd(II) at pH 10 and sulphosalicylic acid for Fe(III) (Hellferich, 1962).

2.3. Determination of partition coefficients

The batch distribution coefficient K_d , is defined by the following equation (Erdem et al., 2004):

$$K_d = \frac{\text{m.equiv metal on resin/g of dry resin}}{\text{m.equiv metal on soln. 1 ml of dry resin}}$$

2.4. Column operation

An aqueous solution of the metal ions concentrations had been immersed with a medium selected for separation in which one of the metals has a very high partition coefficient and the other one should be very low one. A glass column, with stopcock, of 50 cm long and 1.2 cm diameter was used. A small amount of glass wool was placed at the end of the column near to the stopcock. The solution inside the column maintains upper surface of the resin to ensure air bubble between particle gels. Feed and outlet samples were collected in periodical to measure the concentrations of each metal ion, similar to the previous researches (Korkisch and Ahlawalia, 1966, 1967; Aboul-Magd et al., 1988).

3. Results and discussion

3.1. Effect of metal ion concentrations

The effect of Mg(II), Cu(II), Cd(II), Fe(III), Mn(II), Zn(II) and Pb(II) ion concentrations on the sorption uptake on Dowex HYRW₂-Na Polisher has been investigated in the range from 1.0×10^{-2} to 1.0 M in pure aqueous medium and at constant v/m equal to 50 ml/1 g dry resin. Fig. 1 shows that the metal (NO₃⁻-form) concentration determines that the partition coefficient (the uptake of metal ion per gram dry resin) process decreased with the decrease of the metal concentration as expected. It also indicates that the maximum values of sorption capacity of adsorption with metal ion were observed by the resin at initial metal concentration. This behavior is expected because may be due to two reasons, for a fixed initial solute concentration, increasing the adsorbent doses providing greater surface area or adsorption sites (Erdem et al., 2004); and/or the ratio of a number mole of metal ion to the available exchange capacity is lower and consequently the fractional metal

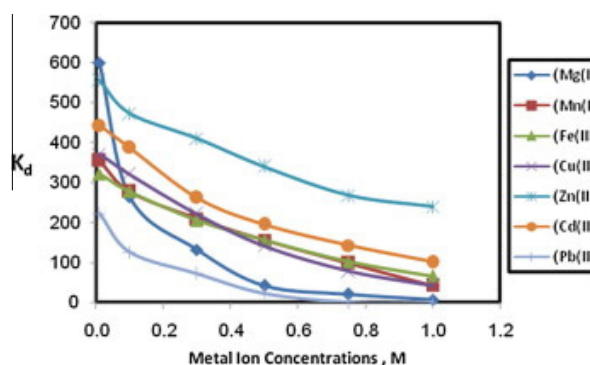


Figure 1 Distribution coefficients of metal nitrates in different molarities on Dowex HYRW₂ cation exchange resin.

ion will not cover all resin's exchange capacity. From this point, the higher removal had marketable by small amount of resin to ensure efficient economical. This behavior of an removing of metal ions from solution by resin was earlier observed by (Korkisch and Ahlawalia, 1966, 1967; Aboul-Magd et al., 1988; Sterolow, 1960). These results also clearly indicated that the removal efficiency would decrease with metal ions beyond the level of very dilute solution therefore, the efficiencies of separation are very difficult and negligible.

It is apparent that the amount of exchanges of metal ion per unit mass decreased by increasing of the metal ion concentration and the retention of metal ions increased with the increasing of resin's exchange capacity ratio. The lowering of the K_d values for these metal ions with the increasing of metal ion concentrations are probably due to the relative amount of ion pairing shown by the inspection of the activity coefficients of these metal ion-salts (Korkisch and Ahlawalia, 1966, 1967).

3.2. Effect of acid concentrations

Investigations with respect to the influence of nitric acid on the sorption of metal ions show that the sorptions of metal ions are affected greatly with increasing the acid concentration (Fig. 2). An increase in acid from 0.01 to 3.0 M considerably lowers the partition coefficient values, this change can be explained as the ability of the element to form negatively charged ions increases. The respective absorption value proceeds

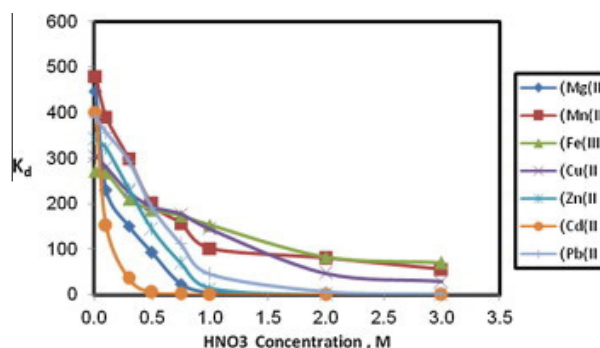


Figure 2 Distribution coefficients of metal nitrates in different molarities of hydrochloric acid on Dowex HYRW₂ cation exchange resin.

according to the following order of the total molar solution $0.01 > 0.1 > 0.3 > 0.5 > 0.7 > 1.0 > 2.0 > 3.0$ M. This effect is different from metal to metal depending on the stability of the dominant acido-complex species in the condition concerned. Such effect generally means that the acidity group competes more effectively in the exchange sites as nitric acid concentration increases and the activity coefficient, which it is increases with decreasing concentration (0.01–3.0 M) (Philips et al., 2007).

Table 1 shows that the partition values tend to be lower in hydrochloric acid than in nitric acid. This difference varies from element to element and may be due to the competitive effect of the chloride ion as strong coordinated to that of the nitrate ion. It is therefore important to optimize the acid concentrations in order to obtain best separations or to give a good variation of the partition coefficients for the elements (Cotton and Wilkinson, 1980; Korkisch and Klakil, 1964).

3.3. Effect of organic solvents

Results for partition coefficients in different proportions of THF, DMSO, isopropyl alcohol and acetone in presence of ni-

tric and hydrochloric acids at 0.1, 0.5, 1.0 and 3.0 M solutions have been investigated and are shown in Tables 2–5.

3.3.1. In HNO_3 –THF media

The absorption coefficient is found increased for metal ions (except Mg(II)) in presence of THF. At a certain concentration of HNO_3 (1.0 and 3.0 M), the partition of Mg(II) ions increases somewhat with THF addition in water. In general, the absorption of elements decreases with increasing of the acid concentration, and leads to in some cases to zero values. The partition coefficient for such elements Mg(II), Mn(II), Fe(III), Cu(II), Zn(II), Cd(II) and Pb(II) has been found higher at aqueous-0.1 M HNO_3 –THF media. A formation of complex in case of Mn(II) as $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, whereas in case of Fe(III) a purple color as liquid anion exchange ligand as tetrahedral adduct has been content, however in case of Cu(II) as THF $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ or $[\text{Cu}(\text{NO}_3)]$, indicating that Cu(II) ion is reduced to mono-valence Cu(I) to give white precipitate CuCl such as pale yellow precipitate in case of CuBr (Cotton and Wilkinson, 1980). Also a review on such media has been published (Janauer et al., 1971) at a media of 20% THF and 3.0 M HNO_3 .

Table 1 Effect of HCl concentration on the K_d -values in pure aqueous medium.

Metal ions	K_d values in HCl concentration (M)							
	0.01	0.10	0.30	0.50	0.75	1.05	2.00	3.00
Mg(II)	440.36	260.00	122.00	81.72	13.22	0.00	0.00	0.00
Mn(II)	245.00	195.00	124.50	88.70	45.50	17.31	8.70	3.31
Fe(III)	136.17	121.14	98.75	66.32	33.45	16.10	7.50	0.00
Cu(II)	151.50	122.91	91.50	67.20	26.00	11.01	4.22	1.50
Zn(II)	180.00	150.00	99.13	33.40	7.20	0.00	0.00	0.00
Cd(II)	77.78	68.20	51.50	16.50	5.55	0.00	0.00	0.00
Pb(II)	PPT	PPT	PPT	PPT	PPT	PPT	PPT	PPT

Note: PPT = precipitate.

Table 2 K_d -values of metal ions in presence of THF–aqueous-hydrochloric acid media.

THF (v/v, %)	Mg(II)	Mn(II)	Fe(III)	Cu(II)	Zn(II)	Cd(II)	Pb(II)
0.1 M HCl solution							
10	231.00	77.50	78.00	125.32	121.91	29.65	PPT
20	139.00	83.25	75.00	119.44	115.00	27.22	PPT
30	249.00	85.00	68.00	117.51	111.00	26.14	PPT
40	255.00	89.01	61.00	115.23	106.04	22.11	PPT
0.5 M HCl solution							
10	71.50	21.00	33.00	88.03	77.00	9.17	PPT
20	73.00	24.00	31.00	81.00	70.61	8.00	PPT
30	77.00	35.00	28.00	79.22	64.22	6.05	PPT
40	83.00	32.00	24.00	71.00	59.00	3.19	PPT
1.0 M HCl solution							
10	3.76	1.17	2.15	62.00	55.10	2.05	PPT
20	5.55	4.00	0.00	61.00	51.67	0.00	PPT
30	7.91	7.53	0.00	55.00	45.66	0.00	PPT
40	8.57	8.85	0.00	53.00	43.20	0.00	PPT
3.0 M HCl solution							
10	0.00	0.00	0.00	0.00	21.00	0.00	PPT
20	0.00	0.00	0.00	0.00	14.00	0.00	PPT
30	0.00	0.00	0.00	0.00	10.00	0.00	PPT
40	0.00	0.00	0.00	0.00	2.03	0.00	PPT

Note: PPT = precipitate.

Table 3 K_d -values of metal ions in presence of aqueous-DMSO-HCl media.

DMSO (v/v, %)	Mg(II)	Mn(II)	Fe(III)	Cu(II)	Zn(II)	Cd(II)	Pb(II)
0.1 M HCl solution							
10	172.00	95.52	63.00	103.00	94.00	26.14	PPT
20	195.31	102.00	59.00	99.00	94.00	36.50	PPT
30	210.31	105.00	51.00	94.00	94.00	45.33	PPT
40	221.40	105.21	46.82	91.00	94.00	45.42	PPT
0.5 M HCl solution							
10	88.32	42.71	26.99	35.50	53.00	7.92	PPT
20	91.50	45.79	18.22	29.41	53.00	8.00	PPT
30	93.47	46.79	17.51	24.37	53.00	8.00	PPT
40	99.85	46.44	13.60	21.70	53.00	12.60	PPT
1.0 M HCl solution							
10	52.00	21.80	0.00	0.00	37.00	0.00	PPT
20	53.21	22.95	0.00	0.00	37.00	0.00	PPT
30	55.25	22.95	0.00	0.00	37.00	0.00	PPT
40	59.00	22.95	0.00	0.00	37.00	1.50	PPT
3.0 M HCl solution							
10	0.00	0.00	0.00	0.00	14.00	0.00	PPT
20	0.00	0.00	0.00	0.00	14.00	0.00	PPT
30	0.00	0.00	0.00	0.00	14.00	0.00	PPT
40	0.00	0.00	0.00	0.00	14.00	0.00	PPT

Note: PPT = precipitate.

Table 4 K_d -values in presence of aqueous-isopropyl alcohol-HCl media.

Isopropanol (v/v, %)	Mg(II)	Mn(II)	Fe(III)	Cu(II)	Zn(II)	Cd(II)	Pb(Li)
0.1 M HCl solution							
10	277.71	73.36	93.01	137.50	45.00	43.10	PPT
20	291.14	74.51	93.11	139.40	47.50	44.00	PPT
30	305.20	75.11	93.15	145.21	47.90	44.00	PPT
40	310.66	77.42	93.15	138.20	50.13	44.00	PPT
0.5 M HCl solution							
10	81.92	13.80	45.60	96.77	9.45	13.50	PPT
20	83.11	17.91	45.60	105.30	10.30	9.10	PPT
30	85.13	20.10	45.92	108.22	10.90	7.00	PPT
40	86.07	22.50	46.10	99.00	11.11	3.15	PPT
1.0 M HCl solution							
10	7.53	4.50	10.12	7.50	0.00	5.14	PPT
20	8.10	7.91	10.12	8.10	0.00	9.10	PPT
30	8.90	11.55	10.12	8.33	0.00	7.00	PPT
40	9.15	14.88	10.12	5.68	0.00	3.15	PPT
3.0 M HCl solution							
10	0.00	0.00	0.00	4.52	0.00	0.00	PPT
20	0.00	0.00	0.00	4.90	0.00	0.00	PPT
30	0.00	0.00	0.00	4.90	0.00	0.00	PPT

Note: PPT = precipitate.

3.3.2. In case of THF-HCl media

Cd(II), Zn(II), Fe(III) and Cu(II) have the same behavior over the entire range of THF-HNO₃ concentration but with lower K_d -values for Cd(II) and Fe(II). Table 2 shows that the effect of THF-HCl solution on the adsorption coefficients of metal ions and the extraction of these metal ion appear to be possible such as; Cd(II)-Zn(II), Cd(II)-Cu(II), Fe(III)-Zn(II) and Fe(III)-Cu(II) in binary system. No separation has appeared for such elements at 3.0 M HCl solution because the most of

these elements give stable chloride-complexes except Zn(II) ion with K_d -values (21.0–2.03). Pb(II) ion is an insoluble matter as a white precipitate has been formed. Results in Table 2 showed a wide variation in the behavior of the partition coefficient in the THF-HCl media as compared to that of THF-HNO₃ media. The investigation that took place over the cation exchanger on Dowex 50-X8 in THF (Fritz and Rettig, 1966) was similar to that of the Dowex HYRW₂-Na Polisher.

Table 5 K_d -values of metal ions in presence of aqueous-HCl-acetone media.

Acetone (v/v, %)	Mg(II)	Mn(II)	Fe(III)	Cu(II)	Zn(II)	Cd(II)	Pb(II)
0.1 M HCl solution							
10	214.00	72.50	92.78	135.12	142.00	46.00	PPT
20	175.00	81.50	92.78	147.15	134.80	39.00	PPT
30	143.00	85.45	92.78	155.32	107.30	35.00	PPT
40	101.00	88.90	92.78	139.14	91.18	27.00	PPT
0.5 M HCl solution							
10	68.15	13.50	41.23	93.77	101.15	13.50	PPT
20	47.00	17.19	33.11	94.21	74.77	9.70	PPT
30	36.20	18.90	28.95	73.55	69.85	4.11	PPT
40	29.00	20.60	25.77	62.70	50.00	1.50	PPT
1.0 M HCl solution							
10	2.15	4.50	0.00	32.88	76.50	2.75	PPT
20	0.00	5.70	0.00	24.60	55.12	1.50	PPT
30	0.00	9.50	0.00	17.90	42.00	0.00	PPT
40	0.00	13.83	0.00	11.10	27.73	0.00	PPT
3.0 M HCl solution							
10	0.00	0.00	0.00	6.50	0.00	0.00	PPT
20	0.00	0.00	0.00	0.00	0.00	0.00	PPT
30	0.00	1.50	0.00	0.00	0.00	0.00	PPT
40	0.00	2.31	0.00	0.00	0.00	0.00	PPT

Note: PPT = precipitate.

3.3.3. In case of DMSO-HNO₃ media

The adsorptions of all metal ions are similar in behavior because their distributions are very high. Nevertheless, these absorption values are still high so no rapid separations for these elements from each other is allowed, i.e., the differences in their partition are not allowed to the possibilities at low percent of DMSO or at high nitric acid concentration of clear-cut separation.

Analogous trends and unfavorable conditions exist in 0.5 M HNO₃-DMSO media: a gradual decrease in adsorption behavior with a gradual increase of acid concentrations is observed due to probably the formation of nitrate-complexes. In 3.0 M HNO₃ solution, a similar trend is found to that at 0.1 M but with lower K_d -values, this behavior can be attributed to the stability of the formation of negatively nitrate complexes. This observation is similar to that has been reported (Aboul-Magd et al., 1988). In Table 3 it is shown that Cd(II), Cu(II) and Fe(III) ions have an enhanced complex formation and that will be preventing the sorption of the metal ions by the resin at 1.0 M HCl-DMSO media. While, the elements of Mg(II), Mn(II) and Zn(II) ions show a retention on the cation exchanger which indicated that the complex formation is not important in these media. The K_d -values for Cd(II), Mn(II) and Mg(II) are increased or decreased with Cu(II) and Fe(III) ions with the addition of DMSO in water solution. A review on this subject has been published by Korkisch and Ahlawalia (1966, 1967), Aboul-Magd et al. (1988), Sterolow (1960), Cotton and Wilkinson (1980), Korkisch and Klakil (1964) and Janauer et al. (1971). On the other hand, Zn(II) ion shows no change in the K_d -values; it is still constant over the entire range of DMSO systems however with lower adsorption has been reported at 3.0 M HCl, i.e., a gradual decrease in the K_d -values with increasing of acid concentrations.

3.3.4. In case of isopropyl alcohol-HNO₃ media

Preliminary investigations of the influence of isopropyl alcohol on the adsorption of Cu(II) on Dowex HYRW₂-Na Polisher. Cu(II) ions are not determined because an insoluble matter has been observed at isopropyl alcohol-1.0-3.0 M HNO₃ solutions. Cu(II) ion may be reduced to Cu(I) ions and reacts with isopropyl alcohol to give a bright yellow insoluble polymer compound in the present form (CUOR) complexes and reasonable stable. (Cotton and Wilkinson, 1980). For this reason isopropyl alcohol is a better organic solvent for separating copper from other metal ions by cation exchanger ion column chromatography. At isopropyl alcohol concentration corresponding to 10%, 20%, 30% and 40%-3.0 M HNO₃ solutions, Fe(III) and Mn(II) have a higher adsorption but show practically identical behavior so that separations are impossible. In general, the sorption behavior with isopropyl alcohol solution in hydrochloric acid is similar to the previous other solvents with nitric acid solution.

Table 4 indicates the adsorption behavior of metal ions in isopropyl alcohol-HCl media can be divided into different groups, at constant acidity of HCl 0.1 M. One group of metal ions is increased with increasing of solvent, such as Mg(II), the other group of metal ions could not be determined with Pb(II) ion, and finally Mn(II), Fe(III), Zn(II) and Cd(II) ions show no change in K_d -values with the increase in isopropyl alcohol concentration. However the sorption of metal ions decreases rather strongly with increasing concentration of HCl, i.e., an increase in HCl concentration from 0.1 to 3.0 M considerably lowers the sorption which tends to be zero for Cd(II), Zn(II), Fe(III), Mn(II) and Mg(II). This change becomes more pronounced as the ability of the elements to form negatively charged ions increases (chiefly negative halo-complexes) (Sterolow, 1960; Cotton and Wilkinson, 1980; Korkisch and Klakil, 1964; Janauer et al., 1971; Fritz and Rettig, 1966).

3.3.5. In case of acetone–HNO₃ media

In partly non-aqueous solutions of nitric acid concentration in the cation exchanger; there are two factors that are causing an increase or decrease in the value of partition coefficients. The first one is an increase in nitric acid concentration while, the second one is an increase in the proportion of acetone by volume in the aqueous solutions. In general, the results of measurement of the partition coefficients of various elements in nitric acid are found to be the same as that observed in previous organic solvents. Therefore, no separation of the elements employed is possible in nitric acid–acetone systems.

3.3.6. In case of acetone–HCl media

Table 5 shows that the differences of the K_d -values for metal ions with increasing of hydrochloric acid and acetone percentage in water medium are obvious up to of 0.5 M HCl. After these concentrations the K_d -values are zero for Cd(II), Mg(II) at 40% (v/v) and also for Fe(III) in presence of all percent of acetone–1.0 M HCl media. Zero K_d -values at 3.0 M HCl–acetone media for all metal ions under investigation. Only Mn(II) shows 2.31 values of K_d at 40% acetone and at 1.5 M HCl in 30% (v/v). Moreover, the acetone–HCl media offer a useful indication for regarding the exchange trend as compared with isopropyl alcohol except for Cu(II), i.e., as increasing the proportion of acetone, the adsorption of the metal ion of Cu(II) by exchanger increases then decreases at certain concentration of acetone media. On the contrary, the K_d -values of Fe(III) ions remain constant in the range of 10–40% (v/v) acetone–0.1 M HCl media as shown in Table 5. The large decrease in adsorption by the resin has been shown at high hydrochloric acid concentration for most of elements reach to zero values of K_d this is attributed to the formation of chlorides-complexes, which are less held strongly by the resin.

The mechanism of the adsorption is based on the chelating between the metal ion and the chelating group of the sulfonated agent in the located resin. The absorption of the chelating agent on the resin is based on both mainly, the exchange and partly molecular adsorption. Therefore, the adsorption of the chelating agent molecule took place by the aid of its chelating group. Such organic solvents, nitric or hydrochloric acids have been taken into consideration (Cotton and Wilkinson, 1980; Fritz and Rettig, 1966; Badawy et al., 2009). However, in the process of the adsorption of metal ion, the chelating group must be free from the resin matrix to form metal legend in the resin phase. Moreover, it might be predicted that not all the chelating groups present in the loaded resin were available for total adsorption. This prediction is proved by the fact that the total adsorption is expected from the values of the total loaded amount of chelating agents as previously presented in Tables 2–5.

4. Separation techniques

The prepared resin column is 50 cm long and 1.2 cm diameter. It was first washed with 0.05 M HCl or nitric acids and then with de-ionized water several times till neutral. A mixture of Fe(III) with K_d -zero and Zn(II) with K_d -51.67 solutions in 20% (v/v) tetra hydro furan–1.0 M HCl with an equal amount of an equivalent resin was taken. Sixty millilitres of the mixture, described before, was then passed through the column at flow rate of 0.3 ml/min. This volume is enough quantitatively to elute out Fe(III). Zn(II) was next eluted with 90 ml of 2.0 M HCl solution. The concentration of Fe(III) and Zn(II) were determined volumetrically with EDTA using suitable indicators. Table 6 shows that the elution percent for the

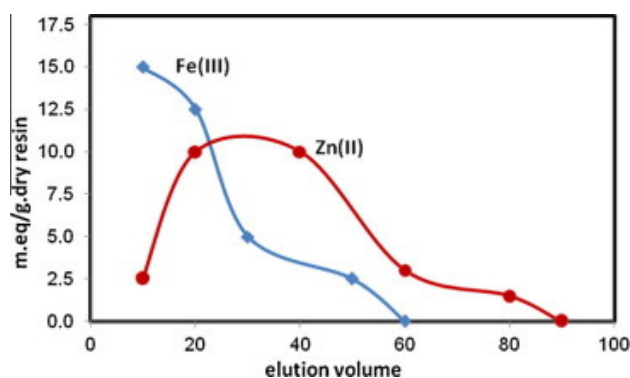


Figure 3 Elution curve of a Fe(III) and Zn(II) separation; 20% tetrahydrofuran–1.0 M HCl for Fe(III) and 2.0 M HCl solutions for Zn(II).

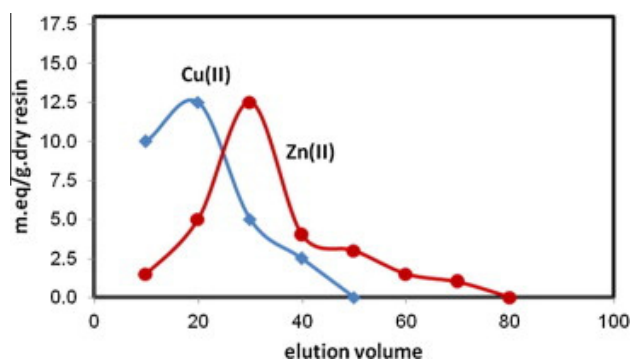


Figure 4 Elution curve of a Cu(II) and Zn(II) separation; 10% dimethylsulfoxide–1.0 M HCl for Cu(II) and 2.0 M HCl solutions for Zn(II).

Table 6 Recovery (%) of metal ions in binary system.

Amount found		Amount taken (m.equiv/g)	Eluting agent	System
%	m.equiv			
98	35.77	36.5	20% THF–1.0 M HCl	1 – Fe(III)
97	26.96	27.8	2.0 M HCl	2 – Zn(II)
93	29.99	32.2	10% DMSO–1.0 M HCl	1 – Cu(II)
96	33.60	35.0	2.0 M HCl	2 – Zn(II)

separation of Fe(III) and Zn(II); taken in an amount 36.5 mequiv. (98%) and 27.8 mequiv. (97%), respectively (Fig. 3). The same procedure was used for the separation of Cu(II) and Zn(II) ions as presented in Fig. 4. For the separation of Cu(II), 10% (v/v) dimethyl sulphoxide–1.0 M HCl is used, whereas for Zn(II), 2.0 M HCl solution only was enough for its separation. Table 6 shows that the elution percent for the separation of Cu(II) and Zn(II); taken in an amount 32.2 mequiv. and (93%) in case of Cu(II) and 35 mequiv. and (96%) in case of Zn(II) (Aboul-Magd et al., 1988; Sterolow, 1960; Cotton and Wilkinson, 1980; Korkisch and Klakil, 1964; Janauer et al., 1971; Fritz and Rettig, 1966; Badawy et al., 2009).

5. Conclusion

In this study, the effects of parameters such as effect of acid concentrations, metal ion concentrations, organic solvents in different proportions and partition coefficients studies have been investigated. The work evaluates the effect of nitric and hydrochloric acids in different concentrations in presence of DMSO, THF, isopropyl alcohol and acetone for removing pollutant elements such as Fe(III), Cu(II) and Zn(II) for the metal ions which were determined at room temperature by using Dowex HRWX₂-Na Polisher resin. The partition coefficients would be useful for developing an appropriate technology for designing a wastewater treatment. Detailed studies will be needed for further evaluation of ion exchange resin in the treatment of the legacy of the factories that are thrown in rivers.

References

- Aboul-Magd, A.S., Mohamed, F.H.K., Hassan, E.A., El-Sabbah, M.M., Ebaid, A.E., 1988. Determination of distribution coefficients of divalent metal ions in aqueous and aqueous-organic mixed solvents on the styrene-butadiene phenol-formaldehyde cation exchangers. *J. Indian Chem. Soc.* 25A, 1097–1101.
- Apiratkul, R., Pavasant, P., 2008. Sorption of Cu(II), Cd(II) and Pb(II) using modified zeolite from coal fly ash. *Chem. Eng. J.* 144, 245–258.
- Badawy, N.A., El-Bayaa, A.A., Abdel-Aal, Y., Garamon, S.E., 2009. Chromatographic separations and recovery of lead ions from a synthetic binary mixtures of some heavy metal using cation exchange resin. *J. Hazard. Mater.* 166, 1266–1271.
- Cotton, F.A., Wilkinson, G., 1980. *Advanced Inorganic Chemistry*, fourth ed. John Wiley and Sons.
- Erdem, E., Karabiner, N., Denat, R., 2004. The removal of heavy metal cations by neutral zeolite. *J. Colloid Interf. Sci.* 280, 309–314.
- Fritz, J.S., Rettig, Th.A., 1966. Separation of metals by cation exchange in acetone–water–HCl. *Anal. Chem.* 35, 1562–1567.
- Gode, F., Pehlivan, E., 2006. Removal of Cr(II) from aqueous solutions using Lewatite S 100. *J. Hazard. Mater. B* 136, 330–337.
- Hellferich, F., 1962. *Ion Exchange*. McGraw-Hill Book Company, New York/San Francisco/Toronto/London, pp. 91–94.
- Janauer, G.E., Korkisch, J., Hubbard, S.A., 1971. Cation exchange separation of uranium in dimethyl sulphoxide. *Talanta* 18, 767–772.
- Karthikeyan, G., Andal, N.M., Anbalagan, K., 2005. Adsorption studies of Fe(III) on chitin. *J. Chem. Sci.* 117 (6), 663–672.
- Kendüzler, E., Turker, A.R., Yalcinkaya, O., 2006. Separation and pre-concentration of trace manganese from various samples with flame atomic adsorption spectrometry. *Talanta* 69, 835–840.
- Korkisch, J., Ahlawalia, S.S., 1966. Separation of large amounts of Fe(III) from Co(II), Ni(II) and Al(II) by combined ion exchange solvent extraction. *Anal. Chem.* 34, 308–313.
- Korkisch, J., Ahlawalia, S.S., 1967. Cation exchange behavior of several elements in HCl–organic solvent media. *Talanta* 14, 155–170.
- Korkisch, J., Klakil, E., 1964. Cation exchange behavior of several elements in HBr–organic solvent media. *Talanta* 16, 377–391.
- Lakshmi, N., Srinivasan, K., 2004. Removal of Ni(II) from water by agricultural waste: cotton seed (CIBA pentadra). *Ori. J. Chem.* 20 (3), 482–492.
- Lin, S.-H., Juong, R.-S., 2000. Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: a review. *J. Environ. Manage.* 90, 1336–1349.
- O'Connell, D.W., Birkinshaw, C., Dwyer, Th.F., 2008. Heavy metal adsorbents from modification of cellulose: a review. *Bioresour. Technol.* 99, 6709–6724.
- Phillips, D.H., Watson, D.B., Pamela, C.S., 2007. Uranium removal from contaminated ground water by synthetic resins. *Water Res.* 42, 4450–4457.
- Srivastava, V.C., Mall, I.D., Mishra, I.M., 2009. Competitive adsorption of Cd(II) and Ni(V) metal ions from aqueous solution onto rice husk ash. *Chem. Eng. Process.: Process Intens.* 48, 370–379.
- Sterolow, F.W.E., 1960. An ion exchange selectivity scale of cations based on equilibrium distribution coefficients. *Anal. Chem.* 32, 1185–1188.
- Vaughan, T., Seo, Ch.W., Marshall, W.E., 2004. Removal of selected metal ions from aqueous solution using modified corn-cobs. *Bioresour. Technol.* 78, 133–139.
- Vogel, A.I., 1966. *A Text Book of Quantitative Inorganic Analysis*, third ed. Longman/Green, London, pp. 415–441.
- Wan Ngah, W.S., Hanafiah, M.A.K.M., 2008. Removal of heavy metal ions from waste water by chemically modified plants as adsorbents: a review. *Bioresour. Technol.* 99, 3935–3948.
- Wang, H.L., Joing, W.F., 2007. Adsorption of di-nitro butyl phenol from aqueous solution by fly ash. *Ind. Eng. Chem. Res.* 46, 5405–5411.