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Separation of toxic Pb^{2+} metal from aqueous solution using strongly acidic cation-exchange resin: analytical applications for the removal of metal ions from pharmaceutical formulation

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ABSTRACT

A strongly acidic cation-exchange resin Amberlite IR-120 was successfully used for the separation of toxic metal ions. The distribution coefficient values for various metal ions were performed in different acidic mediums using Amberlite IR-120 resin columns. On the basis of distribution coefficient values, Amberlite IR-120 was found to be selective for Pb^{2+} ion. A number of important quantitative binary separations of metal ions viz. Cd^{2+}– Pb^{2+}, Hg^{2+}– Pb^{2+}, Cu^{2+}– Pb^{2+}, Zn^{2+}– Pb^{2+}, Cd^{2+}– Al^{3+}, and Mg^{2+}– Al^{3+} were achieved on the columns of this resin. In order to demonstrate the practical utility of these separations, Mg^{2+} and Al^{3+} were determined in commercially available pharmaceutical preparation namely digene using Amberlite IR-120 resin columns. The regeneration studies were carried out which demonstrated a decrease in the recovery of Pb^{2+} from 88 to 74% after five consecutive cycles.

Keywords: Cation-exchange resin; Amberlite IR-120; Separations; Metal ions; Pharmaceutical formulation

1. Introduction

The indiscriminate industrialization and uncontrolled discharge of industrial waste–containing heavy metals has depleted the water quality. The presence of high level of toxic heavy metals in the environment produces considerable adverse effects, not only to the plants and the animals but also to the human being due to their toxicity and nonbiodegradability [1–6]. Toxic heavy metals have no known metabolic or beneficial function on organisms. Therefore, the accumulation of these toxic metals over time in the bodies of living organisms can cause severe damage. It is also known that unlike most organic pollutants, heavy metals are generally refractory and cannot be degraded or readily detoxified biologically [3]. Among various heavy metals; mercury, lead, cadmium, arsenic, chromium, and copper are main toxic metal ions [7,8]. Exposure of humans to heavy metal pollution may occur naturally or by human anthropogenic sources that may include erosion of surface deposits of metal minerals, mining of coal and natural gas, smelting, fossil fuel combustion and industrial application of metals, production of paper, plastics, electroplating and the manufacture of lubricants and chloralkali [9]. The individual affected with heavy metal toxicity may experience symptoms like chronic muscle pain, memory loss, chronic malaise, high blood

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pressure, sleep disabilities, brain fog, chronic infections, such as candida, gastrointestinal complaints such as diarrhea, constipation, bloating, gas, heartburn, indigestion, food allergies, attention/concentration deficits, dizziness, migraines and/or headaches, visual disturbances, mood swings, depression, anxiety, and other nervous system malfunctions [9]. Thus, the removal of toxic heavy metals is the major course that cannot be ignored. Therefore, reliable methods are necessary for the removal of heavy toxic metals from aquatic environment. In recent years, various methods have been developed for the removal of heavy metals from wastewater. Chemical precipitation, solvents extraction, reverse osmosis, adsorption, ion exchange, membrane separation, electrodialysis, etc. are the most widely used techniques for the removal of heavy toxic metals from wastewater streams [10]. Among these techniques, ion exchange and adsorption are the main and cost-effective methods for the removal of metal ions [11–23]. In recent years, researchers have used several types of adsorbents for the removal of metal ions and other pollutants from aqueous medium. Ion-exchange resins have been developed as a major option for the treatment of wastewaters from the last few decades [24–28]. Ion-exchange resins are useful because of the insolubility of the resin phase. After contact with the ion-containing solution, the resin can be separated by filtration. Their insolubility renders them environmentally compatible since the cycle of loading/regeneration/reloading allows them to be used for many years. The hydrogen ions released from the cationic ion exchange resin neutralize the hydroxide ions, so that the equilibrium shifts until all the metal ions are leached into solution and adsorbed onto the ion-exchange resin [29]. Ion-exchange resins have been used for water softening, the removal of toxic metals from water in the environment, wastewater treatment, hydrometallurgy, sensors, chromatography, and biomolecular separations [30].

This work was undertaken in an attempt to explore the use of a strongly acidic cation-exchange resin Amberlite IR-120 for the removal of Pb^{2+} from aqueous system. This resin was successfully used for the separation of Mg^{2+} and Al^{3+} quantitatively from a pharmaceutical formulation, namely Digene. Amberlite IR-120 was effectively used up to five consecutive cycles without any appreciable loss in the percent adsorption of Pb^{2+}.

2. Experimental

2.1. Reagents and instruments

Amberlite IR-120 (H^+) resin was purchased from B.D.H Chemicals Ltd., Poole England. All other reagents and chemicals were of analytical reagent grade. One percent ethanolic solution of 1-[1-hydroxy-2-napthol azo]-5-nitro-2-napthol-4-sulfonic acid sodium salt (Eriochrome black T), 1-[2-prydylazo]-2-napthol (PAN) and 1% aqueous solution of o-cresolsulfonapthalein 3′-3 bis[methyliminodiacetic acid sodium salt] (Xylenol orange) were used as indicator, and 0.01 M solution of disodium salt of ethylene diaminetetraacetic acid (EDTA) was used as titrant. The standard stock solutions of metals were prepared by dissolving appropriate amounts of their corresponding nitrate salts in Milli-Q water except Mn^{2+} and Fe^{3+} for which chloride salts were used. The preconditioning of Amberlite IR-120 resin was performed by washing it with Milli-Q water for three times to remove the adhered impurities from resin surface followed by drying in oven at 40˚C for 10 h. The dried resin was stored in desiccator until used.

Shaker cum incubator (SW22/9550322, Julabo, Germany), Electronic balance (Verbal 100 Super, India), and pH meter (Orion 2 star, Thermo Scientific, USA) were used.

2.2. Distribution coefficient (K_d) of metal ions

In order to get an idea about the partition behavior of Amberlite IR-120 resin for various metal ions of analytical interest, distribution coefficient (K_d) values of different metal ions were determined by batch method in different acidic mediums. Distribution coefficients were actually used to access the overall ability of the material to remove the ions of interest under different sets of conditions. Various portions of (300 mg each) the Amberlite IR-120 resin (H^+ form) were taken in Erlenmeyer flasks and mixed with 30 mL of the above metal salt solutions in the required medium and subsequently shaken for 4 h in temperature-controlled shaker at 25 ± 2˚C to attain the equilibrium. The amount of metal ion before and after the equilibrium was determined by EDTA titration. The distribution coefficients were calculated using the equations.

$$K_d = \frac{\text{Amount of metal ion retained in one gram of the resin (mg g}^{-1}\text{)}}{\text{Amount of metal ion in unit volume of the supernatant solution (mg mL}^{-1}\text{)}}$$

$$K_d = \frac{(I - F)/300\ \text{mg}}{F/30\ \text{mL}}$$

where I is the initial amount of the metal ion in the solution phase, and F is final amount of metal ion in the solution phase after treatment with the resin.

2.3. Removal study of Pb^{2+} ion by batch experiment

2.3.1. Effect of contact time

The equilibration time for maximum adsorption of Pb^{2+} ion on Amberlite IR-120 resin was established by performing a series of adsorption experiments. About 0.5 g Amberlite IR-120 resin was stirred with a known amount of lead(II) nitrate solution for 10–60 min. The amount of Pb^{2+} ion before and after adsorption was determined by titration against the standard solution of 0.01 M di-sodium salt of EDTA.

2.3.2. Effect of pH

To study the effect of pH on the adsorption of Pb^{2+} ion, 0.5 g Amberlite IR-120 resin was shaken continuously with a known amount of lead(II) nitrate solution for 40 min at pH 1–10. The pH of the solution was adjusted by adding acid, base or buffer of desired pH. The amount of Pb^{2+} ion before and after adsorption was determined by the above method.

2.3.3. Effect of temperature

To determine the effect of temperature on the adsorption of Pb^{2+} ions, 0.5 g Amberlite IR-120 resin was equilibrated with lead(II) nitrate solution for 40 min at pH 6 and temperature was varied from 25 to 65℃. The amount of Pb^{2+} ion before and after adsorption was determined by the above method.

2.3.4. Effect of Amberlite IR-120 resin dose

To determine the effect of Amberlite IR-120 resin dose for the removal of Pb^{2+} ion, different amount (0.2–1.0 gm) of Amberlite IR-120 resin was stirred with a known amount of lead(II) nitrate solution for 40 min at pH 9 and 45℃ temperature. The amount of Pb^{2+} ion before and after adsorption was determined following the aforementioned procedure.

2.4. Quantitative binary separation of metal ions

Quantitative binary separations of metal ions were performed by column method using elution technique. About 0.5 g Amberlite IR-120 resin in H^+ form was packed in a glass column having internal diameter of 0.6 cm and a height of 35 cm with a glass wool support at the end. The column was washed 2–3 times with demineralized water. 2.0 mL binary mixture of the metal ions to be separated was poured on to the column and allowed to flow at a rate of 0.5 mL min^{-1}. The column was rinsed with demineralized water to ensure complete absorption of metal ions. Metal ions absorbed by the resin were eluted at a constant flow rate of 0.5 mL min^{-1} using appropriate eluting reagents. The effluent was collected and metal content determined titrimetrically using disodium salt solution of 0.01 M EDTA as a titrant.

2.5. Selective separation of Pb^{2+} from a synthetic mixture of Al^{3+}, Pb^{2+}, Mn^{2+}, Hg^{2+}, Mg^{2+}, and Cd^{2+}

About 0.5 g Amberlite IR-120 resin in H^+ form was packed in a glass column with glass wool support. The column was washed with Milli-Q water, and the mixture solution containing metal ions was applied. Different sets of synthetic mixtures of metal ions solution were taken in which the amount of Pb^{2+} was varied, and the amount of rest metal ions was kept constant. The solution was allowed to flow down at the rate of 0.5 mL min^{-1}. The mixture of metal ions, namely Al^{3+}, Mn^{2+}, Hg^{2+}, Mg^{2+} and Cd^{2+}, eluted together first and Pb^{2+}, which was retained strongly by the Amberlite IR-120 resin, eluted at last. The effluent was collected in 10 mL fractions and titrated with standard 0.01 M EDTA solutions.

2.6. Determination of metal ion contents in pharmaceutical preparation

One tablet of antacid (Digene) containing 103.85 and 8.82 mg of elemental aluminum and magnesium, respectively, was treated with 10 mL concentrated HCl, filtered, and the clear filtrate obtained was diluted to 50 mL with demineralized water. About 1.0 mL of this solution was evaporated just to dryness, and the residue was digested with 1–2 mL demineralized water. This extract of pharmaceutical sample was applied to the column (i.d. 0.6 cm) containing 0.5 g Amberlite IR-120 resin in H^+ form was allowed to flow down the column slowly to ensure complete adsorption of the metal contents. Mg^{2+} was eluted first and Al^{3+} at last using 0.01 HNO_3 solution. The rate of elution was kept constant (0.5 mL min^{-1}) throughout the elution process. The metal contents of the effluent were determined titrimetrically using 0.01 M EDTA solution as titrant.

2.7. Desorption and regeneration studies

Desorption and regeneration studies were also carried out by batch process. Hundred milliliters of 10 mg L^{-1} Pb^{2+} solution was treated with 0.5 g Amberlite IR-120 in conical flask in a temperature-controlled shaker incubator for 1 h. After 1 h, Amberlite IR-120 was washed several times with Milli-Q water to remove excess of Pb^{2+}. Then, Amberlite IR-120 was treated with 100 mL of 0.01 M HNO_3 solution in other flask. The flask was again shaken in temperature-controlled shaker incubator (to desorb Pb^{2+}) for 1 h. The solution was then filtered with Whatman filter No. 41, and the filtrate was titrated against 0.01 M EDTA solution to check the desorbed Pb^{2+}. The desorption studies of Pb^{2+} was also carried out in several other acids (0.01 M formic acid, 0.01 M acetic acid, and 0.01 M succinic acid) by following the aforesaid procedure.

For the regeneration study, 0.5 g of Amberlite IR-120 was saturated with 100 mL of 10 mg L^{-1} Pb^{2+} solution for 1 h. After 1 h, Amberlite IR-120 was washed several times with Milli-Q water to remove excess of Pb^{2+}. To regenerate the spent Amberlite IR-120, it was treated with 100 mL of 0.01 M HNO_3 solution. The same procedure was repeated for five consecutive cycles.

Table 1
Distribution coefficient (K_d) of metal ions on IR-120 cation exchange resin columns in different acidic mediums

Metal ions	Milli-Q water	Nitric acid (0.01 M)	Formic acid (0.01 M)	Acetic acid (0.01 M)	Succinic acid (0.01 M)
Mg^{2+}	348	15	66	126	190
Ca^{2+}	1,068	366	446	691	720
Sr^{2+}	2,015	782	913	1,230	1,433
Ba^{2+}	2,182	1,004	1,133	1,566	2,086
Hg^{2+}	532	120	178	194	324
Cd^{2+}	456	120	166	183	216
Cu^{2+}	3,215	558	1,220	1,356	2,233
Ni^{2+}	3,165	1,182	1955	2,600	3,012
Co^{2+}	1,948	295	942	1,268	1,746
Mn^{2+}	2,215	315	1,133	1,296	1,323
Zn^{2+}	3,215	1,095	1,983	2,233	2,363
Pb^{2+}	8,159	2,195	2,677	3,243	5,180
Fe^{3+}	4,782	580	1,382	2,034	4,234
Al^{3+}	3,882	705	1,430	2,564	3,576

3. Results and discussion

In order to explore the separation potentiality of Amberlite IR-120 cation-exchange resin for the separation of metal ions, distribution coefficients (K_d) of several metal were performed in Milli-Q water, 0.01 M nitric acid, 0.01 M formic acid, 0.01 M acetic acid, and 0.01 M succinic acid. It is apparent from Table 1 that all metal ions had the lowest K_d values in nitric acid medium in comparison with other acidic mediums. It was due to the presence of high concentration of H^+ ions in nitric acid medium which reversed the process of adsorption and the process of regeneration predominated over the process of removal [31]. The order of K_d values of alkaline earth metal ions was $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. This sequence was in accordance with the hydrated ionic radii. The ions with smaller hydrated radii easily enter the pores of resin, resulting in higher adsorption [32]. It was also noted that Pb^{2+} had the highest K_d values in all the acidic mediums as compared to other metal ions. The utility of Amberlite IR-120 to remove Pb^{2+} ion by sorption at different time, pH, temperature, and resin dose was studied. It was observed that sorption was very fast at beginning and 45% sorption took place within 5 min, and equilibrium was established after 40 min where 97% sorption was noted (Fig. 1(a)). The difference in the rate of sorption may be due to the fact that initially all resin sites were vacant so the sorption was high. Later, due to the decrease in number of vacant sites as well as Pb^{2+} concentration, the uptake rate of Pb^{2+} by Amberlite IR-120 was decreased significantly. The optimal pH for the maximum removal of Pb^{2+} ion using Amberlite IR-120 column was found to be 6 (Fig. 1(b)). At lower pH (i.e. ≤2), the removal was low. This is due to high H^+ ion concentration that reversed the process of sorption and the process of regeneration predominated over the process of removal [33]. As the pH increased, the adsorption of Pb^{2+} was also increased, and maximum adsorption took place at pH 6. After pH 6, the adsorption became constant because at pH > 6.0, the Pb^{2+} gets precipitated due to the hydroxide anions formed lead hydroxide precipitate [3]. It was also interesting to note that the uptake of Pb^{2+} ion by Amberlite IR-120 was favored with the increase in temperature up to 45˚C and after that it became constant (Fig. 1(c)). The removal of Pb^{2+} increased from 62 to 97.5% for 25–45˚C. The continuous increase in the percentage removal of Cd^{2+} up to 45˚C indicated that sorption was endothermic in nature. The effect of Amberlite IR-120 dose for the removal of Pb^{2+} ion was studied, and it was noted that the removal percentage of Pb^{2+} was increased from 62 to 96% as the dose of Amberlite IR-120 was increased from 0.2 to 0.5 g. Nonetheless, after dosage of 0.5 g, there was no any change in percentage removal of Pb^{2+} which may be due to the decrease in the total sorption surface area available for Pb^{2+} ions due to aggregation or overlapping of active sites at higher dosage. So 0.5 g of Amberlite IR-120 was

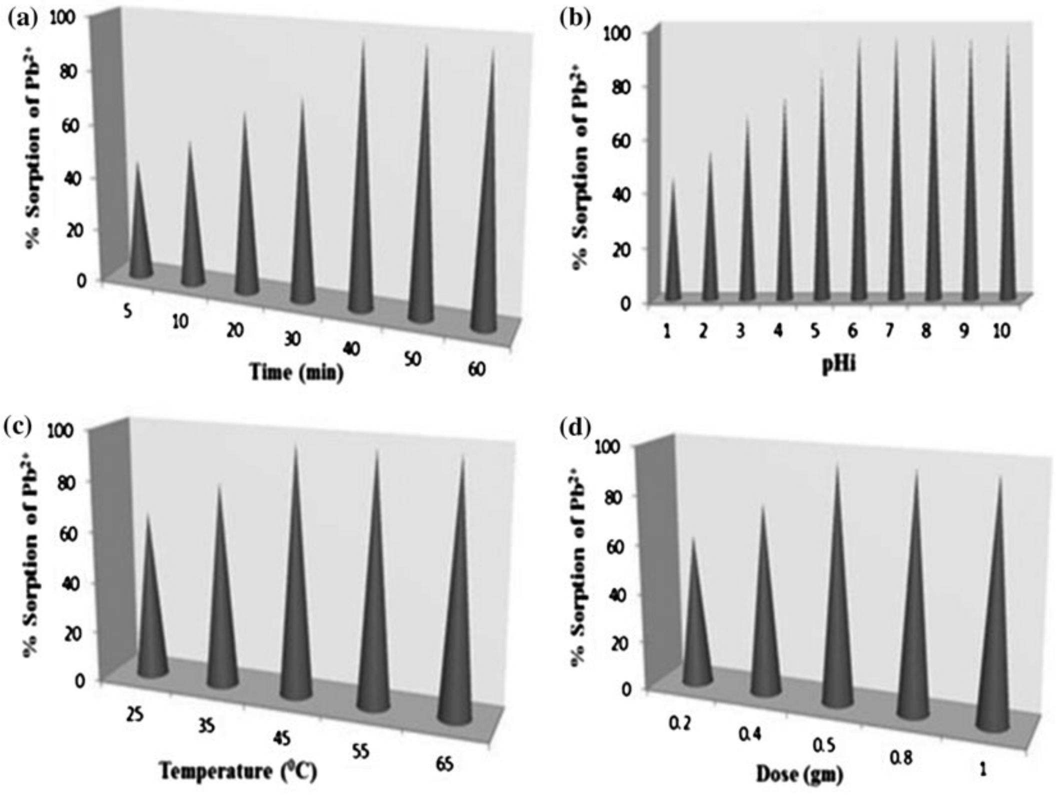


Fig. 1. Percent sorption of Pb^{2+} at different (a) time, (b) pHi, (c) temperature, and (d) resin dose.

Table 2
Binary separations of metal ions from the synthetic mixture of metal ions using Amberlite IR-120 columns

Binary mixtures	Amount loaded (mg)	Amount found[a] (mg)	% Recovery	Eluent used	Volume of eluent required for complete elution of metal ions (mL)
Cd^{2+}	11.24	10.40	92.5	0.01 M HNO_3	70
Pb^{2+}	20.72	20.10	97.0	0.01 M HNO_3	70
Hg^{2+}	20.05	19.20	95.8	0.01 M HNO_3	70
Pb^{2+}	20.72	20.10	97.0	0.01 M HNO_3	70
Cu^{2+}	6.35	5.82	91.7	0.01 M HNO_3	70
Pb^{2+}	20.72	20.10	97.0	0.01 M HNO_3	70
Zn^{2+}	6.53	5.94	90.9	0.01 M HNO_3	70
Pb^{2+}	20.72	20.10	97.0	0.01 M HNO_3	70
Cd^{2+}	11.24	10.40	92.5	0.01 M HNO_3	70
Al^{3+}	2.69	2.43	90.3	0.01 M HNO_3	70
Mg^{2+}	2.43	2.20	90.5	0.01 M HNO_3	70
Al^{3+}	2.69	2.43	90.3	0.01 M HNO_3	70

[a] Average of three replicate determinations.

considered as optimum dose and taken for further studies.

The practical efficiency of Amberlite IR-120 was demonstrated by achieving a number of binary separations of some important metal ions viz.– Cd^{2+}– Pb^{2+}, Hg^{2+}– Pb^{2+}, Cu^{2+}– Pb^{2+}, Zn^{2+}– Pb^{2+}, Cd^{2+}– Al^{3+}, and Mg^{2+}– Al^{3+}. The sequential elution of metal ions through the column depends upon the metal-ligand stability. The weakly retained metal ions eluted first and strongly retained at last (Table 2). The order of

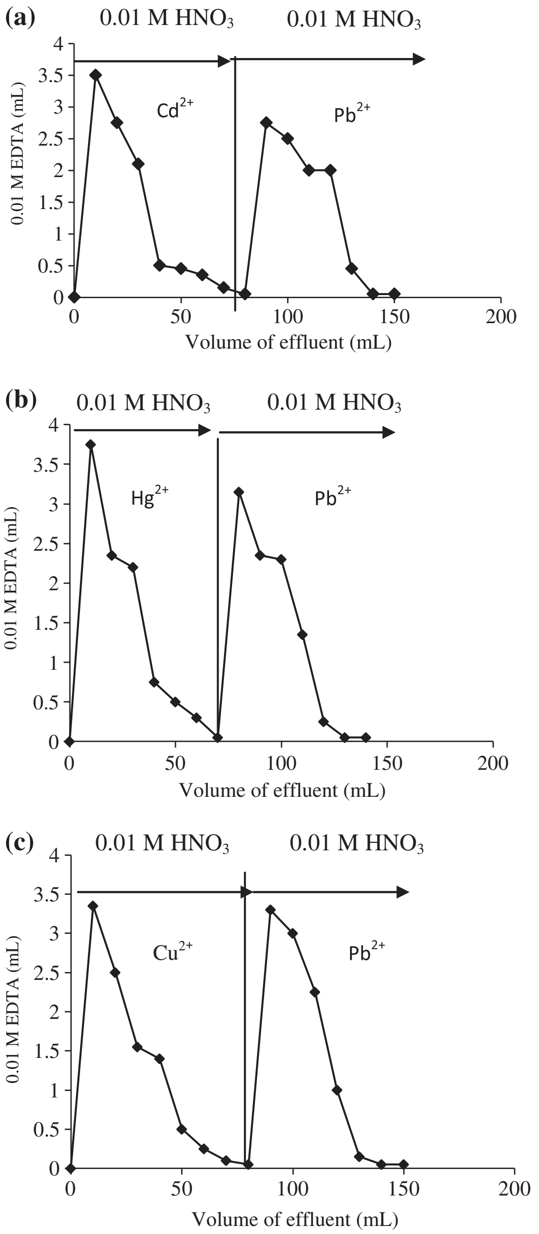


Fig. 2(a–c). Chromatograms of metal ions separations of binary mixtures (Cd^{2+}- Pb^{2+}, Hg^{2+}- Pb^{2+}, Cu^{2+}- Pb^{2+}) on Amberlite IR-120 resin columns.

elution and eluents used for each binary separation are shown in Figs. 2 and 3. Pb^{2+} was also selectively separated from a synthetic mixtures of metal ions containing Al^{3+}, Pb^{2+}, Mn^{2+}, Hg^{2+}, Mg^{2+}, and Cd^{2+} (Table 3). The utility of these separations on the columns of Amberlite IR-120 cation-exchange resin has been further demonstrated by achieving quantitative separations of Mg^{2+} and Al^{3+} contents of a commercially available pharmaceutical formulation namely digene (Table 4).

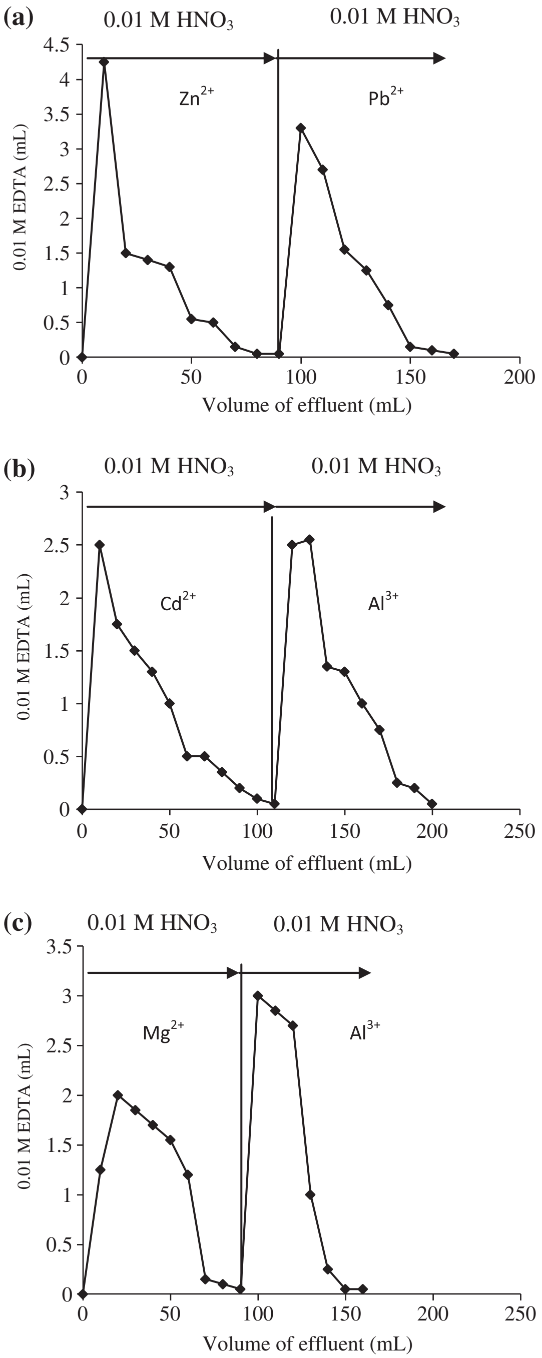


Fig. 3(a–c). Chromatograms of metal ions separations of binary mixtures (Zn^{2+}- Pb^{2+}, Cd^{2+}- Al^{3+} and Mg^{2+}- Al^{3+}) on Amberlite IR-120 resin columns.

To keep the process of sorption more economical, it is very important to regenerate the resin. Desorption and regeneration studies were carried out to check the recovery of sorbed Pb^{2+} from Amberlite IR-120 cation-exchange resin. Different types of acids were used as eluents and optimum Pb^{2+} recovery was observed by

Table 3
Selective separation of Pb^{2+} from a synthetic mixture containing Al^{3+}, Pb^{2+}, Mn^{2+}, Hg^{2+}, Mg^{2+}, and Cd^{2+} on the columns of Amberlite IR 120

Amount loaded (mg)	Amount found[a] (mg)	% Recovery	Eluent used	Volume of eluent required for complete elution of metal ions (mL)
5.18	5.05	97.5	0.01 M HNO_3	60
10.36	10.1	97.5	0.01 M HNO_3	60
20.72	20.1	97.0	0.01 M HNO_3	70

[a]Average of three replicate determinations.

Table 4
Separations of Mg^{2+} and Al^{3+} contents of pharmaceutical formulation (Digene) on Amberlite IR-120 resin columns

Binary mixtures	Amount loaded (mg)	Amount found[a] (mg)	% Recovery	Eluent used	Volume of eluent required for complete elution of metal ions (mL)
Mg^{2+}	2.0	1.78	89.0	0.01 M HNO_3	60
Al^{3+}	0.18	0.16	86.5	0.01 M HNO_3	60
Mg^{2+}	4.0	3.54	88.7	0.01 M HNO_3	70
Al^{3+}	0.36	0.31	86.0	0.01 M HNO_3	70
Mg^{2+}	6.0	5.16	86.0	0.01 M HNO_3	70
Al^{3+}	0.54	0.46	86.0	0.01 M HNO_3	70

[a]Average of three replicate determinations.

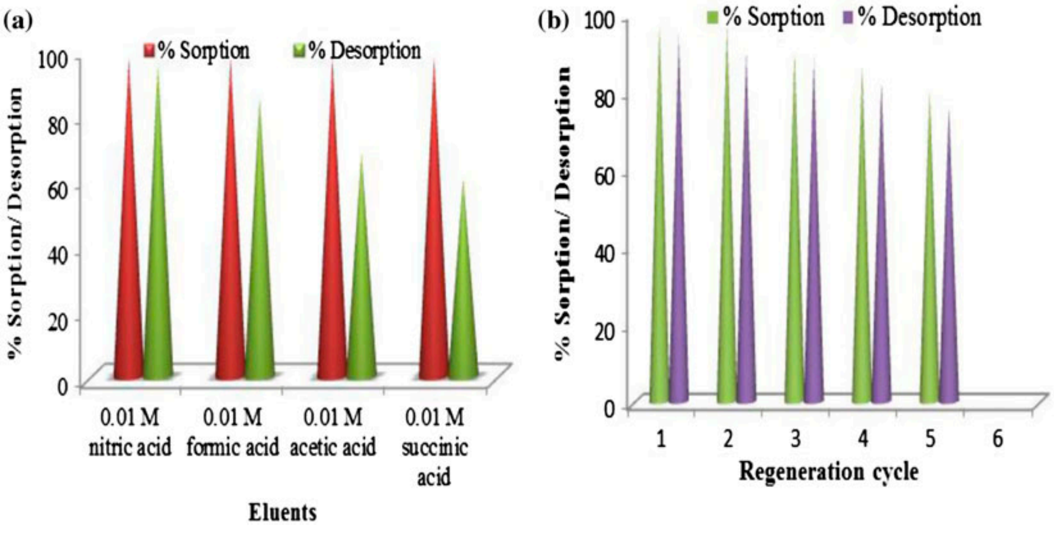
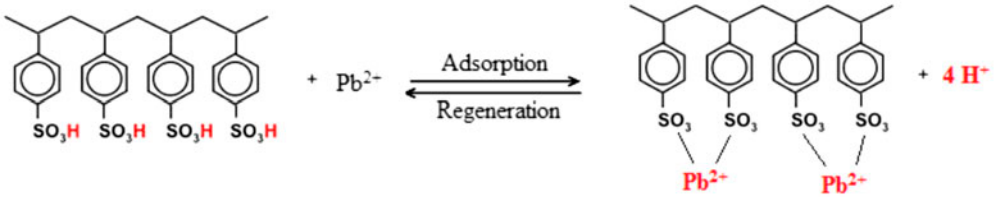


Fig. 4. Sorption/desorption studies of Pb^{2+} on Amberlite IR-120 using various eluents and batch studies to regenerate the Amberlite IR-120.

0.01 M HNO_3 (Fig. 4). Regeneration studies were conducted to check the reusability of exhausted Amberlite IR-120. It is clear from Fig. 4 that the sorption was reduced from 90 to 79% after five consecutive cycles, and the recovery was reduced from 88 to 74%. The regeneration studies showed that Amberlite IR-120 could be proficiently utilized for the removal and recovery of Pb^{2+} without any appreciable loss in the sorptive performance. The process of adsorption and regeneration was demonstrated by the following mechanism:



4. Conclusion

In this study, a strongly acidic cation-exchange resin Amberlite IR-120 was used for the separation of toxic metal ions. This resin showed the highest K_d values for Pb^{2+} ion. The sorption of Pb^{2+} by Amberlite IR-120 was very fast, and 45% sorption took place within 5 min. On the basis of distribution coefficient values, a number of binary separations of some important metal ions were achieved. Amberlite IR-120 was successfully used for the selective separation of Pb^{2+} from a synthetic mixture of metal ions containing Al^{3+}, Pb^{2+}, Mn^{2+}, Hg^{2+}, Mg^{2+}, and Cd^{2+}. The practical utility of the resin was performed by separating Mg^{2+} and Al^{3+} from a commercially available pharmaceutical formulation namely digene. The sorbed Pb^{2+} was recovered using 0.01 M HNO_3 solution and the regenerated Amberlite IR-120 was effectively used up to five consecutive cycles without any appreciable loss in the percent adsorption of Pb^{2+}.

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