Selective removal of toxic Pb(II) ion by solid phase extraction with carboxylate derivative of C_3-symmetric triphenoxy methane platform.

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Abstract

A new solid phase extraction reagent was developed by impregnating an ion-exchange ligand tris(3,5-di-*tert*-butyl-2-carboxymethoxyphenyl)methane into Amberlite SAD-7 resin. Sorption behavior of the resin towards Pb(II) and some other divalent transition metal was studied as a function of various experimental parameters by batch as well as continuous sorption experiments. The resin showed excellent selectivity for sorption of Pb(II) over other divalent metal ions. The sorption process was found to follow pseudo-second kinetics, and sorption equilibrium was fitted with Langmuir isotherms model. In continuous column experiment, traces of Pb(II) ions were selectively captured in the packed bed of the resin over excess of Zn(II) ions. The results infer that the new impregnated resin is a promising material as an efficient sorbent for selective removal of lead from contaminated streams.

Keywords:

Solid phase extraction, lead ion, selectivity, removal, column experiment

1. Introduction:

Lead is a relatively rare but toxic element. It is a constituent of some copper alloys and tin base white metal alloys. Lead chemistry is of prime interest because of its cumulative toxicity and harmful influences on animals and human health. The cumulative poisoning effect of lead causes hematological damage, anemia, kidney malfunctioning, brain damage, sore muscles, fatigue, irritation and distribution in the central nervous system [1].

Because of the presence of lead in various environmental and biological samples at low levels, designing new approaches and development of convenient and effective techniques concerning preconcentration, separation and determination of lead are necessary and have a vital importance. Obviously, trace level separation of metallic toxicant Pb(II) poses a challenging problem to the analytical chemists. The most widely used techniques for the separation and preconcentration of trace level Pb(II) include, but not limited to, liquid-liquid extraction [2-3], co-precipitation [4], ion-exchange [5], adsorption [6], reverse osmosis [7], cloud point extraction [8], electrochemical deposition [9], and solid phase extraction (SPE) [10]. Solvent extraction methods have been widely reported in the literature for separation, removal and recovery of various metal ions [11]. Conventional classical methods are frequently time consuming, harsh and labor intensive. Among the common separation techniques, solid-phase extraction has been widely used because of its various advantages such as higher preconcentration factor, lesser waste generation, lower matrix effect, easy recovery of the solid phase material and thereby more reusability [12-13]. For solid phase extraction solvent impregnated resins (SIRs) can be considered as alternative sorption active materials since they are similarly capable of selective sorption. SIRs, which combine the unique features and process advantages of liquid-liquid extraction and ion exchange, comprise a polymeric matrix impregnated with readily available liquid ionic extractant, and are relatively easy to prepare.

The concept of SIRs is based on the incorporation of an ionic liquid extraction reagent into a macroporous polymer matrix by a physical impregnation technique. The highlighted characteristics of SIRs include: i) the specificity and selectivity of readily available extractants ii) the straightforward mechanism of interaction of metal ions with liquid/liquid extractants iii) lack of third phase formation iv) the possibility of treating unclarified solutions and/ or adopting a continuous liquid - solid separation process [14-19]. Amberlite resins have been commonly used as supports for preparation of SIRs [20]. They have been designed with different characteristic of porosity. In this series, Amberlite XAD-7 is widely used for impregnation with different extractants.

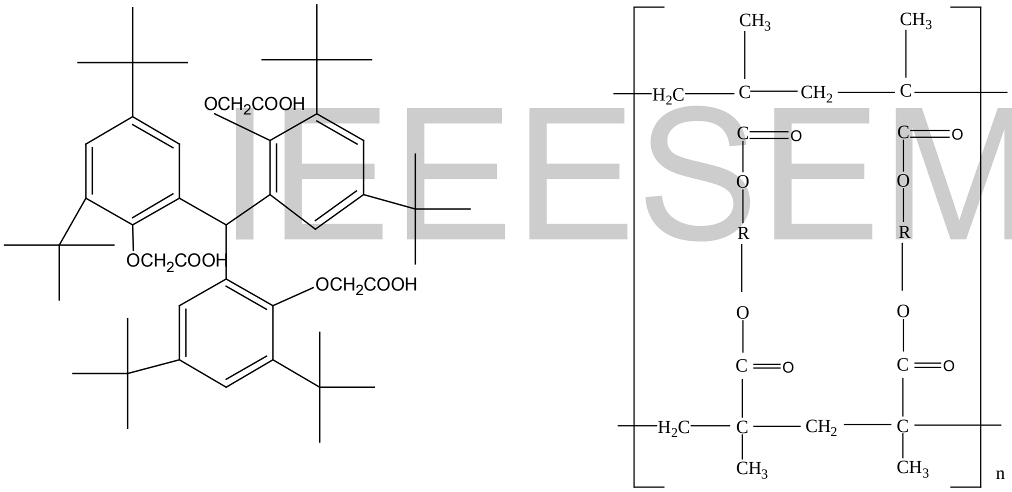
Previous work reported on the preparation of solvent-impregnated resins using various carboxylic acid derivatives of phenolic oligomers, such as cyclic hexamer, cyclic tetramer, linear trimer derived from *p*-*tert*-octylphenol impregnated in XAD-7 resin [21]. Though these resins exhibited remarkable Pb(II) selectivity, they had poor loading capacity for Pb(II). Later on, carboxylic acid derivatives of *p*-*tert*-butyl[4]arene and *p*-*H*-calix[4]arene (debutylated one) were impregnated in XAD-7, which exhibited improved Pb(II) sorption capacity [22].

In the present work, we prepared resin impregnated with carboxylic acid derivatives of tris-(3,5,di-*tert*-butyl-2-hydroxyphenyl)methane into Amberlite XAD-7 and investigated the sorption behavior of the resin towards Pb(II) ion. Selectivity behavior of the resin towards Pb(II) ion, resin's maximum Pb(II) uptake capacity and its efficiency for mutual separation of the toxic cations from the mixture of other divalent cations in dynamic sorption condition was explored.

2. Experimental

2.1. Reagents

The impregnation reagent tris phenoxy carboxylate **1** was synthesized as before [23]. Amberlite XAD-7 purchased from Organo Co., Ltd. was employed as a polymer matrix, the substance of which is acrylic ester. This resin is macroporous with interesting textural properties such as high pore volume (35-50 mesh), pore diameter (90 Å) and the surface area (450m^2/g). Before using, Amberlite XAD-7 was washed with methanol three times, followed by drying *in vacuo*. The chemical structure of the impregnated extractant and the macroporous polymer matrix are shown in Figure1.



Extractant **1**

Amberlite XAD-7

Figure 1: Chemical structures of the impregnated extractant (**1**) and macroporous polymer.

2.2. Impregnation process

The extractant-impreganated Amberlite XAD-7 resin was prepared by the dry impregnation method. In this, one gram of the extractant **1** was dissolved in analytical grade chloroform and the dried XAD-7 (3.00 g) was immersed in the chloroform solution of **1** overnight. Chloroform was then removed slowly *in vacuuo* and the resin was further dried under high vacuum.

2.3. Two-phase solvent extraction

2.4. Sorption experiments

The sorption experiments were carried out by the conventional batch method. In a typical experiment, 0.1 mM aqueous metal solution was prepared by dissolving individual metal nitrates in 0.1 M nitric acid and 0.1 M HEPES buffer solution. Both solutions were arbitrarily mixed to adjust the desired pH. To 10 cm^3 of the aqueous solution was added 0.020 g of the resin and the mixture was stirred for 24 h at 303 K. After separation of the resin by filtration, the metal concentration and pH of the aqueous solution were measured by Shimadzu ICPS 8100 ICP-AES and a pH meter, respectively.

2.5. Chromatographic separation of lead and zinc ions

In the column experiment, the aqueous feed solution was prepared by dissolving zinc and lead nitrates in dilute nitric acid solution, the pH of which was 3.9. The feed solution containing large excess of zinc (1000 ppm) and small amount of lead (10 ppm) was passed through the column packed with resin (100 mg). Glass beads (diameter = 1.3 mm) were used on either side of the packed bed of the adsorbent to provide support. After washing with distilled water, the adsorbed metal was eluted with 1 M hydrochloric acid. In both cases, the feed rate was 7.02 cm^3 h^{-1}. The metal concentrations in the collected sample solution were determined by ICP-AES.

3. Results and discussion

3.1. Two phase extractive behavior of the extractant

As a preamble to determine the selectivity and extraction profile of different divalent cations, two-phase solvent extraction behavior of the extractant **1** was performed by conventional batch method. The experimental results of pH dependency on single species extraction of Pb(II), Cu(II), Zn(II), Co(II) and Ni(II) metal ion mixture with the extraction reagent are shown in Figure 2. The selectivity order for the extraction of metal ions was Pb > Cu > Zn, Co, Ni, which resembles to that of other carboxylic acid type of extraction reagents . While extraction of Pb(II) increased significantly after pH 3.0, that of Cu(II) occurred only after pH 4.0 indicating that 1 is selective for recognition and extraction of Pb(II) over Cu(II) and other divalent cations. Extraction of these cations after pH 3.0 is in accordance to the pka of carboxylic acid and indicates that ion-exchange mechanism is taking place in the extraction.

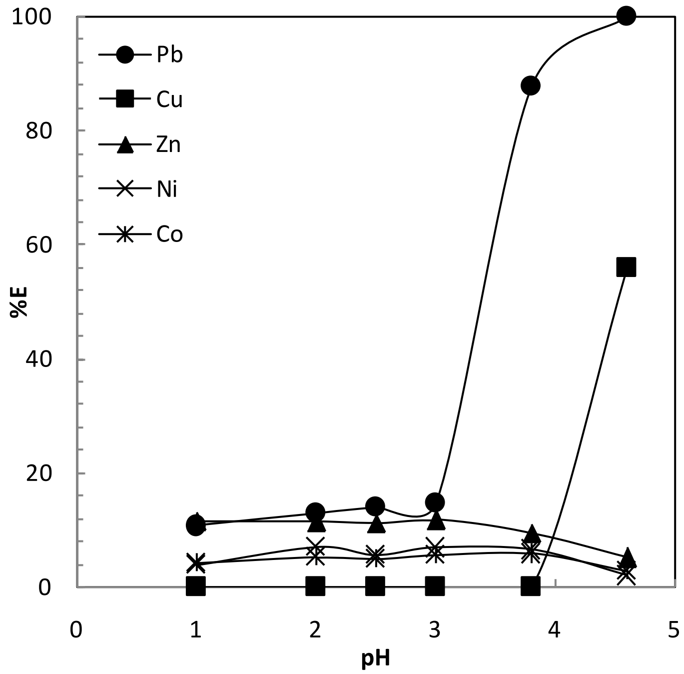


Figure2: Effect of pH on the percentage extraction of metal ions by extractant **1**. [Metal ion] = 0.1 mM, [**1**] = 5 mM, adjustment of pH = 0.1 M HNO_3 - 0.1 M HEPES buffer, shaking time = 12 h at 303 K.

3.2. Solid phase extraction of impregnated extractant

3.2.1. Effect of shaking time

The effect of contact time on the adsorption of Pb(II) ion by using impregnated XAD-7 at room temperature was investigated (Figure 3). The amount of metal ion sorbed increased sharply at the initial stages by increasing shaking time and sorption equilibrium was achieved in 24 hours shaking.

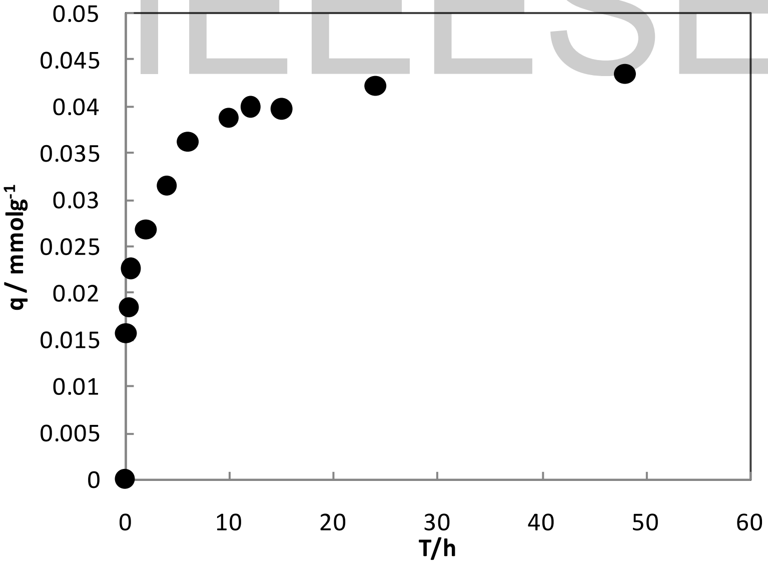


Figure3: Effect of shaking time on amount of Pb(II) sorption on impregnated resin. Weight of impregnated resin = 20 mg, initial pH = 4.40

3.2.2. Sorption kinetic modeling

Pseudo-second –order model is presented in the following equation,

$$\frac{t}{q}=\frac{1}{k_2 q_e^2}+\frac{t}{q_e} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots1$$

Plot of t/q versus t gave a linear relationship, as illustrated in Figure 4, which allows computation of q_e and rate constant, k_2. The value of k_2 was found to be 0.606 g/mmol min, and the value of the calculated q_e was found to be 0.042 mmol/g which is very close to the experimental value, and high correlation coefficient was obtained ($R^2 > 0.99$) therefore ,the pseudo-second order model was applicable for the sorption process.

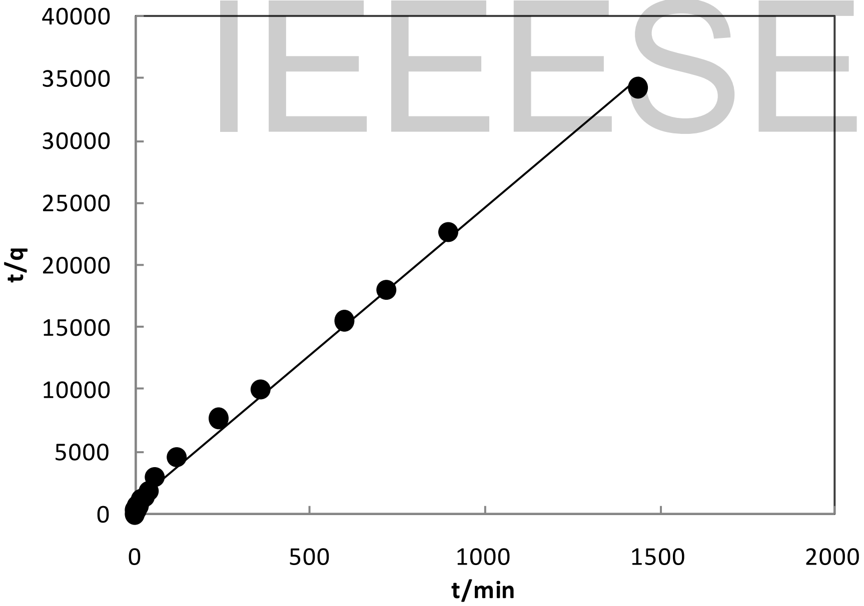


Figure4: Second order kinetics model for sorption of Pb^{2+} ion at room temperature and pH 4.40 using impregnated resin.

3.2.3. Effect of pH on sorption selectivity

The effect of pH on sorption selectivity of divalent metal ions on the present impregnated resin is shown in Figure 5a, where the percentage adsorption, %A is defined by

$$\%A = \frac{Ci - Ce}{Ci} x100 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..2$$

where, C_i and C_e are the initial and equilibrium concentrations of divalent metal ions in aqueous solution.

The selectivity order is the same as observed in solvent extraction experiments (Figure 2) and reflects that the extractant maintains the same selectivity behavior when impregnated in macroporous resin. The pH of extraction was, however, shifted to higher pH value by 0.5 unit, i.e. extraction of Pb(II) occurred after pH 3.5 and that of Cu(II) occurred after pH 4.5. This is attributable to the fact that the bulk macroporous resin is ineffective in sorption.

For comparison, the sorption behavior of polymer matrix XAD-7 alone was also evaluated (Figure 5b).. The polymeric matrix itself exhibit only poor adsorption for these metals ions. The observed very little sorption efficiency may be due to coordination from carbonyl/ester groups.

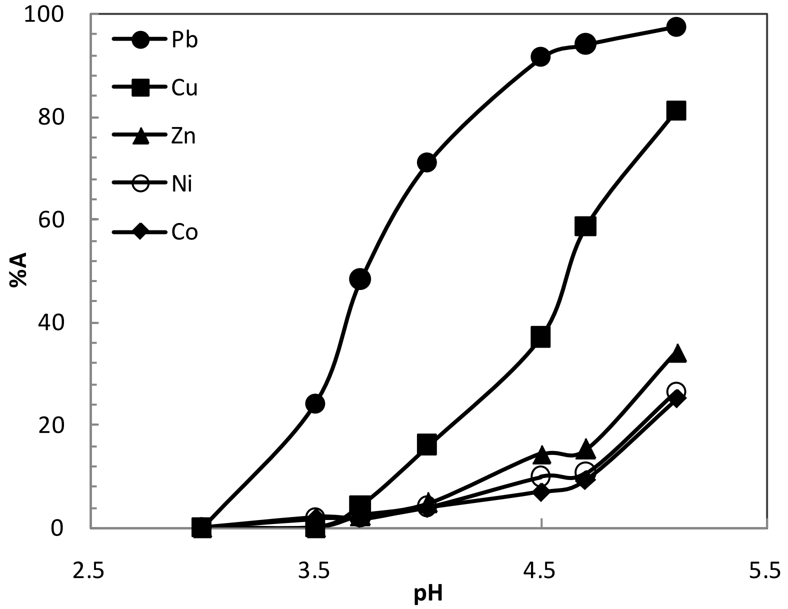


Figure5: Effect of equilibrium pH on percentage adsorption of metal ions on impregnated resin. [Metal ion] = 0.1 mM, volume of aqueous solution = 10 cm^3, weight of resin = 10 mg, shaking time = 12 h, adjustment of pH = 0.1 M HNO_3 - 0.1 M HEPES buffer.

The effect of pH on the distribution ratio of lead ion on impregnated resin is shown in Figure 6, where the distribution coefficient, K_d is defined by,

$$K_d = \frac{q}{C_e} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..3$$

Plot of log distribution coefficient; log K_d, against equilibrium pH, gave a straight line with a slope equals to 1.6 nearly equals to two, which is equal to the charge of lead. It also suggested that the adsorption phenomenon was also progressed by ion-exchange phenomenon with the proton of the carboxylic acid functional group of the extractant impregnated. The specifically high selectivity of lead is due to the presence of carboxylate oxygen atoms and forming stable complex.

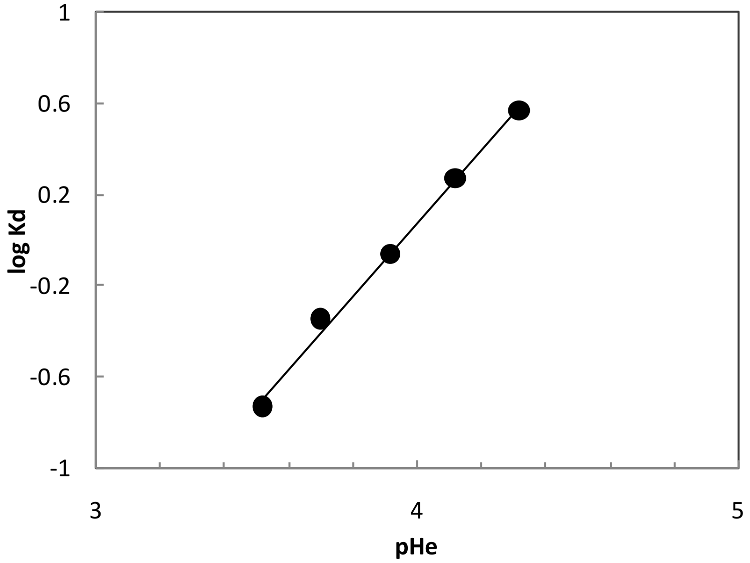


Figure6: Effect of pH on distribution ratio of lead ion. Weight of impregnated resin = 20 mg, 0.1 M HNO_3 – 0.1 M HEPES.

3.2.4. Sorption capacity

The batch method was used for the evaluation of the sorption capacity of resin for lead ions. As the resin has significant lead selectivity, the maximum lead uptake capacity of the resin was examined by equilibrating the resin with varying concentration of metal ion at constant initial pH. The quantity of lead loaded on the resin, q ($mmol \cdot g^{-1}$) was evaluated by the equation,

$$q = \frac{C_i - C_e}{W} \times V \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..4$$

where C_i and C_e are the initial and equilibrium concentrations of metal ions in aqueous solution respectively, W (mg) and V (cm^3) are weight of the resin and volume of aqueous solution respectively.

As it is obvious from the results of Figure7, the amount of lead loaded on the resin (q) increases with increasing lead concentration in low concentration region and reaches a constant value at higher concentration region. The maximum binding capacity of the resin towards lead as calculated from the plateau region of figure 7 was 0.20 mmol g^{-1}, which is comparable to our previous resin impregnating carboxylic acid derivative of calix[4]arene. The observed maximum adsorption capacity is not commendable for industrial application of the resin. However, the effective separation of Pb(II) is worth noting.

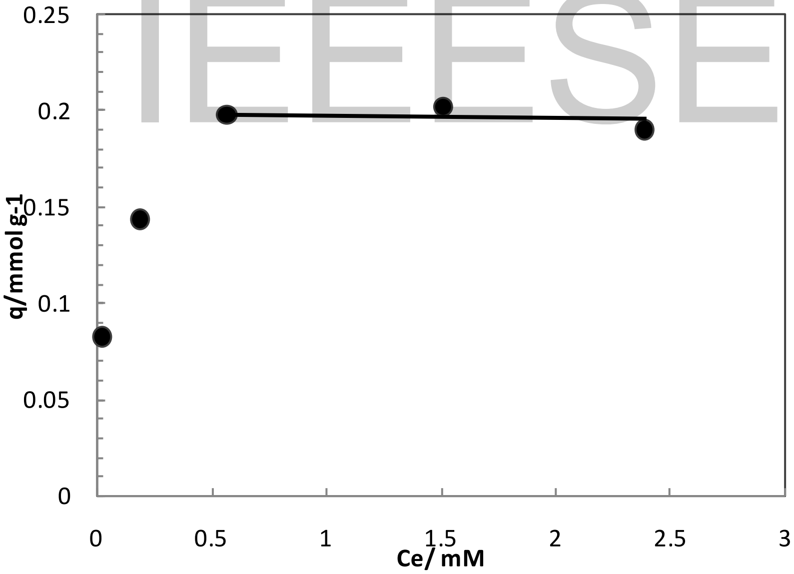


Figure7: Adsorption isotherms of lead (II) on the impregnated resins. Weight of resin = 20 mg, volume of solution = 10 cm^3, initial pH = 4.40.

The binding capacity of XAD-7 impregnated resin containing calix[3]arene was found to be 0.18 mol kg^{-1} and the stoichiometry was found to be 1:2 (lead : extractant) . One molecule of the present extractant also contain three carboxylic acid functional groups, and the stoichiometric ratio is found to be 1:1(lead: extractant) This suggest the loading of lead depends on the stoichiometric proportion of the extraction reagent impregnated.

3.2.5. Sorption isotherm modeling

Analysis of equilibrium data is important to design and optimize an operating procedure. The Langmuir equations are commonly used for describing sorption equilibrium for water and wastewater treatment applications. Langmuir isotherm is valid for monolayer sorption onto a surface containing a finite number of sorption active sites. Langmuir sorption equation based on sorption on a homogenous surface can be expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{bQ} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

where, Q is the monolayer sorption capacity, and b is constant related to the free energy of sorption. A straight line was obtained on plotting Ce versus Ce/q_e (Figure 8). The values of Q and b were determined from the slope and the intercept of the equation of the straight line, respectively.

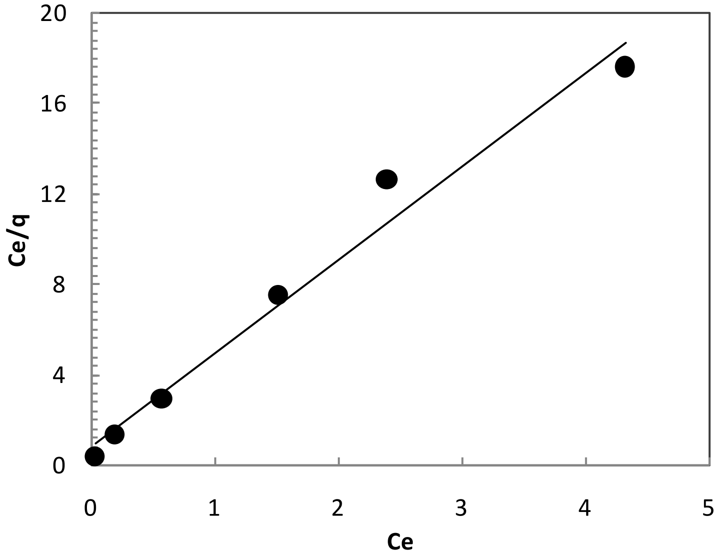


Figure8: Langmuir isotherm for adsorption of Pb^{2+} at pH 4.40.

The calculated value of Q and b from the equation of straight line of Figure 8 were 0.24 mol kg-1 and 5.1 lit/mol, respectively. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant [24], separation factor or equilibrium parameter, R_L which is defined by:

$$R_L = \frac{1}{1+bC_o} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..6$$

where, *b* is the constant related to free energy of sorption and C_o is the initial concentration. The R_L value indicates the type of isotherm, whether it is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). A plot of R_L against the increasing initial concentration (Figure 9) demonstrates that the R_L value ranges in between 0-1 indicating that the sorption of Pb(II) on the present resin is a favorable process.

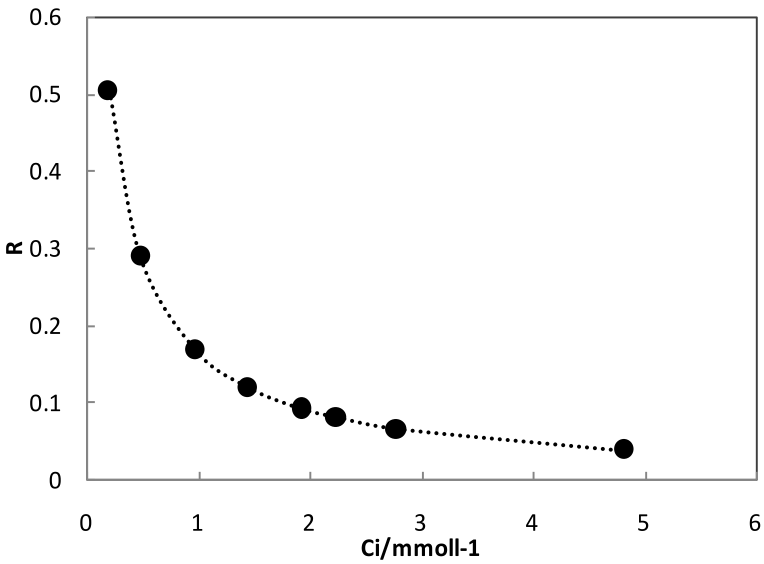


Figure 5.9: Relation between separation factor (R_L) and initial concentration of lead ion.

3.3. Chromatographic separation of Pb(II) from Zn(II)

As observed from selectivity experiment, the impregnated resin possessed good separation capacity towards lead over the other ions studied, and it was anticipated that the resin is suitable for selective removal of trace amount of lead from large amount of other metal ion present in a real industrial effluent. For example, the waste solution of zinc plating, which contains trace amount of lead ion as a toxic contaminant and it is necessary to remove traces of Pb(II) in a very selective way. By means of break through followed by elution using the column packed with the present resin, the small amount of lead should be adsorbed on the resin and get separated from the excess amount of zinc. The breakthrough profile of zinc and lead on passing the mixture through the packed bed of the resin is shown in Figure 10a. The bed volume (abbreviated as B.V.) represents the ratio of volumes for the solution passed through column and the packed resin. As can be seen in the figure, breakthrough of zinc ion took place immediately after feeding the mixture through the column without being trapped in the bed. On the contrary, the breakthrough of lead began to take place after 40 B.V. These results clearly suggested that the complete separation of trace amounts of lead from large amount of zinc was successfully achieved by using a column packed with the present resin. The elution profiles of the loaded metal ions from the column with 1M HCl are shown in Figure 10b. Sharp elution profiles for both the cations were observed at about 60 B.V. The elution profiles demonstrated that lead can be concentrated by a preconcentration factor of nearly five as compared to that of the feed solution. On the other hand, concentration of zinc in the eluted sample was six times lower than that of the feed solution indicating that the resin had almost no affinity for sorption of Zn(II) in continuous column experiemnt. These results are promising as they suggest that the present resin would be useful in achieving selective and effective removal of trace amount of lead from the polluted water and industrial streams.

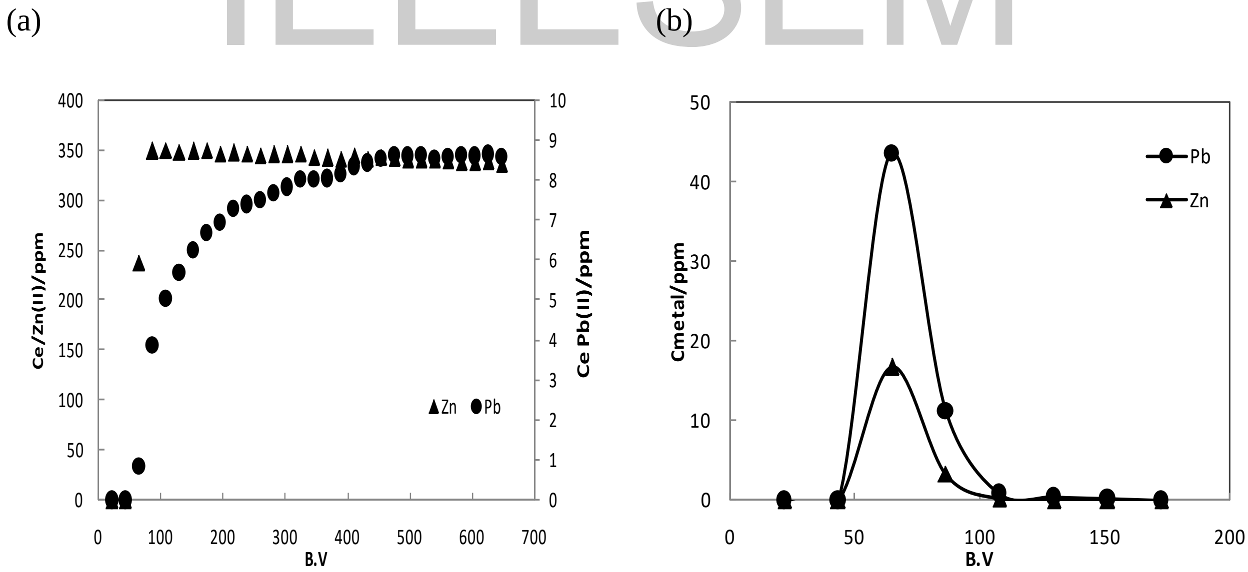


Figure10: Breakthrough (a) and elution (b) profiles of lead and zinc ions. [Pb(II)] = 10 ppm; [Zn(II)] = 1000 ppm; weight of resin = 100 mg, flow rate = 7.02 $cm^3 h^{-1}$, pH of feed solution = 3.90, eluent = 1 M HCl.

4. Conclusion

We developed a solid phase extraction material by impregnating a tricarboxylic acid ligand on Amberlite XAD-7 resin. The results obtained from sorption experiments demonstrated the effectiveness of the impregnated resin as a sorbent for selective lead removal from aqueous solution. The sorption equilibrium was described by Langmuir isotherm model, and the process followed pseudo-second order kinetics. The loaded lead was easily and completely eluted with acid solution regenerating the resin. All our results led us to conclude that Amberlite XAD-7 impregnated with a tricarboxylic acid ligand is an efficient sorbent for the removal of toxic lead ion from aqueous streams.

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