CHAPTER 3

Applicability of Cerium (IV) and Thorium (IV) Phosphates as Cation Exchangers

3.1 INTRODUCTION

Ion exchange is a process, whereby an insoluble substance removes an ion of positive or negative charge from an electrolyte solution and releases another ion of like charge into the solution in a chemically equivalent manner. The process occurs with no structural changes in the ion exchanger. At some point, during the exchange process, ion exchange equilibrium is established. A typical ion exchange occurring in water softening is presented as,

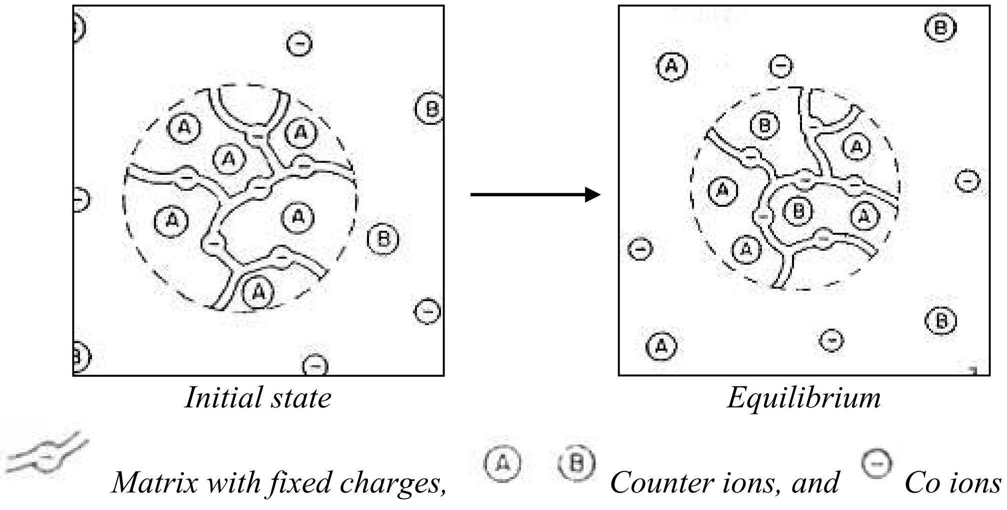
$$2\,NaR + CaCl_{2(aq)} \Leftrightarrow CaR_2 + 2NaCl_{(aq)} \qquad \textbf{(Eq. 3.1)}$$

where, R represents the structural unit of the ion exchanger. Here, the exchanger in the Na^+ form is converted to the Ca^{2+} form. Complete conversion to the Ca^{2+} form can be achieved by treating the exchanger with a sufficient excess solution of a Ca^{2+} salt.

Ion exchange is, with very few exceptions, a reversible process. In water softening, a cation exchanger which has lost all its Na^+ ions and thus has become exhausted, can be regenerated with a solution of sodium salt such as NaCl. In regeneration, the process is reversed, and the ion exchanger is reconverted to the Na^+ form. Ion-exchange equilibrium is attained when an ion exchanger (spherical ion exchanger beads of uniform size containing the counter ion A) is placed in an electrolyte solution BY, containing a counter ion which is different from that in the ion exchanger. Ion A in the exchanger is partially replaced by B expressed as,

$$\overline{RA} + B \leftrightarrows \overline{RB} + A \qquad \textbf{(Eq. 3.2)}$$

where R is the exchanger matrix and A and B are exchanging ions.**(Figure 3.1)**



Initial state *Equilibrium*

Matrix with fixed charges, *Counter ions, and* *Co ions*

Figure 3.1*Ion exchange equilibrium***[1]**

As equilibrium is approached, A ions diffuse out of the beads into the solution, and B ions diffuse from the solution into the beads. This interdiffusion of counter ions is called ion exchange.

Ion exchange is inherently a stoichiometric process. Any counter ions, which leave the ion exchanger, is replaced by an equivalent amount of other counter ions. This is a consequence of electro neutrality requirement. When a counter ion moves out into the solution, the ion exchanger is left with an electric surplus charge which it must compensate by taking up another counter ion. The total counter ion content thus remains constant, irrespective of ionic composition.

Apparent deviations from stoichiometric behaviour can occur because of electrolyte sorption and desorption which may accompany ion exchange and which change the co-ion content of the ion exchanger. Under normal conditions, however, Donnan exclusion keeps co-ions, in substantial amounts, from entering the ion exchanger during the entire process, however, this does not hinder the exchange of counter ions.

The exchange is, as a rule, reversible. Thus, it makes no difference from which side equilibrium is approached, that is, whether A is exchanged for B, or B for A. The final equilibrium distribution of the counter ions is the same in either case, provided that the amounts of all the components in the system are the same.

At equilibrium, the concentration ratios of the competing counter ion species, in the ion exchanger and in the solution are not the same. The ion exchanger prefers one species to the other. This shows that the redistribution of the counter ions is not purely statistical. The preference for one species may have several causes. The most important of these are,

a) The electrostatic interactions between the charged framework and the counter ions, depends on the size and, in particular, on the valence of the counter ion.
b) In addition to the electrostatic forces, other interactions between the ions and their environment are effective.
c) Large counter ions may be sterically excluded from the narrow pores of the ion exchanger.

The above mentioned factors depend on the nature of the counter ion and thus may lead to preferential uptake of a species by the ion exchanger. The ability of the ion exchanger to distinguish between various counter ion species is called selectivity. A theoretical background of thermodynamics of ion exchange combined with operating parameters notably temperature, pressure, concentration of electrolyte etc. is thus very important to improve selectivity, and efficiency of the exchange process. When characterizing the ion exchange properties of ion exchange materials, the feasibility and mechanism of the ion exchange process is very important.

3.2 THERMODYNAMICS OF EXCHANGE

Thermodynamics is a powerful tool to study an ion exchange reaction at equilibrium and determines feasibility of the exchange process. The importance of a thermodynamic study is its ability to predict correlations among experimental results in the absence of detailed knowledge of the structure of the system **[2]**.

The ion-exchange process occurring on the surface of an ion exchanger, can be represented by the equation:

$$2(H^+ - R) + M^{2+} \leftrightarrows M^{2+}(R)_2 + 2H^+ \quad \textbf{(Eq. 3. 3)}$$

where M^{2+} = bivalent metal ion and R = Ion exchange material.

This equation can also be written in a generalized form as:

$$\bar{C}_H + C_M \leftrightarrows \bar{C}_M + C_H \qquad \textbf{(Eq. 3.4)}$$

where the barred and unbarred quantities represent the concentrations in the exchanger and solution phases, respectively. The equivalent ionic fractions of the counter-ions in the exchanger and solution phases($\overline{X}_M$, $\overline{X}_H$, X_M and X_H) are calculated from the expressions:

$$\overline{X}_M = \frac{\overline{C}_M}{\overline{C}}; X_M = \frac{C_M}{C}; \overline{X}_H = \frac{\overline{C}_H}{\overline{C}}; X_H = \frac{C_H}{C} \qquad \textbf{(Eq. 3.5)}$$

where, $\overline{C}$ and C are the total electrolyte concentrations in the solid $\left(\overline{C} = \overline{C}_M + \overline{C}_H\right)$ and solution phases $(C = C_M + C_H)$.

For equilibrium as presented in equation - (iii), the selectivity coefficient (K_c) is calculated from the expression,

$$K_c = \frac{\overline{X}_M (X_H)^2}{\left(\overline{X}_H\right)^2 X_M} \qquad \textbf{(Eq. 3.6)}$$

The corrected selectivity coefficient (K_c') is defined by,

$$K_c{}' = \frac{\overline{X}_M (X_H)^2}{\left(\overline{X}_H\right)^2 X_M} \frac{(\gamma_H)^2}{\gamma_M} \qquad \textbf{(Eq. 3.7)}$$

where, $\overline{X}_M$ and $\overline{X}_H$ are equivalent ionic fractions of metal ions and hydrogen ions in the ion exchanger phase and X_M and X_H are equivalent ionic fractions of metal ions and hydrogen ions in solution phase, respectively. $\gamma_M$and$\gamma_H$are the activity coefficients of metal ion and hydrogen ion, respectively, in the solution phase and n is the valence of the metal ion. The solution phase activity coefficients for hydrogen and metal ions are calculated using the Debye-Hückel limiting law.

$$\log \gamma_i = -AZ_i^2\sqrt{\mu_i} \qquad \textbf{(Eq. 3.8)}$$

Where, $\gamma_i$is the activity coefficient, A is a constant, the values of which have been taken from the table of Manov**[3]**, Z_i is charge of the ions and μ_i is the ionic strength. The thermodynamic equilibrium constant K is calculated at different temperatures from plots of $\ln K_c^{'}$ versus equivalent ionic fractions of metal ions in the exchanger phase$\overline{X}_M$,following the expression given byGaines and Thomas **[4]**.

$$\ln K = (Z_M - Z_H) + \int_0^1 \ln K_c^{'}\, d\,\overline{X}_M \qquad \textbf{(Eq. 3.9)}$$

where, Z_M and Z_H are charges on the competing metal and hydrogen ions. The integrals are evaluated from the areas under the curve of $\ln K_c^{'}$ versus $\overline{X}_M$ using the computer (curxpt) software.

The standard Gibbs free energy change, $\Delta G°$, is calculated from the thermodynamic equilibrium constant K, using the general equation,

$$\Delta G^o = \frac{-RT\ln K}{Z_M Z_H} \qquad \textbf{(Eq. 3.10)}$$

The standard enthalpy change, $\Delta H°$, is calculated from the van't Hoff isochor,

$$\Delta H^o = [\ln K_2 - \ln K_1]\left[\frac{T_1T_2}{T_2-T_1}\right]R \qquad \textbf{(Eq. 3.11)}$$

The standard entropy change, $\Delta S°$, is calculated using the expression,

$$\Delta S^o = \frac{(\Delta H^o - \Delta G^o)}{T} \qquad \textbf{(Eq. 3.12)}$$

where, R is the gas constant, K_1 and K_2 are equilibrium constants at the temperatures T_1 and T_2, respectively.

For an ion exchange process in aqueous medium, the most important factor is size of the cation and hence the hydrated ionic radii. Smaller the size of the cation, more heavily it is hydrated, with the result that the hydrated ionic radius is large. The values of $\Delta H°$, $\Delta G°$ and $\Delta S°$appear to be a function of the hydrated ionic radii of the exchanging metal ions.

When a solid ion exchanger is in contact with electrolyte solution, mainly two reactions may take place, either ion exchange or sorption. As physical forces are responsible for sorption, the value of equilibrium constant (K) may decrease with increasing temperature **[5-7]**. Ion exchange being a chemical reaction, some energy is required for crossing the barrier (energy of activation). In such cases therefore, as the temperature increases metal ion exchange will increase. Therefore, the interaction is temperature dependent.

The enthalpy change for an ion exchange reaction can be either of the five reasons or a net effect of these factors: (a) The heat consumed in bond breaking, as H^+ is released from the resin (b) The heat released in the formation of bonds with the incoming cation (c) The heat corresponding to the energy required for crossing the barrier (distance between exchange phase and solution phase) (d) The enthalpy change accompanying hydration and dehydration of exchanging ion in the solution (e) Introduction of a high degree of disorder into the resin matrix due to the ion exchange process. A negative enthalpy change ($\Delta H°$) indicates that the exchange reaction is exothermic and a positive enthalpy change indicates that the exchange reaction is endothermic. As dehydration is a must for ion exchange to occur, some energy must be supplied, to the cation, as it leaves the hydration sphere to undergo ion exchange **[8]**.

The entropy change ($\Delta S°$)normally depends on the extent of hydration of the exchangeable and exchanging ions along with any change in water structure around ions that may occur when they pass through the channels of the exchanger **[9]**.

In general, Gibbs free energy change (ΔG^o) values decrease with increase in temperature which shows increase in feasibility and spontaneity of the sorption/ion exchange process with rise in temperature. Negative values of $\Delta G°$ indicate that the exchange process is feasible and spontaneous in nature and attainment of a more stable energy level after ion exchange of metal ions. $\Delta G°$depends on temperature, as well as heat consumed and released during M^{2+}-H^+ exchange in terms of hydration and dehydration as well as the size of the hydrated cationic radii.

3.2.1 The Rate Determining Step

In the course of ion exchange, a counter ion A must migrate from its place within the ion exchanger into the solution. Simultaneously, a counter ion B must go the other way and occupy the place left by ion A. There is a transfer of ions in both the ion exchanger and the solution. In the bulk solution, any concentration differences are constantly leveled out by agitation. Agitation, however, affects neither the interior of the beads nor a liquid layer, which adheres to the bead surfaces. Within the beads and through this layer, the so-called “film”, transport can occur by diffusion only. Thus we come across two potential rate-determining steps:

(a) Interdiffusion of counter ions within the ion exchanger itself (particle diffusion).

(b) Interdiffusion of counter ions in the adherent films (film diffusion).

The rate controlling mechanism can be film diffusion, if the slow step is diffusion across the hydrodynamic film that surrounds the exchanger particles, or particle diffusion, if the slow step is diffusion inside the exchanger beads themselves. In the first case, a concentration gradient is set up within the liquid film, whereas inside the exchanger, a uniform concentration of ion, prevails. In the second case, the concentration gradient occurs within the exchanger, while the film has a uniform composition. A high metal ion concentration, relatively large particle size of the exchanger and a vigorous shaking of the exchanging mixture favours a particle diffusion controlled process **[1, 10]**.

3.3 ADSORPTION ISOTHERMS

The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid is known as adsorption. Adsorption is a general term that refers to the disappearance of solutes from solution with the presumption of adsorption on a solid phase. It is the accumulation at the solid-solution interface, and may result from either physical or chemical interaction with the surface.Adsorption refers to attraction and bonding onto a surface, while absorption is a process in which the solute is taken up throughout the bulk.

In some cases distinction is difficult and the generic term ***sorption***has been used. Sorption is determined by the extent of solute removal from solution in either batch studies or in elution studies with columns of adsorptive materials. Sorption is the process in which both adsorption and adsorption take place simultaneously. Adsorption is not necessarily a physical phenomena always. It may be a process involving chemical interaction between adsorbent and adsorbate. This type of adsorption is known as chemisorption. Physisorption is a relatively weak bonding to the surface, while chemisorption is a stronger interaction which involves ionic or covalent bonding, in addition to van der Waal’s and dispersion forces operative in physical adsorption.

A typical technique is to supply a known concentration of sorbate to a known mass of adsorbent. After the solution and solid have come to equilibrium, solution concentration is then measured and the difference between the initial concentration and final equilibrium concentration adjusted for the solution volume is assumed to be the amount of sorption per unit mass of the sorbent.

Adsorption models deal with the equilibrium between the ions, adsorption solution and exchange matrix. It is well understood that the adsorption phenomena for a given pair of ions and a solid surface is mainly a function of the particular ion concentration and the concentration of other ions, especially the H^+ ions (pH) **[11]**. Sorption of ions, mainly depends on the degree of surface heterogeneity due to the existence of crystal edges, broken bonds and imperfection on the surfaces. In the modeling of ion adsorption, effects of surface heterogeneity have been taken into account in the last decade **[11]**.

Equilibrium behaviour is described in terms of equilibrium isotherms which depend on the system temperature, concentration of the solution, contact time and pH **[12, 13]**. Adsorption equilibrium is usually established when the concentration of an adsorbate (metal ions) in a bulk solution is in dynamic balance with that of the adsorbent (exchanger) interface. The variation in adsorption with concentration and temperature is generally expressed in terms of adsorption isotherms - Langmuir and Freundlich adsorption isotherms.

Generally, both Langmuir and Freundlich isotherms are used for explaining the adsorption of metal ions on materials, since they are simple and have an ability to describe experimental results in a wide range of concentrations. Linear regression is the widely used method for fitting the transformed forms of original Langmuir and Freundlich isotherm equations **[11]**. Both isotherm models can be easily transformed into linear forms to obtain adjustable parameters, just by graphical means or by linear regression analysis. The application of Langmuir and Freundlich models have been further extended, considering the influence of adsorption sites and the competition between different ions for adsorption on the available sites. Kinniburgh et al **[14]** derived the competitive Langmuir isotherm characterized by site affinity, maximum adsorption capacity and a parameter describing mutual replacement of H^+ and M^{2+} on an adsorbing site **[11]**.

Langmuir Isotherms

TheLangmuir relationship has originally been derived for the adsorption of gases onto solid surfaces but it can be applied to solution systems as well. It is based on a model with the following basic assumptions:

- There is only a mono-molecular layer of adsorbed molecules.
- The equilibrium is characterized by the fact that the rates of adsorption and desorption are equal.

The linearized form of the Langmuir isotherm equation is given as:

$$C_e/(X/m) = 1/(bV_m) + C_e/V_m, \qquad \textbf{(Eq. 3.13)}$$

where X is the amount of adsorbate, m, the amount of adsorbent, C_e, the equilibrium concentration of the adsorbate in the solution, '*b*' is a constant that represents adsorption bond energy, which is related to the affinity between the adsorbent and adsorbate which is also a direct measure for the intensity of the sorption process. V_m is a constant related to the area occupied by a monolayer of sorbate, reflecting the maximum adsorption capacity **[12, 13]**.A dimensionless constant equilibrium parameter R_L can also be used to express an essential characteristic of the Langmuir isotherm. The R_L value indicates the shape of the isotherm and is expressed as $R_L = 1/(1 + bC_0)$. A value $0 < R_L < 1$ indicates favourable adsorption, $R_L = 0$ irreversible adsorption and $R_L = 1$ means linear adsorption while a value, $R_L > 1$ indicates an unfavorable adsorption **[12]**.

Freundlich Isotherms

The Freundlich isotherm is applied to deduce the adsorption intensity of the adsorbent and towards the adsorbate. Unlike Langmuir isotherm, the Freundlich isotherm assumes that the removal of metal ions occurs on a heterogeneous surface involving a multilayer adsorption of metal ions. Freundlich equation is an empirical relationship describing the sorption of solutes from a liquid to a solid surface. It gives relationship between the magnitude of adsorption and concentration, and can be expressed mathematically by an empirical equation known as Freundlich adsorption isotherm. Freundlich isotherm is expressed as,

$$\log(X/m) = \log K + (1/n)\log C_e, \qquad \textbf{(Eq. 3.14)}$$

where, X and m have the same meaning as described in Langmuir isotherm, K and $1/n$ are the Freundlich constants, describing the adsorption capacity and intensity respectively. A value, $0 < 1/n < 1$ indicates a normal isotherm, while $1/n > 1$ is indicative for cooperative sorption, for $n = 1$ the partition between the two phases is independent of the concentration **[12, 13]**.

The isotherm constants are important in understanding the adsorption mechanism and their subsequent application for prediction of some important design parameters. Plots of $C_e/(X/m)$ versus C_e and $log(X/m)$ versus $log\ C_e$ are drawn for Langmuir and Freundlich isotherms respectively which are straight lines from which the constants can be determined by the slopes and intercepts. In order to decide which type of isotherm fits better, the R^2 values (goodness of fit criterion) computed by linear regression for both type of isotherms and a value $0 < R^2 < 1$ indicates that the isotherm provides a good fit to the sorption experimental data, where R^2 values should be close to unity.

3.4 CONCEPTS IN ION EXCHAGE AND METAL SEPARATIONS

Ion exchange is a physico-chemical process. Chemical variables include *p*H, nature of ions being exchanged/separated, concentration of ions in solution, tendency of ions to hydrate, chemical composition of ion exchanger etc. The exchange capacity of a cation exchanger generally increases with increase in pH of the solution, while that of an anion exchanger decreases. Sorption ability of ions increases with increase in charges, atomic masses, ionic radii and ionic potential. Physical variables include rate of flow of solution in column, size of exchanger particles, the height of column, temperature of the solution, amount of ion exchanger etc.

Ion exchangers can be used, in both, batch and column operations. Since a column operation effects several equilibrations as the solution passes through the column, many difficult separations can be achieved relatively easily. The applications of an ion exchange column, offers some advantages such as: (a) simple working technique (b) elements concentrated on an ion exchanger can be eluted as whole or in separated groups or even as individual elements, using a suitable gradient elution procedure.

Practically, all ion-exchange reactions are reversible. At equilibrium, the favoured direction of an exchange reaction is determined by the relative affinity of the ion exchanger for the ions entering into the exchanger matrix. Better separation takes place if there is equilibrium between the ions in the solution and on the ion exchanger.

An increase in the surface area of the ion exchanger also improves the attainment of an equilibrium and separation. A rise in temperature alters the equilibrium constant of the exchange which improves the separation in some cases.

3.4.1 Factors Affecting Selectivity

Selectivity coefficient (K_c): Selectivity coefficient can also be used for describing ion exchange equilibria. The selectivity coefficient is defined as the ratio of the concentrations of the two ions, in the exchanger phase and solution phase, at equilibrium. It is thus a direct measure of the preference of the exchanger for one ion relative to the other. The exchange reaction between monovalent ions is represented as,

$$A + RB \leftrightarrows RA + B \qquad \textbf{(Eq. 3.15)}$$

At equilibrium, selectivity coefficient is given by the expression,

$$K_c = \frac{[RA^+][B^+]}{[RB^+][A^+]} \qquad \textbf{(Eq. 3.16)}$$

where$R$ is exchanger matrix and A and B are exchanging ions. In this respect, selectivity coefficient is quite different from separation factor when the valencies of the competing counter ions are not equal. Selectivity coefficient (K_c) can be evaluated from experimental data for strongly acidic or strongly basic exchanger. The number of equivalent exchangeable ions in the exchanger is equal to total exchange capacity. If, K_c> 1.0, 'A' has more affinity for exchanger, K_c< 1.0 indicates ion 'B' is held strongly by exchanger and needs strong external solution as an eluant to accomplish exchange reaction while K_c = 1.0 indicates no preferential selectivity for both ions.

The exchange reaction between two ions of different valency as 'a' and 'b' is represented as,

$$A^{b+} + RB^{a+} \leftrightarrows RA^{b+} + B^{a+} \qquad \textbf{(Eq. 3.17)}$$

At equilibrium, selectivity coefficient is given by the expression,

$$K_c = \frac{[RA^+]^b[B^+]^a}{[RB^+]^a[A^+]^b} \qquad \textbf{(Eq. 3.18)}$$

Selectivity coefficient contains the ionic valencies as exponents. In such cases, the selectivity coefficient remains more or less constant, when the experimental conditions, particularly the total solution concentration are varied. Selectivity coefficient depends upon the nature of the ion, the nature of the exchanger, external factors such as temperature, and the degree of saturation of the ion exchange material.

Distribution coefficient (K_d): Distribution coefficient (K_d) is a measure of fractional uptake of metal ions in solution, competing for H^+ ions, in case of a cation exchange material. It can be determined by batch experiments, in which a small known quantity of the ion exchange material is shaken with a solution containing a known concentration of the solute (metal ion), followed by analysis of the two phases, after equilibrium has been attained.

The presence of other electrolytes in metal ion solution, strongly affects the $K_d$value of the metal ion. K_d values change, depending on the ionic strength and pHof the electrolyte. The degree of ionization of the ionogenic groups of the exchanger, depends on the acid or base strength of the groups, i.e. on their pK values and on the pH. When the pH drops below the pK value of the groups, the acid groups become predominantly nonionic, the apparent capacity and hence the K_d values thus fall off. Based on such a study, a proper electrolyte can be selected for the elution of a particular metal ion from the exchanger column.

Breakthrough capacity (BTC): The selectivity of an ion exchanger for a particular metal ion can also be assessed by break through capacity (BTC). BTC is expressed in millimoles, milligrams, micrograms, or other appropriate units related to 1 g of dry resin or 1 mL of swollen resin. For BTC determination, ion exchanger is taken in a column and fractions of metal ion solution passed through the column and effluent collected, till the amount of metal ion concentration is same in feed and effluent.The break through capacity depends on, flow rate of feed solution through the column, bed depth, selectivity coefficient, particle size and temperature. BTC is the dynamic capacity or operating capacity of a known amount of ion exchange material towards metal ion in column operating condition. $K_d$values also give an idea of affinity of metal ion towards ion exchanger. It is therefore expected that the selectivity order based on$K_d$values and BTC should be same. However, in practice, the selectivity order based on $K_d$valuesand BTC may not be matching due to the fact that $K_d$values are determined by batch process while BTC is determined by column process.

Separation factor (α): The preference of an ion exchanger for one of the two counter ions is also expressed by the separation factor. It is used as a measure of the chromatographic separation possible on an ion exchange column. K_d is an important factor for determining the analytical potential of an ion exchanger. Separation factor α is the rate at which any two constituents separate on a column and is defined as the ratio of the two corresponding distribution coefficients K_{d1} and K_{d2}. The separation factor α is given by the equation,

$$\alpha = K_{d1}/K_{d2} \qquad \textbf{(Eq. 3.19)}$$

where, K_{d1} and K_{d2} are the distribution coefficients of the two constituents in a given medium. The greater the deviation of α from unity, better is the separation.

Conclusions on factors affecting selectivity

Selectivity/affinity of a particular metal ion towards an ion exchanger depends on (a) the ion exchanger: the factors responsible being particle size, the presence of functional groups that indicate the nature of the exchanger weak or strong, the ion exchange capacity, the degree of cross linking, and the structural complexity of the ion exchanger (b) the exchange media: the factors responsible being concentration, pH, and the nature of the electrolyte, weak or strong, as well as the temperature, and (c) the exchanging metal ion: the factors responsible being ionic radius and the ionic charge on the metal ion, with higher valent ions having more affinity for the exchanger **[15]**. Over and above these three factors the exchange process itself, i.e., the rate of exchange and equilibrium also play an important role in determining the selectivity.

On immersing the exchanger in solution, equilibrium is established between the exchanger and the electrolyte solution, the rate of exchange depending on the size of the exchanging ion and the grain/particle size of the exchanger. Smaller the size of the cation, greater is its tendency to be hydrated and greater is the hydrated ionic radii. Larger ions being less hydrated, less energy is utilized for dehydration of the metal ions to occupy a site on the exchanger, which plays a prominent role in determining the selectivity of metal ions **[16]**. The overall effect is a result of the contribution of the above mentioned factors. Depending on the predominant factor, the affinity of metal ions towards the ion exchanger varies in each case.

Other General Guidelines

- At low concentrations (aqueous) and ordinary temperatures, the extent of exchange increases with increasing valency of the exchanging ion: ($Na^+ < Ca^{2+} < Al^{3+} < Th^{4+}$).
- At low concentrations (aqueous) ordinary temperatures and constant valence, the extent of exchange increases with increasing atomic number of the exchanging ion ($Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$; $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$).

- At high concentrations, the difference in the exchange “potentials” of ions of different valence (Na^+ versus Ca^{2+}) diminish and, in some cases, the ion of lower valence has the higher exchange “potential”.
- The relative exchange “potentials” of various ions may be approximated from their activity coefficients - the lesser the activity coefficient, the greater the exchange “potential”.
- The exchange “potential” of the hydrogen ion (H_3O^+ versus OH^-) vary considerably with the nature of the functional group, and depends on the strength of the acid or base formed between the functional group and either the hydroxyl or hydrogen ion. The stronger the acid or base, the lower the exchange potential.
- As a rule, the K_d values increase with increasing charge on the ion. There are however two contradictory factors, (a) an increase in charge increases the attraction for the cation (K_d high), (b) an increase in charge also increases hydrated ionic radii (K_d low).

3.4.2 Factors Affecting Separations

An efficient ion exchange separation may be influenced by load of metal ion, electrolyte used for elution, flow rate of eluent, diffusion of metal ions in mobile and stationary phases, pH, nature of ion exchange material and the particle size and length of the column. Other factors responsible are distribution coefficient (K_d), Breakthrough capacity (BTC), Separation factor (α), Selectivity coefficient (K_c), retardation factor (R), retention volume (V_r), column capacity and temperature.

Proper use of solution for sorption/elution, enhances the scope of an ion exchange separation which may be enhanced by using for fixation or for elution, a solution capable of complexing the ions exchanged. The formation of complexes may assist separations by diminishing the concentrations of free ions and also by producing complexes of different stabilities, thus leading to significantly different behaviour with selected eluents. As explained earlier, the presence of other electrolytes such as inorganic acids and certain salt solutions, strongly affects the K_d values of the metal ions. Thus, all investigations for the development of metal ion separations are based on $K_d$values, determined both in aqueous and various electrolyte media.

The efficiency of an ion exchange separation depends on the condition under which α has a useful value, or influencing in a direction favourable to separation. Since, α is the ratio of the $K_d$valuesof the constituent counter ions, the K_d values are determined under the expected solution conditions on the selected ion exchange material.

In many cases, the efficient separation of a mixture requires that the eluent concentration be changed during the course of elution, which may be done in a stepwise manner or by continuous change in the concentration, as in gradient elution.

To understand the behaviour of solute (such as metal ions in solutions), the following terminologies should be understood.

***Partition/Distribution coefficient (K_d)*:**

$$K_d = C_S/C_M \qquad \textbf{(Eq. 3.20)}$$

where, C_S and C_M are concentrations of solute in stationary and mobile phases, respectively.

***Retardation factor* (*R*):** is the ratio of the displacement velocity of solute to velocity of solvent (electrolyte in present case). *R* represents fraction of time spent by species in mobile phase i. e.

$$R = t_M/(t_M + t_S) \qquad \textbf{(Eq. 3.21)}$$

where, t_M and t_S represent retention time of solute in stationary and mobile phases respectively.

***Retention Volume* (V_r):** At appearance of peak, half of the solute is eluted in retention volume, while other half remains on the column in mobile phase, plus volume of stationary phase.

This indicates the time period for which solute/metal ion resides in mobile phase/electrolyte, which is expressed as,

$$V_r = L\,F\,(V_M + K_d\,V_S/\,v\,V_M) \qquad \textbf{(Eq. 3.22)}$$

where, *L* = length of column, *F* = flow rate, *v* = linear flow rate or average velocity, and V_M and V_S are volume of mobile and stationary phase respectively.

***Column capacity*:** Column capacity is related to retention volume. It is given by,

$$k = (V_r - V_M)/\,V_M \qquad \textbf{(Eq. 3.23)}$$

where, V_r = retention volume and V_M = volume of mobile phase.

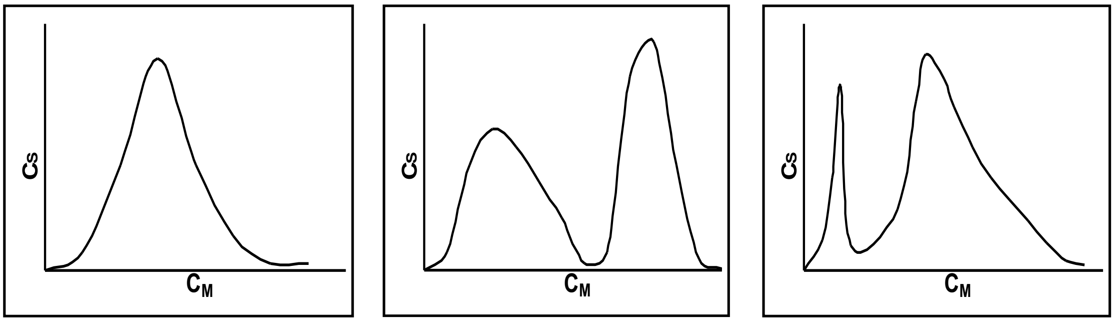
***Temperature*:** Since temperature influences K_d, resolution is also affected by temperature.

Elution behaviour**:** When solution containing metal ions is passed through a column containing exchanger, based on differential affinity, the various species get strongly or weakly bound on the exchanger. During the elution process, pure electrolyte is eluted first, followed by weakly bound species and finally the strongly bound species. A plot of concentration of metal ion in stationary phase vs. mobile phase provides partition isotherm. Generally, three types of curves are observed (**Figure 3.2**).

Linear isotherm: is symmetric bell shaped Gaussian curve where $C_S \alpha C_M$.

Classical isotherm: also referred to as Langmuir curve, is observed in adsorption chromatography.

Anti classical isotherm: is referred to as non Langmuir curve. Here, micro peak is followed by broad peak. Such curves are observed in cases where the solute has low solubility in stationary phase.



(a) **(b)** **(c)**

Figure 3.2*Types of elution curve (a) linear isotherm (b) classical isotherm and (c) anti classical isotherm*

As seen from **Figure 3.2**, linear isotherm (**Figure 3.2a**) is considered to be best for chromatographic separation. In practice, for single ion elution, symmetrical bell shaped curves are observed. In binary and ternary separations, separation efficiency is indicated by (a) percentage recovery and (b) peak shapes/elution curves of the constituent metal ions, in terms of Langmurian/non-Langmurian which indicates how well one metal ion is separated in presence of another metal ion. However, in binary metal separations in columns, generally '**Figure 3.2b**' or '**Figure 3.2c**' type curves are obtained. Further tailing effects are attributed to (a) high K_d values (due to which the metal ion is retained for long time on stationary phase) and (b) irregular flow/flow rate.

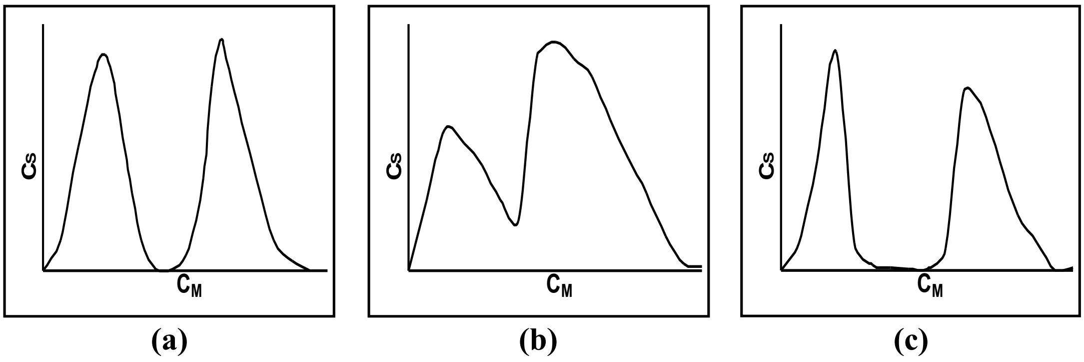
Zone spreading**:** Another factor that affects peak shape is due to a phenomenon called "zone spreading" that occurs due to differential migration of solute in mobile phase. Separation efficiency depends on differential migration of metal ion in mobile/stationary phase. Deviations are observed referred to as "zone spreading", caused by diffusion of metal ion in stationary phase (eddy diffusion), concentration gradient in stationary/mobile phase (longitudinal diffusion) and mass transfer of metal ion in stationary phase (exchanger) and mobile phase (electrolyte).

Eddy diffusion:There are a multitude of pathways by which an ion finds its way through a packed column, which is directly proportional to the diameter of the particles making up the column.

Longitudinal diffusion: this is due to, concentration gradient of solutes, ahead and behind the zone center. Longitudinal diffusion is directly proportional to mobile phase diffusion coefficient and inversely proportional to mobile phase velocity.

Mass transfer: occurs in stationary as well as mobile phase. Time is required for solute molecules to diffuse from the interior of exchanger phases to the interface, where transfer occurs. This time lag results in the persistence of non equilibrium conditions. A column is always operated at non equilibrium condition. Thus metal ion is swept ahead before they have time to equilibrate with the stationary phase. This unequal distribution in stationary and mobile phases also leads to zone spreading. Typical elution curves indicating separation efficiency is presented in **Figure 3.3**.

A controlled flow rate gives good separation of peaks, however irregular flow rate results in tailing effect. Peak shapes with ideal time break between two peaks indicate efficient separation.



(a) **(b)** **(c)**

Figure 3.3*Types of elution curve with (a) controlled flow (b) tailing/not good flow and (c) ideal time break*

Elution techniques

Generally three types of elution techniques are practiced.

Frontal:passing electrolyte containing metal ion continuously through a column. In this case, electrolytes are eluted first, followed by weakly bound/exchanged species and then strongly exchanged species.

Elution: This is the most popular technique, wherein separation is effected due to differential migration of solute in mobile phase and the electrolyte, exhibits behaviour of symmetrical bell shaped curve in ideal case. Here, the eluent which may be a pure electrolyte is passed through the column, which in turn, leads to the differential migration of metal ion in mobile phase. If the flow rate is fixed, separation depends on K_d.

Displacement: In this technique, separation is achieved by running a more strongly exchanged displacement agent into the column. The main advantage of this technique is that heavy loading of the column is possible. Gradient elution is the variation of eluting condition during the course of separation.

3.5 OBJECTIVESOF THE PRESENT WORK

The main objective of the present study was to explore the feasibility of CP and TP as cation exchangers towardstransition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and heavy metal ions (Cd^{2+}, Hg^{2+}, Pb^{2+}).The study deals with the following aspects:

- ✓ The equilibrium exchange of metalions with H^+ ions contained in CP and TP have been studied varying temperature, at constant ionic strength. On the basis of the exchange isotherms, thermodynamic parameters equilibrium constant (K), standard Gibbs free energy change ($\Delta G°$), entropy change ($\Delta S°$) and enthalpy change ($\Delta H°$) have been evaluated and correlated.
- ✓ Adsorption isotherms (Langmuir and Freundlich) have been studied by varying metal ion concentration, pH, contact time and temperature. Langmuir constants (b and V_m) and Freundlich constants (K and $1/n$) have been evaluated using Langmuir and Freundlich isotherms respectively. R^2 value (goodness of fit criterion) has been computed by linear regression for both types of isotherms.
- ✓ Distribution coefficient (K_d) has been determined at optimized conditions (optimum pH, optimum metal ion concentration and optimum equilibrium

time) in aqueous as well as various electrolyte media/concentration (HNO_3, NH_4NO_3, $HClO_4$ and CH_3COOH of 0.2 M and 0.02 M).

- ✓ Breakthrough curves have been plotted, breakthrough capacity (BTC) determined and compared with K_d values to confirm the selectivity order of metal ions.
- ✓ Elution behaviour of metal ions has been studied using acids and electrolytes (HNO_3, NH_4NO_3, $HClO_4$ and CH_3COOH of 0.2 M and 0.02 M). Based on the separation factor α a few binary and ternary metal ion separations have been performed.
- ✓ To explore the performance ability, CP and TP have been regenerated and reused.

3.6 LITERATURE SURVEY IN THE CURRENT AREA OF STUDY

Several studies have shown that cerium (IV) phosphates (CPs) are interesting inorganic materials for cation exchange. Clearfield et al have reported the ion exchange behavior of crystalline CP with alkali metal ions **[17]**. Varshney et al have reported kinetics of ion exchange of alkali and transition metal ions using acrylamide and acrylonitrile based fibrous CP**[18-20]**. Sorption studies of strontium and uranium ions on fibrous cerium (IV) hydrogenphosphatehave been reported **[21]**. Nilchi et al have reported analytical applications of disodium, dipotassium and distrontiumsubstitutedcerium phosphate and molybdate as cation exchangers for alkaline earth metal ions **[22]**. Varshney have reported synthesis, characterization and adsorption behaviourof triton X-100 based CP as a new Hg(II) selective, surfactant based fibrous ion exchanger **[23]** and analytical applications of Pb(II) selective, surfactant-based sodium dodecyl sulphate cerium phosphate **[24]**. Analytical applications of pyridine basedCP as fibrous ion exchangers has been reported byVarshney**[25]**.Suzuki et al **[26]**have reported synthesis and characterization of Pb(II) selective membrane filter,fabricated from fibrous CP $\{CeO(H_2PO_4)_2 \cdot H_2O\}$ by blending with cellulose fiber.Preetha et al **[27]**have reported synthesis, characterization and application of cerium zirconium phosphate as cation exchanger for metal ion separations of some transition metal ions.

Many fibrous thorium (IV) phosphates (TPs) have been synthesized and characterized. They are interesting inorganic materials for cation exchange as it can be made in various forms as per the requirement like granules, membrane, filters etc.**[28-34]**. Khan et al have reported synthesis, characterization and application of organo-inorganic composite polypyrrole-TP **[28]** and nano-composite poly-*o*-toluidine-TP **[29]** as cation exchangers. Varshney et al have reported synthesis, characterization and analytical applications of pyridine based TP **[30]**, Cd(II) selective polystyrene-TP **[31]** and Pb(II) selective polyacrylonitrile-TP **[32],** as novel hybrid fibrous ion exchangers. Mahamudar et al have reported synthesis and characterization of polyacrylamide-TP **[33]** and polycinnamamide-TP **[34]** as important fibrous ion exchangers for removal of Pb^{2+}, and fluoride adsorption from aqueous solution using hybrid TP as a composite material has been studied. BrandelandGemethave reported synthesis and characterization for series of TPs**[35-37]** and reported adsorption study of trivalent actinides **[37]**. A K De et al have reported distribution coefficient measurement and selective metal ion separations usingTP as a cationexchanger**[38]**.

3.7 EXPERIMENTAL

3.7.1 Materials and Methods

CP and TP has been synthesized and characterized, and discussed in details in **Chapter II, Section 2.3 and 2.4.**Metal salts of AR grade were obtained from E Merck, India. Disodium salt of ethylene diamine tetra acetic acid (EDTA) was procured from Fluka.Perchloric acid, acetic acid, ammonium nitrate, nitric acid, indicators and reagents used were of AR grade. Deionized water (DIW) was used for all the studies. For all experiments, the exchanger particles of definite mesh size [30 - 60 mesh (ASTM)] in H^+ form and a shaker bath having a temperature variation of ± 0.5 °C was used.

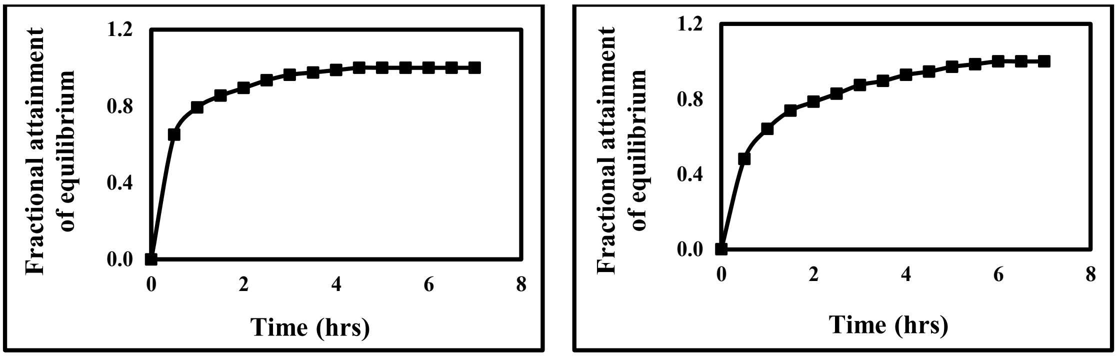
3.7.2 Thermodynamic Studies

Equilibrium time determination: This experiment was performed for Co^{2+} and the values obtained, utilized for other metal ions (Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}).

100mg of exchanger was shaken with 0.002 M metal ion solution in stoppered conical flasks, varying time in the range of 30 min to 6 h, with 30 min interval at a particular temperature (303K). Plots of the fractional attainment of equilibrium

*U(τ)*versus time (*t*) for CP **(Figure 3.4a)** and TP **(Figure 3.4b)** shows equilibriumto have attained within 6 h (optimum equilibrium time).

Equilibrium experiments:The equilibrium experiments were performed by shaking 100 mg of the exchanger particles at the desired temperature (303 K to 333 K with 10 K interval) in a shaker bath for optimum equilibrium time (6 h) with 20 mL of a mixture of solution containing 0.06 M HCl and the appropriate metal ion of varying volume ratios (1, 3, 5,…19 mL 0.02 M metal ion solution and 19, 17, 15,...1 mL of 0.06 M HCl, respectively were prepared) having constant ionic strength (0.06 M). After every prescribed time interval, metal ion concentration was determined by EDTA titration [**39**]. From this experiment, thermodynamic parameters equilibrium constant (*K*), standard Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) have been determined.



(a) **(b)**

Figure 3.4*A plot of the fractional attainment of equilibrium for* Co^{2+}*-*H^{+} *exchange verses time using (a) CP and (b) TP*

3.7.3 Adsorption Studies

Effect of pH, Contact Time and Temperature: Adsorption/ion exchange of metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (transition metal ions) and Cd^{2+}, Hg^{2+}, Pb^{2+} (heavy metal ions) using CP and TPwas carried out in the pH range 1–7. To 0.1 g of the exchanger, 10 mL of 0.002 M metal ion solution was added and pH adjusted in acidic range using dilute HNO_3 and in alkaline range using dilute NaOH and the mixture shaken for 30 min. The supernatant liquid was used to determine the metal ion concentration by EDTA titration**[40]**. The % uptake has been calculated using formula,

$$[(C_o - C_e)/C_o] \times 100 \qquad \textbf{(Eq. 3.24)}$$

where C_o is the initial concentration of metal ion in mg/L and C_e is the final concentration of metal ion in mg/L. A maximum % uptake gives optimum pH for the sorption of respective metal ion. The metal ion solution (10 mL) of 0.002 M was equilibrated in stoppered conical flasks at the desired temperatures (303 K to 333 K with 10 K interval) and at specific time intervals with increments of 10 min. (10 – 200 min). In each case, the pH of the solution is adjusted to the value at which maximum sorption of respective metal ion takes place. After every prescribed time interval metal ion concentration was determined by EDTA titration [**39**].

3.7.4 Separation Studies

Distribution Studies: Effect of metal ion concentration on distribution coefficient (K_d) values for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (transition metal ions) and Cd^{2+}, Hg^{2+}, Pb^{2+} (heavy metal ions) has been determined by batch method **[39- 41]**.

0.1 g of CP/TP in the H^+ form was equilibrated with 20 mL of varying metal ion concentration (0.002 - 0.01 M with interval of 0.002 M) for 6 h (optimum equilibrium time) at room temperature. The metal ion concentration, before and after exchange was determined by EDTA titration.

K_d was also evaluated at optimum condition (optimum metal ion concentration, pH of maximum adsorption andoptimum equilibrium time) with 0.1 g of the exchanger in aqueous as well as various electrolyte media like NH_4NO_3,HNO_3, $HClO_4$ and CH_3COOH of 0.02 and 0.2 M concentration at room temperature. The distribution coefficient (K_d) is evaluated using the expression,

$$K_d = \frac{(I-F)}{F} \times \frac{V}{W}\ (\mathrm{mL{\cdot}g^{-1}}) \qquad \textbf{(Eq. 3.25)}$$

where, I = total amount of the metal ion in the solution initially; F = total amount of metal ions left in the solution after equilibrium; V = volume of the solution; W = weight of the exchanger.

Column Preparation: For determination of BTC, elution studies and separation studies, column was prepared as follows. A dry glass column [30 cm (length) × 1 cm (internal diameter)] was filled with glass-wool at bottom (height = ~1 cm) and washed thoroughly with DIW. 0.5 g of the ion exchanger CP/TP, was now introduced into the column (bed height = 1.3 cm), and packed with glass-wool (height = ~1 cm) at the top and washed thoroughly with DIW to remove air bubbles from the column and flow rate adjusted to 0.5 $mL{\cdot}min^{-1}$ for all studies.

Breakthrough Capacity (BTC): For determination of BTC, 0.5 g of ion exchanger, CP/TP was taken in glass column and washedthoroughly with DIW and flow rate adjusted to 0.5 mL/min.5 mL fractions of each individual metal ion solution (0.001 M) was passed through the column and effluent collected, till the amount of metal ion concentration was same in feed and effluent. A breakthrough curve was obtained by plotting the ratio C_e/C_oagainst the effluent volume, where $C_o$andC_e are the concentrations of the initial solution and effluent, respectively. BTC is calculated using formula,

$$BTC = \frac{C_0 V_{(10\%)}}{W} \qquad \textbf{(Eq. 3.26)}$$

where, $C_o$is concentration of metal ion ($mol{\cdot}L^{-1}$), $V_{(10\%)}$is the volume of metal ion solution passed through column when exit concentration reaches 10 % of the initial concentration in mL and W is the weight of the exchanger in g.

Elution Studies: For all metal ions under study 0.001 M, 10 mL of each metal ion, was loaded onto the column. Each metal ion loaded was eluted with reagents like HNO_3, $HClO_4$, $CH_3COOH$and NH_4NO_3 of 0.02 M and 0.2 M concentration. The amount of metal ion eluted (% E) was calculated using the expression,

$$\%\,Metal\ eluted\ (\%\,E) = \frac{Conentration\ of\ metal\ ion\ eluted\ (Ce)}{Conentration\ of\ metal\ ion\ loaded\ (Co)} \times\ 100 \textbf{(Eq. 3.27)}$$

Binary and Ternary Separations: For binary and ternary separations, mixture of the metal ions (0.001 M, 10 mL of each metal ion) to be separated was loaded onto the column. Metal separations were achieved by passing suitable eluents through the column. For a given metal ion pair, the eluent was selected based on K_d values of respective metal ions (in a particular medium) in which separation factor was highest. Metal ion concentration was determined quantitatively by EDTA titration. The amount of each metal ion eluted (% E) was calculated using the above equation (**Eq. 3.27**).

3.7.5 Regeneration and Reusability Studies

Regeneration and reuse of ion exchangers CP and TP was performed in the case of Pb^{2+} by batch method. 0.006 M (Optimum metal ion concentration) Pb^{2+} solution was treated with 0.1 g of CP and TP and kept for 6 h (maximum equilibrium time) after which metal ion concentration was determined by EDTA titration and K_d value determined. Pb^{2+} exchanged onto material was eluted out by treating with HNO_3 (1 M, 50 mL) for 30 minutes with occasional shaking. The materials CP and TP were separated from acid by decantation and treated with deionized water to remove adhering acid. This process was repeated at least five times to ensure complete removal of Pb^{2+} from exchanger. The regenerated exchangers were used to determine K_d value for Pb^{2+}. The process was repeated till wide variation in K_d values was observed. % retention in K_d values $K_{d(R)}$ was determinedusing the expression, $K_{d(R)} = [K_{d(C)}/K_d] \times 100$ where K_d= Initial value obtained,$K_{d(C)}$ =$K_d$determined in each subsequent cycle.

3.8 RESULTS AND DISCUSSION – PART I

3.8.1 Thermodynamic Studies using CP

Thermodynamics of ion exchange has been studied for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (transition metal ions) and Cd^{2+}, Hg^{2+}, Pb^{2+} (heavy metal ions).Equilibrium constant (K), standard Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) have been evaluated using standard equations discussed earlier in text **(Eqs.3.10-3.12)** and results presented in **Table 3.1**.

Equilibrium constant (K) values increase with increase in temperature for all metal ions under study (**Table 3.1**), indicating that the metal ions have higher affinity for the exchanger and that the mechanism is ion exchangeas discussed earlier in text [**42**].

The free energy change ($\Delta G°$) for all the exchange reactions is negative, over the entire temperature range, indicating that the exchanger has a greater preference for metal ions than H^+ ions. Further, $\Delta G°$ values become more negative with increasing temperature indicating increase in feasibility and spontaneity of the sorption process,and that the exchange is favoured with increasing temperature**[42]**. At any given temperature, $\Delta G°$ follows the order (increasing negativity): $Zn^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+}$ amongst the transition metal ions and $Pb^{2+} > Cd^{2+} > Hg^{2+}$ amongst the heavy metal ions.

The enthalpy change ($\Delta H°$)is positive in all cases indicating that the exchange process is endothermic. $\Delta H°$ follows the order $Zn^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+}$ and $Pb^{2+} > Cd^{2+} > Hg^{2+}$. Higher/positive values of enthalpy change indicate more endothermicity of the exchange process and requirement of more energy for dehydration to occur.The $\Delta H°$ values indicate that probably complete dehydration occurs in case of Zn^{2+} and Pb^{2+}. Further, trends in $\Delta H°$values arealso supportive to trends in $\Delta G°$ values.

Δ*S*° also follows same trend as Δ*H*°. Higher values observed in case of Zn^{2+} and Pb^{2+}, are attributed to greater dehydration, which indicates the greater disorder produced during the exchange.

Table 3.1*Thermodynamic parameters for M^{2+}-H^{+} exchange at various temperatures using CP*

Exchanging System	Temperature (K)	K_a	ΔG^O (k J mol^{-1})	*ΔH^O (k J mol^{-1})	ΔS^O (J mol^{-1} K^{-1})
$Co^{2+} - H^{+}$	303	1.64	-0.62	82.15	273.22
	313	3.30	-1.55		267.44
	323	3.68	-1.75		259.78
	333	28.36	-4.60		260.62
$Ni^{2+} - H^{+}$	303	1.74	-0.69	84.76	282.04
	313	4.69	-2.01		277.23
	323	11.67	-3.30		272.63
	333	35.50	-4.94		269.37
$Cu^{2+} - H^{+}$	303	1.45	-0.47	64.50	214.44
	313	4.32	-1.90		217.12
	323	8.02	-2.79		208.65
	333	23.89	-3.74		204.94
$Zn^{2+} - H^{+}$	303	3.54	-1.59	87.19	293.02
	313	10.87	-3.10		288.48
	323	23.39	-4.22		283.05
	333	78.96	-6.04		280.00
$Cd^{2+} - H^{+}$	303	3.77	-1.67	46.25	158.16
	313	4.15	-1.85		153.68
	323	6.04	-2.41		150.67
	333	12.18	-3.46		149.28
$Hg^{2+} - H^{+}$	303	2.06	-0.91	9.89	35.66
	313	2.20	-1.03		34.89
	323	2.27	-2.41		34.03
	333	2.90	-3.46		34.14
$Pb^{2+} - H^{+}$	303	6.35	-2.33	168.19	562.78
	313	33.11	-4.55		551.91
	323	214.86	-7.21		543.08
	333	2440.60	-10.79		537.51

**Average value calculated from the van't Hoff isochore equation.*

3.8.2 Adsorption Studies using CP

The effect of experimental conditions such as pH, contact time and temperature were studied to set the conditions for maximum adsorption/ion exchange for the metal ions by the ion exchanger.

The effect of pH on the sorption behaviour of metal ions (under study) have been presented in **Table 3.2**. At pH values less than ~3, very less sorption has been observed for all metal ions. The lack of sorption at low pH could be attributed to high concentration of hydrogen ions competing with the metal ions for sorption/exchange sites. A precipitation was observed in case of Ni^{2+}, Cu^{2+} and Pb^{2+} at pH 6, in case ofCo^{2+} and Cd^{2+} at pH 8 and in case of Zn^{2+} and Hg^{2+}atpH 5.The observed order for % uptake of metal ion at optimum pH, is $Zn^{2+}>Ni^{2+}>Co^{2+}>Cu^{2+}$ (amongst transition metal ions) and $Pb^{2+}>Cd^{2+}>Hg^{2+}$ (amongst heavy metal ions) **(Table 3.2)**.

The time taken for attainment of equilibrium for each metal ion in $mg \cdot L^{-1}$ has been presented in **Table 3.3**.Sorption of metal ions varying contact time and temperature has been presented in **Tables 3.4 to 3.10** and illustrated in **Figures 3.5 to 3.11** [plot of uptake (%) versus time]. It is observed that sorption increases gradually with increase in contact time and reaches a maximum value after which randomness is observed. Increase in % uptake could be attributed to two different sorption processes, namely, a fast ion exchange followed by chemisorption **[43,44]**. It is observed that % uptake of each metal ion increases with increase in temperature, which indicates the uptake to be an ion exchange mechanism [**43**].

Langmuir constants (b and V_m) and Freundlich constants (K and $1/n$)obtained from the slopes and intercepts of the linear plots{**Figures 3.12(a-g) and 3.13 (a-g)** respectively}are listed in **Table 3.11**. It is observed thatR^2 values are found to be close to unity for both isotherms and provides a good fit to the experimental data for sorption of all the metal ions taken (except Cd^{2+} for Freundlich isotherm and Hg^{2+} for both isotherms). Variation in R^2 values is attributed to the fact that the surface adsorption is not a monolayer with single site. Two or more sites with different affinities may be involved in metal ion sorption **[43,44]**. In the present study, low values of b indicate favorable adsorption. V_m values, reflect maximum adsorption capacity of metal ions towards exchanger, follows the order $Co^{2+}>Zn^{2+}>Cu^{2+}>Ni^{2+}$amongst transition metal ions and $Pb^{2+}>Cd^{2+}>Hg^{2+}$amongst heavy metal ions at 303 K. The values of $1/n$ and R_L are obtained between 0 and 1 which indicates normal isotherm and favourable adsorption.Langmuir and Freundlich isotherms have been presented in **Figures 3.12(a-g) and 3.13 (a-g)** respectively.

Table 3.2*%Uptake of metal ions at various pH using CP*

pH	**Uptake of metal ion (%)**						
	Co^{2+}	**Ni^{2+}**	**Cu^{2+}**	**Zn^{2+}**	**Cd^{2+}**	**Hg^{2+}**	**Pb^{2+}**
1	18.51	1.00	2.10	15.12	18.10	1.20	27.64
2	12.28	4.76	22.75	28.25	16.00	1.73	36.54
3	**29.30**	15.61	**25.55**	**46.80**	21.00	2.50	55.45
4	18.08	**32.16**	11.76	11.20	37.00	**2.90**	**76.22**
5	11.15	16.25	17.97		**55.50**		76.00
6	4.42				28.00		
7	2.24				31.00		

Maximum deviation in % uptake of metal ion =±2%

Table 3.3*Time taken for attainment of equilibrium using CP*

Metal ion	**Equilibrium time (min)**			
	303 K	**313 K**	**323 K**	**333 K**
Co^{2+}	60	60	50	50
Ni^{2+}	60	60	40	40
Cu^{2+}	60	60	50	40
Zn^{2+}	60	50	40	40
Cd^{2+}	90	90	70	60
Hg^{2+}	40	40	40	40
Pb^{2+}	170	170	120	100

Table 3.4*% Uptake of* Co^{2+} *on CP*

Time	% Uptake of Co^{2+}			
mins	303K	313 K	323 K	333K
10	20.7	22.0	27.7	38.4
20	22.8	24.1	32.3	41.8
30	25.0	25.9	38.2	46.0
40	28.7	29.4	43.4	51.8
50	30.8	33.0	45.0	52.5
60	33.1	35.7		

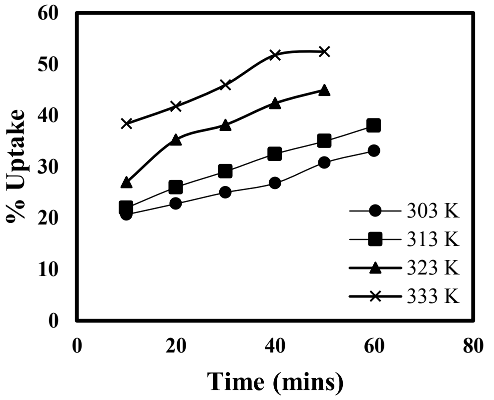


Figure 3.5% Uptake of Co^{2+} *on CP*

Reaction conditions*: Amount of CP=100 mg; metal ion concentration=0.001M; total volume of metal ion = 10 mL; pH = 3*

Table 3.5*% Uptake of* Ni^{2+} *on CP*

Time	% Uptake of Ni^{2+}			
mins	303K	313 K	323 K	333K
10	12.4	15.7	19.7	21.2
20	14.1	18.2	21.2	24.8
30	17.5	20.6	25.5	26.9
40	21.1	21.2	27.1	30.5
50	23.3	24.8		
60	25.2	27.0		

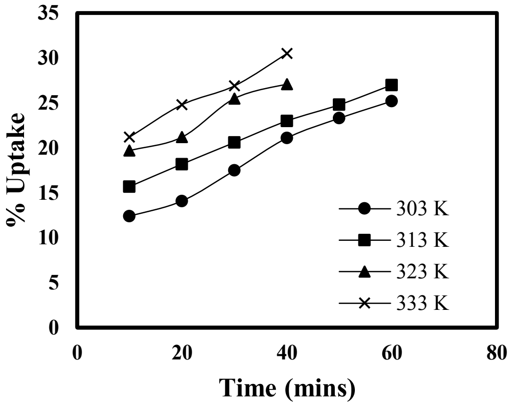


Figure 3.6*% Uptake of* Ni^{2+} *on CP*

Reaction conditions*: Amount of CP=100 mg; metal ion concentration=0.001M; total volume of metal ion=10 mL; pH=4*

Table 3.6*% Uptake of* Cu^{2+} *on CP*

Time	% Uptake of Cu^{2+}			
mins	303K	313 K	323 K	333K
10	13.1	14.6	15.2	17.0
20	15.0	17.0	18.1	20.1
30	16.2	19.5	21.1	23.6
40	19.7	22.0	24.2	28.5
50	21.4	24.5	26.8	31.3
60	23.0	26.0		

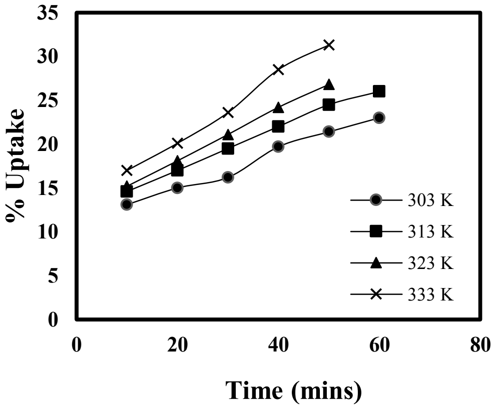


Figure 3.7*% Uptake of* Cu^{2+} *on CP*

Reaction conditions*: Amount of CP=100 mg; metal ion concentration=0.001M; total volume of metal ion=10 mL; pH= 3*

Table 3.7 *% Uptake of Zn^{2+} on CP*

Time	% Uptake of Zn^{2+}			
mins	303K	313 K	323 K	333K
10	10.1	11.4	13.5	16.1
20	11.2	12.9	15.0	19.6
30	14.1	15.6	18.5	22.4
40	16.3	19.2	22.7	26.5
50	17.7	22.0		
60	19.1			

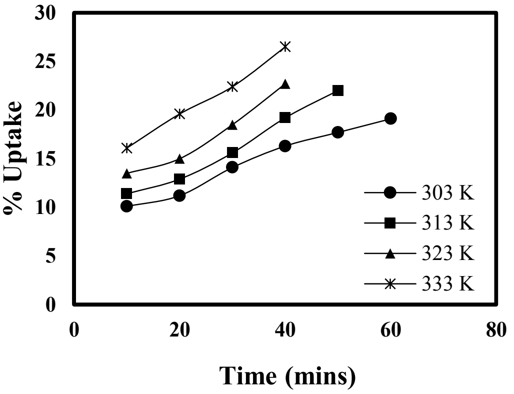


Figure 3.8 *% Uptake of Zn^{2+} on CP*

Reaction conditions: *Amount of CP=100 mg; metal ion concentration=0.001M; total volume of metal ion=10 mL; pH= 3*

Table 3.8 *% Uptake of Cd^{2+} on CP*

Time	% Uptake of Cd^{2+}			
mins	303 K	313 K	323 K	333 K
10	26.3	32.7	35.2	36.4
20	27.7	34.2	39.0	42.5
30	30.1	34.4	42.7	47.5
40	30.3	34.9	45.1	49.8
50	31.4	36.2	46.2	52.2
60	31.6	38.2	47.8	55.0
70	32.3	39.6	49.5	
80	34.5	42.5		
90	36.0	46.4		

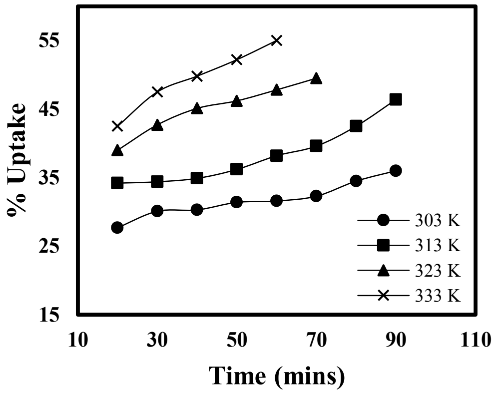


Figure 3.9 *% Uptake of Cd^{2+} on CP*

Reaction conditions: *Amount of CP =100 mg; metal ion concentration=0.001M; total volume of metal ion=10 mL; pH= 5*

Table 3.9 *% Uptake of Hg^{2+} on CP*

Time	% Uptake of Hg^{2+}			
mins	303 K	313 K	323 K	333 K
10	1.2	1.8	2.2	2.5
20	1.8	2.9	3.4	4.1
30	2.0	3.0	4.1	5.0
40	2.7	3.5	4.9	5.5

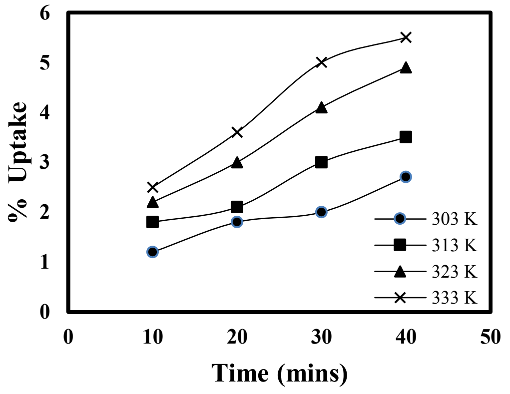


Figure 3.10 *% Uptake of Hg^{2+} on CP*

Reaction conditions: *Amount of CP=100 mg; metal ion concentration=0.001M; total volume of metal ion =10 mL; pH = 4*

Table 3.10 *% Uptake of Pb^{2+} on CP*

Time	% Uptake of Pb^{2+}			
mins	303 K	313 K	323 K	333 K
10	30.1	34.3	42.6	48.4
20	33.8	43.6	49.2	68.2
30	36.5	46.3	57.4	73.9
40	41.8	51.8	62.4	77.3
50	46.2	56.8	70.5	89.2
60	48.4	56.8	71.1	91.1
70	52.0	58.7	74.2	92.4
80	54.7	62.8	78.7	93.7
90	55.1	59.3	80.5	93.6
100	58.4	65.1	87.0	96.8
110	61.9	68.4	90.2	
120	64.2	70.5	90.8	
130	66.9	72.8		
140	70.8	74.5		
150	71.3	77.5		
160	73.1	78.8		
170	76.4	79.3		

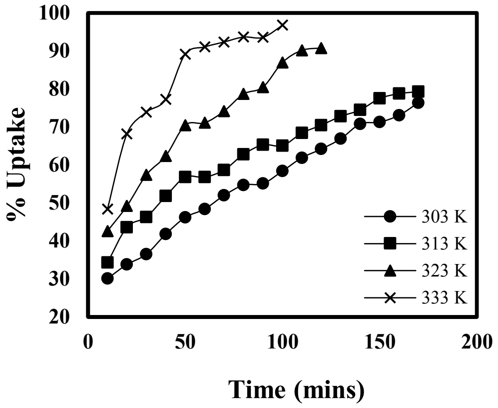
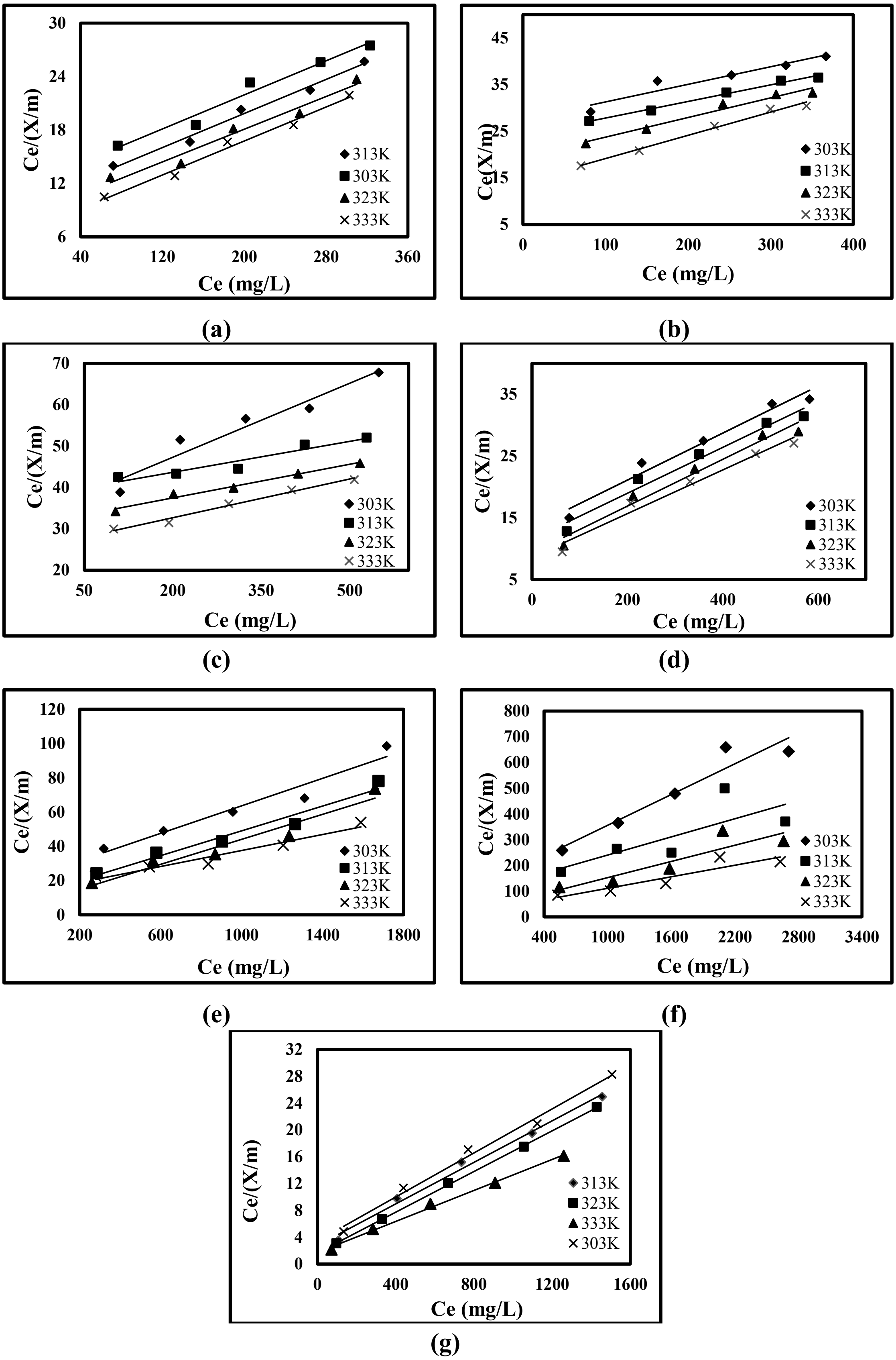


Figure 3.11 *% Uptake of Pb^{2+} on CP*

Reaction conditions: *Amount of CP=100 mg; metal ion concentration=0.001M; total volume of metal ion=10 mL; pH= 4*



(a) (b)

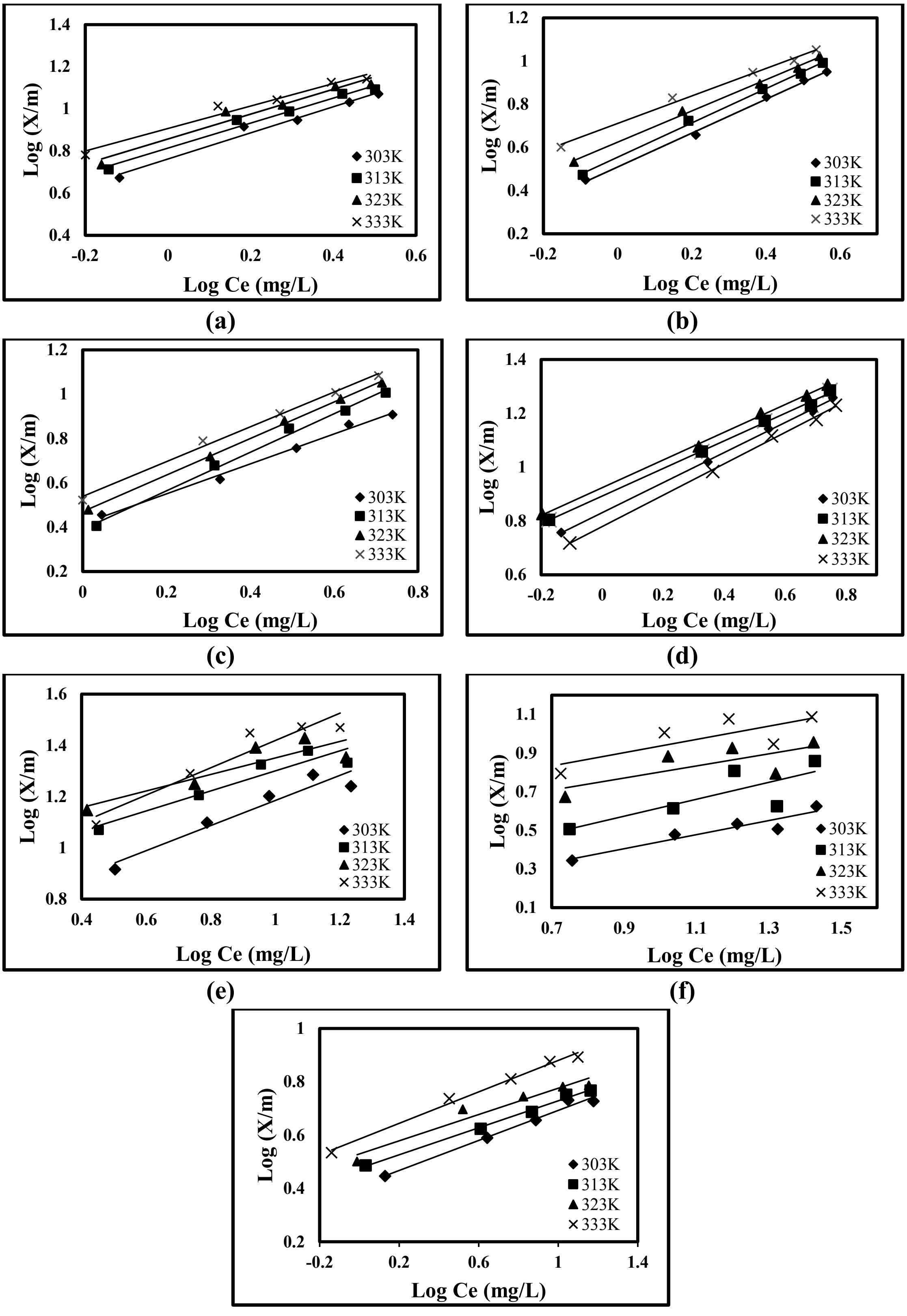
(c) (d)

(e) (f)

(g)

Reaction conditions: *Amount of CP = 100 mg; total volume of metal ion solution = 10 mL*
pH of metal ion solution: pH 3 for Co^{2+}, Cu^{2+}, Zn^{2+}; pH 4 for Ni^{2+}, Hg^{2+}, Pb^{2+} and pH 5 for Cd^{2+}

Figure 3.12 (a-g)*Langmuirplots for (a) Co^{2+}; (b) Ni^{2+}; (c) Cu^{2+}; (d) Zn^{2+}; (e) Cd^{2+}; (f) Hg^{2+} and (g) Pb^{2+}using CP*



(a) (b) (c) (d) (e) (f) (g)

Reaction conditions: *Amount of CP = 100 mg; total volume of metal ion solution = 10 mL*
pH of metal ion solution: pH 3 for Co^{2+}*,* Cu^{2+}*,* Zn^{2+}*; pH 4 for* Ni^{2+}*,* Hg^{2+}*,* Pb^{2+} *and pH 5 for* Cd^{2+}

Figure 3.13 (a-g)*Freundlichplots for(a)* Co^{2+}*; (b)* Ni^{2+}*; (c)* Cu^{2+}*; (d)* Zn^{2+}*; (e)* Cd^{2+}*; (f)* Hg^{2+} *and (g)* Pb^{2+}*using CP*

Table 3.11*Langmuir and Freundlichconstants for transition and heavy metal ions using CP*

Metal Ion	**Temp. (*K*)**	**Langmuir Constants**				**Freundlich Constants**		
		R^2	**b (dm³·mg⁻¹)**	**V_m (mg·g⁻¹)**	**R_L**	**R^2**	***K***	***1/n***
Co^{2+}	303	0.917	0.0011	27.02	0.994	0.993	4.33	0.993
	313	0.941	0.0024	27.02	0.991	0.997	6.20	0.997
	323	0.989	0.0015	28.57	0.981	0.996	5.27	0.996
	333	0.988	0.0030	20.40	0.981	0.997	6.09	0.997
Ni^{2+}	303	0.917	0.0012	23.25	0.999	0.996	5.80	0.764
	313	0.934	0.0016	27.02	0.996	0.998	6.22	0.794
	323	0.957	0.0011	29.41	0.995	0.996	6.50	0.813
	333	0.925	0.0020	30.30	0.986	0.995	6.09	0.825
Cu^{2+}	303	0.942	0.0009	25.64	0.999	0.991	6.65	0.823
	313	0.915	0.0006	41.66	0.998	0.994	7.39	0.869
	323	0.981	0.0008	37.03	0.997	0.999	6.66	0.824
	333	0.983	0.0012	32.25	0.994	0.994	6.08	0.784
Zn^{2+}	303	0.969	0.0031	26.31	0.996	0.998	3.26	0.514
	313	0.971	0.0032	27.02	0.990	0.997	3.25	0.512
	323	0.971	0.0044	27.02	0.981	0.998	3.62	0.559
	333	0.973	0.0040	28.57	0.974	0.997	3.82	0.583
Cd^{2+}	303	0.945	0.0026	25.00	0.993	0.920	3.08	0.489
	313	0.958	0.0032	27.77	0.980	0.890	2.46	0.391
	323	0.938	0.0052	27.77	0.950	0.780	2.09	0.322
	333	0.950	0.0024	37.03	0.972	0.912	3.39	0.531
Hg^{2+}	303	0.919	0.0011	5.02	0.993	0.617	2.20	0.344
	313	0.600	0.0014	8.54	0.989	0.552	2.05	0.313
	323	0.813	0.0020	9.61	0.965	0.633	2.73	0.437
	333	0.838	0.0021	13.51	0.959	0.896	2.31	0.364
Pb^{2+}	303	0.991	0.0061	64.51	0.977	0.984	2.59	0.282
	313	0.999	0.0100	65.78	0.927	0.994	3.01	0.253
	323	0.995	0.0072	86.20	0.921	0.944	3.40	0.246
	333	0.990	0.0051	62.50	0.866	0.991	3.88	0.294

3.8.3 Distribution Studies using CP

The effect of metal ion concentration ondistribution coefficient *(K_d)* was studiedin aqueous medium (**Table 3.12**).With increase in metal ion concentration K_d values increase. Above a particular concentration K_d values are constant which could be explained to be due to the fact that at lower concentrations, almost all the ions are exchanged due to availability of exchangeable sites, which are not available at higher concentrations.

K_d values were also evaluated in aqueous andvarious electrolyte media {HNO_3, NH_4NO_3,$HClO_4$and CH_3COOH of 0.2 M and 0.02 M}at optimum conditions (optimum metal ion concentration, optimum pH and optimum equilibrium time) (**Table 3.13)**. In general, it is observed that K_d values are lower in high concentration of electrolyte and vice versa. In strong electrolyte media,K_d values are lower as compared to weak electrolyte and aqueous media. This may be attributed to the high competition amongst ions for exchange in strong electrolyte media.K_d values in aqueous medium follows the order: Zn^{2+}> Ni^{2+}> Co^{2+} > Cu^{2+} amongst the transition metal ions and Pb^{2+}> Cd^{2+} > Hg^{2+} amongst the heavy metal ions. The most promising features of CP are, high K_d values observed in case of Zn^{2+} andPb^{2+} (aqueous medium), no sorption observed in case of Ni^{2+} (0.2 M $HClO_4$), while Co^{2+} (0.2 M HNO_3), Cu^{2+} (0.2 M HNO_3& 0.2 M $HClO_4$) and Hg^{2+} (0.2 M $HClO_4$) exhibit very low $K_d$values(**Table 3.13)**.

Breakthrough curves (a plot of C_e/C_0 versus effluent volume) are presented in **Figure 3.14 (a-g)**. Breakthrough capacity (BTC) is the dynamic capacity or operating capacity of a known amount of ion exchange material towards metal ion in column operation. K_d is, however determined by a batch process. Thus, the metal ion affinity towards CP, based on K_d and BTC values should be the same, which is observed (**Table 3.13**) in the present study confirming the order of metal ion affinity towards CP.

3.8.4 Elution and Separation Studies using CP

The elution behaviour of single metal ions (under study) are carried out using different eluents such as HNO_3, $HClO_4$, CH_3COOH and NH_4NO_3 of 0.2 and 0.02 M concentration, and results presented in **Table 3.14**. The % metal eluted in all cases, are in the range 81 to 97 % (transition metal ions) and 78 to 98 % (heavy metal ions). Good elution is observed due to presence of single metal ion and non interference of elements. Higher concentration of eluent and acids in general, are better eluents. 0.2 M HNO_3 is the best eluent for most metal ions. Order of % metal eluted amongst the transition metal ions using 0.2 M $HNO_3$is Cu^{2+} (97.22) > Co^{2+} (97. 05) > Ni^{2+} (97.00) > Zn^{2+} (96.03) and amongst the heavy metal ions is Hg^{2+}(98.14) > Cd^{2+} (95.05) > Pb^{2+} (91.34). This observation is in keeping with the fact that metal ions with high K_d values are less eluted and vice-versa **[39, 40]**. All elution curves are symmetrical bell shaped indicating elution efficiency {**Figure 3.15(a-g)**}.

Binary separations for following metal ion pairs, Co^{2+}-Zn^{2+}, Ni^{2+}-Zn^{2+}, Cu^{2+}-Zn^{2+} (transition metal ions) and Hg^{2+}-Pb^{2+}, Hg^{2+}-Cd^{2+}, Cd^{2+}-Pb^{2+} (heavy metal ions) have been performed using concept of high separation factor in a particular medium as discussed earlier in the text (**Section 3.4**). In binary separations, separation efficiency is in the range 79-87 % amongst the transition metal ions and 73-92% amongst the heavy metal ions (**Table 3.15**). In all cases of binary separations, irrespective of metal ion pair, maximum % metal eluted is Ni^{2+} (87.35), Cu^{2+} (86.20), Co^{2+} (84.50), Zn^{2+} (80.95) amongst the transition metal ions and Hg^{2+}(92.50), Cd^{2+} (91.00), Pb^{2+} (85.50) amongst the heavy metal ions. This observation is in keeping with separation factor (α) and K_d values of metal ions. % metal eluted decreases with decreasing separation factor and increases with increasing separation factor and as explained earlier, metal ions with high K_d values are less eluted and vice-versa. Efficient binary separations for all metal ion pairs under study could be attributed to high α values and symmetrical bell shaped curves {**Figure 3.16(a-f)**}.

In ternary separations for Ni^{2+}- Cu^{2+}- Zn^{2+} (transition metal ions) and Hg^{2+}-Cd^{2+}- Pb^{2+} (heavy metal ions) % metal eluted is in the range 47-55 % and 41-62 % respectively (**Table 3.16**). In all cases, three distinct peaks are observed {**Figure 3.17(a-b)**}, however, with tailing effects for every metal ion eluted. % metal eluted is also lower as compared to single and binary metal ion separations. Probably the separation process becomes complex, attributed to the loss of metal ions during the changeover of the eluent, interference of metal ions, pH, simultaneous elution of two or more metal ions with the same eluent, and lastly, experimental errors involved in the determination of metal ions in the presence of other ions, etc. **[39,40]**.

3.8.5 Regeneration and Reusability Studies using CP

A study on regeneration and reuse was performed as described in experimental section. It is observed that the exchanger, once used, can be converted back to its original form by desorption of the metal ions with 1 M HNO_3. A plot of % retention in $K_d$values versus number of cycles is presented in **Figure 3.18** which shows that % retention in K_d values is almost the same ~100 % upto 4 cycles, indicating that CP could be regenerated and reused without much decline in performance

Table 3.12 *Distribution coefficient (K_d) values ($mL\cdot g^{-1}$) varying metal ion concentration using CP*

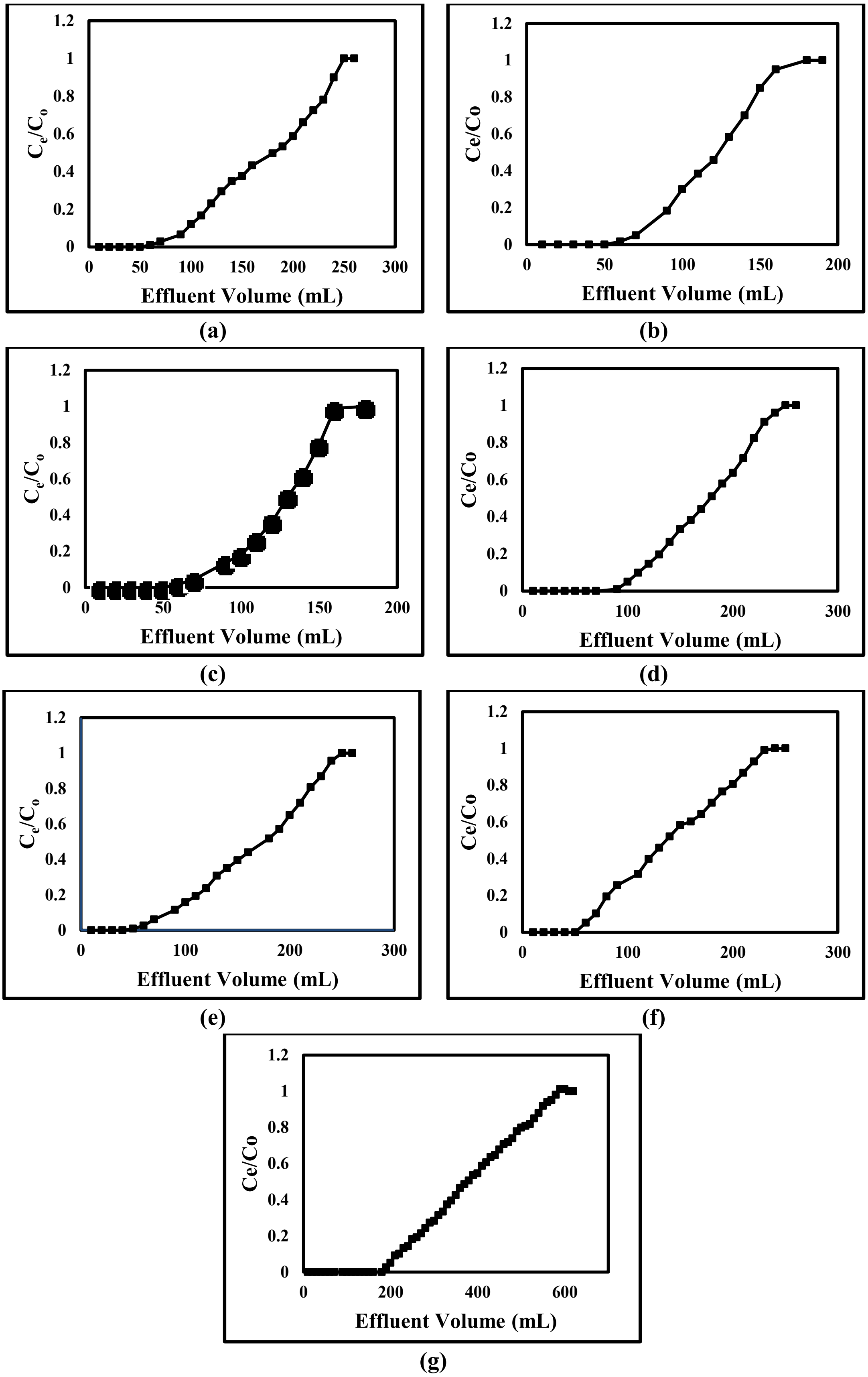
Metal Ions	Distribution coefficient (K_d) values ($mL\cdot g^{-1}$)				
	0.002 M	**0.004 M**	**0.006 M**	**0.008 M**	**0.010 M**
Co^{2+}	115.60	**154.00**	155.00	158.00	158.00
Ni^{2+}	147.10	**189.00**	192.00	193.00	193.00
Cu^{2+}	177.00	**210.00**	210.00	212.00	212.00
Zn^{2+}	205.00	235.00	**260.00**	260.00	261.00
Cd^{2+}	290.00	325.00	**345.30**	347.00	348.00
Hg^{2+}	7.00	15.20	**29.50**	32.00	32.00
Pb^{2+}	2410.00	2500.00	**2590.00**	2600.00	2600.00

Table 3.13 *BTC ($mmol\cdot g^{-1}$) and K_d ($mL.g^{-1}$)values in aqueous and various electrolyte media using CP*

Metal Ions	Ionic Radii (Å)	BTC	K_d*values in aqueous and various electrolyte media/concentration								
			DIW	NH_4NO_3		HNO_3		$HClO_4$		CH_3COOH	
				0.02 M	0.2 M	0.02 M	0.2 M	0.02 M	0.2 M	0.02 M	0.2 M
Co^{2+}	0.72	0.37	201.20	117.00	42.00	27.40	5.00	30.00	16.00	236.50	200.50
Ni^{2+}	0.72	0.47	232.10	134.00	34.00	26.80	15.00	5.50	NS	235.00	155.00
Cu^{2+}	0.74	0.36	194.00	205.00	95.60	70.10	7.00	14.00	6.70	330.00	269.80
Zn^{2+}	0.74	0.50	298.00	196.00	84.70	81.00	28.10	46.80	32.00	304.10	214.00
Cd^{2+}	0.97	0.78	476.50	322.00	96.00	110.00	40.10	90.00	102.50	560.00	820.00
Hg^{2+}	1.44	0.04	31.00	79.50	48.50	78.30	55.80	30.00	4.50	94.00	68.00
Pb^{2+}	1.10	1.16	3640.10	3810.00	2235.20	3450.0	290.50	1528.00	2700.00	5180.20	2210.20

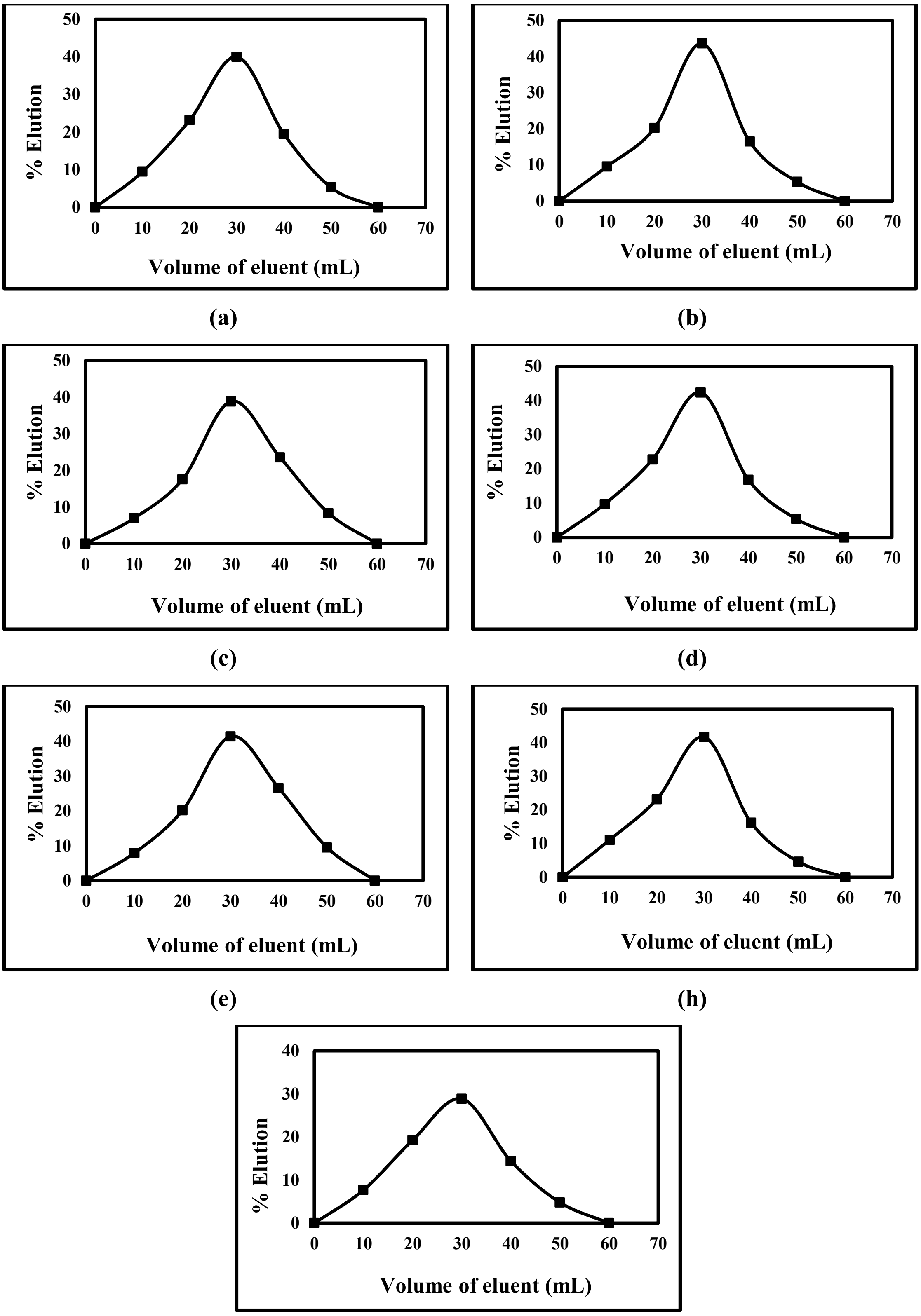
*K_d*Values obtained at optimum condition (Optimum metal ion concentration, Optimum pH of solution and optimum equilibrium time);*

DIW = Deionized water, NS = No sorption



(a) (b) (c) (d) (e) (f) (g)

Figure 3.14(a-g)*Breakthrough curves for, (a) Co^{2+}; (b) Ni^{2+}; (c) Cu^{2+}; (d) Zn^{2+}; (e) Cd^{2+}; (f) Hg^{2+} and (g) Pb^{2+}using CP*



(a) (b)

(c) (d)

(e) (h)

(g)

Figure 3.15(a-g)*Elution behaviour oftransition and heavy metal ions with 0.2 M* HNO_3,*(a)* Co^{2+}; *(b)* Ni^{2+}; *(c)* Cu^{2+};*(d)* Zn^{2+};*(e)* Cd^{2+}; *(f)* Hg^{2+}*and (g)* Pb^{2+}*using CP*

Table 3.14*% Elution (% E) of metal ions in different electrolyte media using CP*

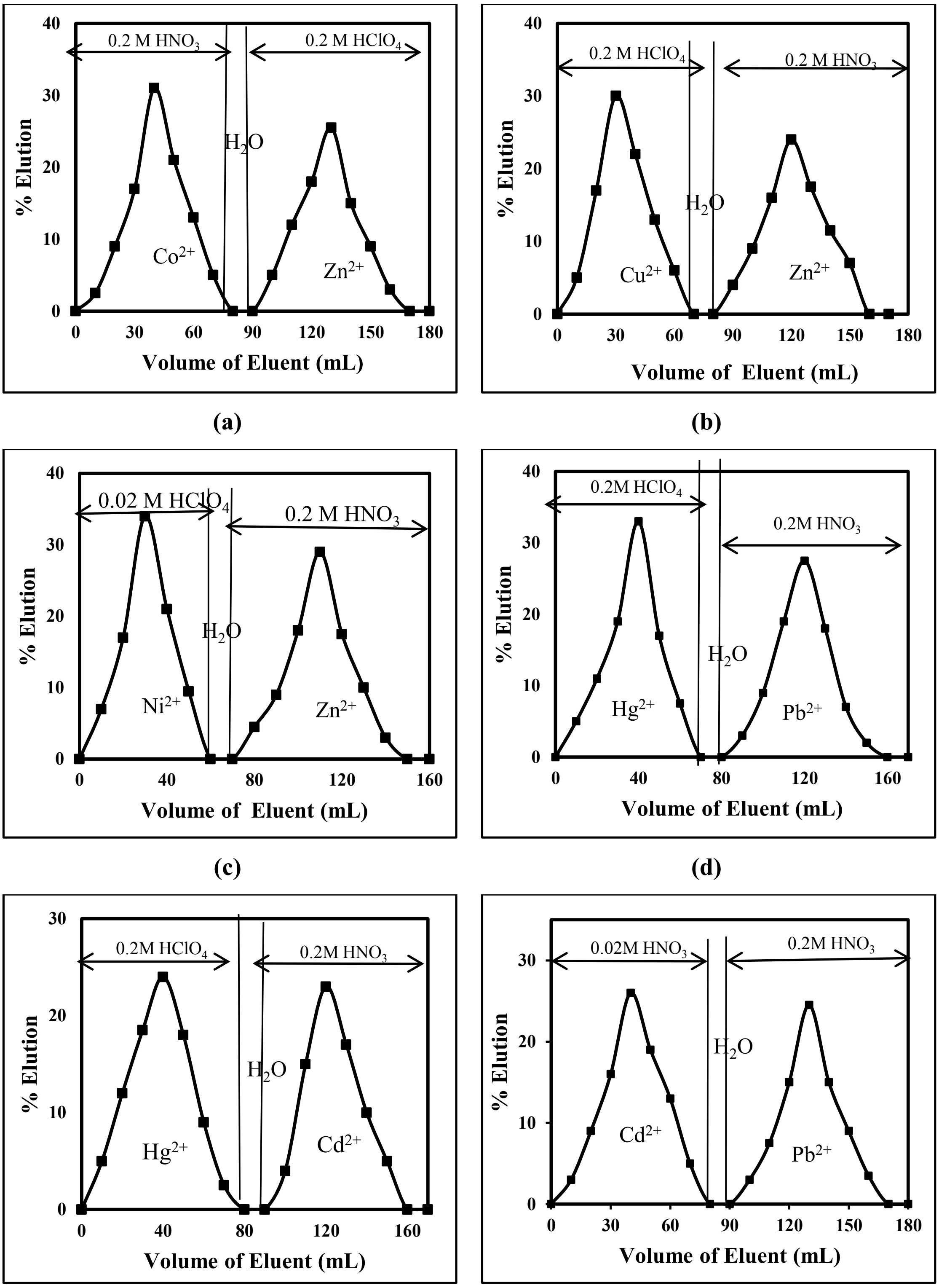
Metal Ions	**NH_4NO_3**		**HNO_3**		**$HClO_4$**		**CH_3COOH**	
	0.02 M	**0.2 M**	**0.02 M**	**0.2 M**	**0.02 M**	**0.2 M**	**0.02 M**	**0.2 M**
Co^{2+}	81.30	83.35	92.15	97.05	92.64	94.10	85.80	88.70
Ni^{2+}	87.00	90.25	94.50	97.00	91.00	93.50	87.90	89.80
Cu^{2+}	87.00	90.30	94.40	97.22	92.10	93.50	86.20	89.40
Zn^{2+}	85.20	87.50	93.10	96.03	93.10	95.10	90.15	92.15
Cd^{2+}	85.10	89.35	94.70	95.05	91.50	93.60	89.20	95.40
Hg^{2+}	91.66	92.60	96.30	98.14	93.50	96.75	89.20	92.10
Pb^{2+}	84.20	86.50	88.45	91.34	86.55	89.40	78.80	80.35

**Eluent volume = 60 mL and 50 mL for 0.02 M and 0.2 M electrolytes respectively*
Maximum deviation in % elution of metal ions = ±2

Table 3.15*Binary separations of transition and heavy metal ions using CP*

Separation achieved	**Separation Factor (α)**	**Eluent**	**Metal ion [mg]**		**Elution [%]**
			Loaded (C_o)	**Eluted (C_e)**	
Co^{2+}-Zn^{2+}	1.5	a) 0.2 M HNO_3(Co^{2+})	0.5893	0.4980	84.50
		b) 0.2 M $HClO_4$ (Zn^{2+})	0.6540	0.5295	80.95
Cu^{2+}-Zn^{2+}	1.5	a) 0.2 M $HClO_4$(Cu^{2+})	0.6354	0.5480	86.25
		b) 0.2 M HNO_3(Zn^{2+})	0.6540	0.5244	80.20
Ni^{2+}-Zn^{2+}	1.3	a) 0.02 M $HClO_4$ (Ni^{2+})	0.5869	0.5126	87.35
		b) 0.2 M $HClO_4$ (Zn^{2+})	0.6540	0.5185	79.30
Hg^{2+}-Pb^{2+}	121.3	a) 0.2 M $HClO_4$(Hg^{2+})	2.0059	1.8554	92.50
		b) 0.2 M HNO_3 (Pb^{2+})	2.0720	1.7715	85.50
Hg^{2+}-Cd^{2+}	15.8	a) 0.2 M $HClO_4$(Hg^{2+})	2.0059	1.8354	89.00
		b) 0.2 M HNO_3 (Cd^{2+})	1.1241	0.8317	73.90
Cd^{2+}-Pb^{2+}	7.6	a) 0.02 M HNO_3(Cd^{2+})	1.1241	1.0229	91.00
		b) 0.2 M HNO_3 (Pb^{2+})	2.0720	1.5430	74.50

Maximum deviation in % elution =±2



(a) (b)

(c) (d)

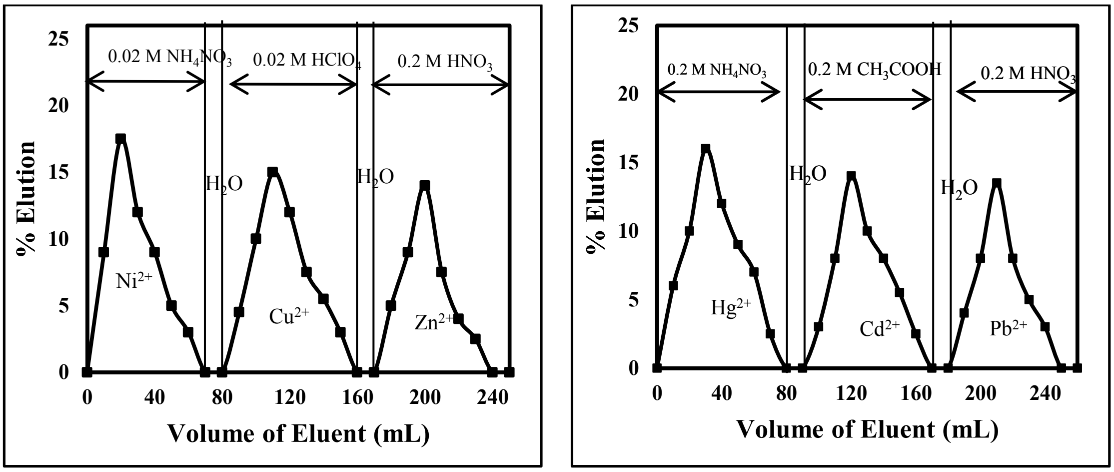
(e) (f)

Figure 3.16(a-f)*Binary separations of transition and heavy metal ions using CP, (a)* Co^{+2}*-*Zn^{+2}*, (b)* Cu^{2+}*-*Zn^{2+}*, (c)* Ni^{2+}*-*Zn^{2+}*, (d)* Hg^{2+}*-*Pb^{2+}*, (e)* Hg^{2+}*-*Cd^{2+} *and (f)* Cd^{2+}*-*Pb^{2+}

Table 3.16*Ternary separations of transition and heavy metal ions using CP*

Separations achieved	Eluent	Metal ion [mg] Loaded (C_o)	Metal ion [mg] Eluted (C_e)	Elution [%]
Ni^{2+}-Cu^{2+}-Zn^{2+}	a) 0.02 M NH_4NO_3 (Ni^{2+})	0.5869	0.3257	55.50
	b) 0.02 M $HClO_4$ (Cu^{2+})	0.6354	0.3113	49.00
	c) 0.2 M HNO_3 (Zn^{2+})	0.6540	0.3099	47.40
Hg^{2+}-Cd^{2+}-Pb^{2+}	a) 0.2 M NH_4NO_3 (Hg^{2+})	2.0059	1.2536	62.50
	b) 0.02 M CH_3COOH (Cd^{2+})	1.1241	0.5732	51.00
	c) 0.2 M HNO_3 (Pb^{2+})	2.0720	0.8598	41.50

Maximum deviation in % elution =±2



(a) **(b)**

Figure 3.17 (a-b)*Ternary separation of transition and heavy metal ions using CP, (a) Ni^{2+}-Cu^{2+}-Zn^{2+} and (b) Hg^{2+}-Cd^{2+}-Pb^{2+}*

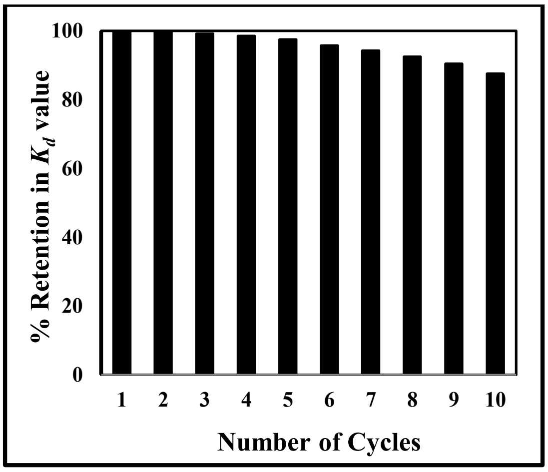


Figure 3.18*A plot of % retention in K_d values versus number of cycles using CP*

3.9 RESULTS AND DISCUSSION – PART II

3.9.1 Thermodynamic Studies using TP

Thermodynamics of ion exchange has been studied for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (transition metal ions) and Cd^{2+}**,** Hg^{2+}, Pb^{2+} (heavy metal ions). Equilibrium constant (K), standard Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) have been evaluated using standard equationsdiscussed earlier in text **(Eqs.3.10-3.12**)and results presented in **Table 3.17.**

Equilibrium constant (K) values increase with increase in temperature for all metal ions under study (**Table 3.17)**, indicating that the metal ions have higher affinity for the exchanger and that the mechanism is ion exchangeas discussed earlier in text [**42**].

The free energy change ($\Delta G°$) for all the exchange reactions is negative, over the entire temperature range, indicating that the exchanger has a greater preference for metal ions than H^+ ions. Further, $\Delta G°$ values become more negative with increasing temperature indicating increase in feasibility and spontaneity of the sorption process,and that the exchange is favoured with increasing temperature **[42]**. At any given temperature, $\Delta G°$ follows the order (increasing negativity): $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$ amongst the transition metal ions and $Pb^{2+} > Cd^{2+} > Hg^{2+}$ amongst the heavy metal ions.

The enthalpy change ($\Delta H°$)is positive in all cases indicating that the exchange process is endothermic. $\Delta H°$ follows the order $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$ and $Pb^{2+} > Cd^{2+} > Hg^{2+}$. Higher/positive values of enthalpy change indicate more endothermicity of the exchange process and requirement of more energy for dehydration to occur.The $\Delta H°$ values indicate that probably complete dehydration occurs in case of Cu^{2+} and Pb^{2+}. Further, trends in $\Delta H°$values arealso supportive to trends in $\Delta G°$ values.

$\Delta S°$ also follows same trend as $\Delta H°$. Higher values observed in case of Cu^{2+} and Pb^{2+}, are attributed to greater dehydration, which indicates the greater disorder produced during the exchange.

Table 3.17 *Thermodynamic parameters for M^{2+}-H^+ exchange at various temperatures using TP*

Exchanging System	Temperature (K)	K_a	ΔG° (k J mol^{-1})	ΔH° (k J mol^{-1})*	ΔS° (J mol^{-1} K^{-1})
$Co^{2+} – H^+$	303	1.52	-0.53	2.69	10.62
	313	1.56	-0.58		10.46
	323	1.60	-0.63		10.30
	333	1.67	-0.72		10.22
$Ni^{2+} – H^+$	303	1.73	-0.69	12.04	42.06
	313	1.78	-0.75		40.90
	323	2.28	-1.10		40.74
	333	2.65	-1.34		40.23
$Cu^{2+} – H^+$	303	2.31	-1.05	69.37	230.69
	313	3.77	-1.72		227.51
	323	10.01	-3.09		224.91
	333	16.26	-3.86		220.46
$Zn^{2+} – H^+$	303	2.08	-0.92	43.59	145.62
	313	2.50	-1.19		143.96
	323	2.96	-1.45		140.27
	333	3.10	-1.56		137.57
$Cd^{2+} – H^+$	303	1.78	-0.68	40.74	136.60
	313	2.06	-0.94		133.17
	323	3.55	-1.70		131.40
	333	6.96	-2.68		130.41
$Hg^{2+} – H^+$	303	1.48	-0.49	18.47	63.93
	313	2.25	-1.06		62.42
	323	2.75	-1.36		61.42
	333	3.44	-1.71		60.64
$Pb^{2+} – H^+$	303	4.75	-1.96	138.14	462.39
	313	11.47	-4.47		455.64
	323	64.07	-6.92		449.13
	333	249.63	-9.02		441.94

**Average value calculated from the van't Hoff isochore equation.*

3.9.2 AdsorptionStudies using TP

The effect of experimental conditions such as pH, contact time and temperature were studied to set the conditions for maximum adsorption/ion exchange for the metal ions by the ion exchanger.

The effect of pH on the sorption behaviour of metal ions (under study) have been presented in **Table 3.18**. At pH values less than ~3, very less sorption has been observed for all metal ions. The lack of sorption at low pH could be attributed to high concentration of the hydrogen ions competing with the metal ions for sorption/exchange sites. A precipitation was observed in case of Ni^{2+}, Cu^{2+} and Pb^{2+} at pH 6, in case ofCo^{2+} and Cd^{2+} at pH 8 and in case of Zn^{2+} and Hg^{2+}atpH 5.The observed order for % uptake of metal ion at optimum pH, is $Cu^{2+}>Ni^{2+}>Zn^{2+}>Co^{2+}$ (amongst transition metal ions) and $Pb^{2+}>Cd^{2+}> Hg^{2+}$ (amongst heavy metal ions) **(Table 3.18).**

The time taken for attainment of equilibrium for each metal ion in $mg{\cdot}L^{-1}$ has been presented in **Table 3.19**.Sorption of metal ions varying contact time and temperature has been presented in **Tables 3.20 to 3.26** and illustrated in **Figures 3.19 to 3.25** [plot of uptake (%) versus time]. It is observed that sorption increases gradually with increase in contact time and reaches a maximum value after which randomness is observed. Increase in % uptake could be attributed to two different sorption processes, namely, a fast ion exchange followed by chemisorption **[43, 44]**. It is observed that % uptake of each metal ion increases with increase in temperature, which indicates the uptake to be an ion exchange mechanism**[43]**.

Langmuir constants (b and V_m) and Freundlich constants (K and $1/n$)obtained from the slopes and intercepts of the linear plots {**Figures 3.26(a-g) and 3.27(a-g)** respectively} are listed in **Table 3.27**. It is observed thatR^2 values are found to be close to unity for both isotherms and provides a good fit to the experimental data for sorption of all the metal ions taken (except Hg^{2+} for Freundlich isotherm). Variation in R^2 values is attributed to the fact that the surface adsorption is not a monolayer with single site. Two or more sites with different affinities may be involved in metal ion sorption **[43,44]**. In the present study, low values of b indicate favorable adsorption. V_m values, reflect maximum adsorption capacity of metal ions towards exchanger, follows the order $Zn^{2+}>Cu^{2+}>Ni^{2+}>Co^{2+}$amongst transition metal ions and $Pb^{2+}>Cd^{2+}>Hg^{2+}$amongst heavy metal ions at 303 K. The values of $1/n$ and R_L are obtained between 0 and 1 which indicates normal isotherm and favourable adsorption. Langmuir and Freundlich isotherms have been presented in **Figures 3.26(a-g) and 3.27(a-g)** respectively.

Table 3.18% *Uptake of metal ions at various pH using TP*

pH	**Uptake of metal ion (%)**						
	Co^{2+}	**Ni^{2+}**	**Cu^{2+}**	**Zn^{2+}**	**Cd^{2+}**	**Hg^{2+}**	**Pb^{2+}**
1	8.00	2.20	5.50	3.00	10.40	2.00	21.11
2	10.30	4.35	19.55	15.40	14.60	3.50	33.69
3	**23.50**	11.25	**35.15**	**24.30**	17.50	4.10	40.52
4	20.08	**26.76**	16.43	10.50	26.38	**5.00**	**63.55**
5	13.85	14.20	11.00		**40.20**		34.50
6					20.20		
7					18.70		

Maximum deviation in % uptake of metal ion =±2%

Table 3.19 *Time taken for attainment of equilibrium using TP*

Metal Ion	**Equilibrium time (min)**			
	303 K	**313 K**	**323 K**	**333 K**
Co^{2+}	60	60	50	50
Ni^{2+}	60	60	40	40
Cu^{2+}	60	60	50	50
Zn^{2+}	60	50	40	40
Hg^{2+}	40	40	40	40
Cd^{2+}	90	90	70	60
Pb^{2+}	170	170	120	120

Table 3.20 *% Uptake of Co^{2+} on TP*

Time	% Uptake of Co^{2+}			
mins	303K	313 K	323 K	333K
10	8.5	10.1	12.0	13.9
20	11.4	12.9	13.2	15.0
30	13.1	14.5	16.4	17.8
40	16.7	17.5	18.7	20.1
50	19.0	20.0	21.6	22.6
60	20.1	22.7		

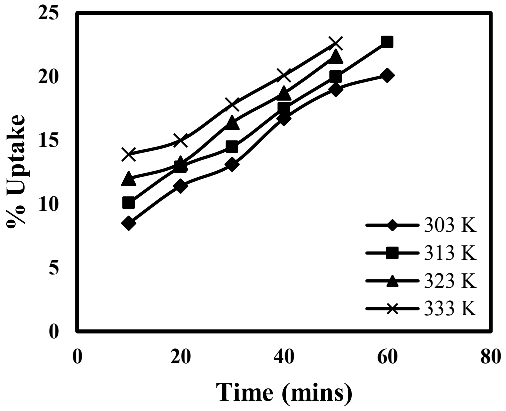


Figure 3.19 *% Uptake of Co^{2+} on TP*

Reaction conditions: *Amount of TP=100 mg; metal ion concentration=0.001M; total volume of metal ion = 10 mL= pH, 3*

Table 3.21 *% Uptake of Ni^{2+} on TP*

Time	% Uptake of Ni^{2+}			
mins	303K	313 K	323 K	333K
10	10.0	11.7	14.0	16.2
20	12.0	13.5	15.2	19.1
30	14.2	16.6	18.8	21.9
40	15.5	19.3	22.1	24.5
50	18.8	21.0		
60	20.2	23.0		

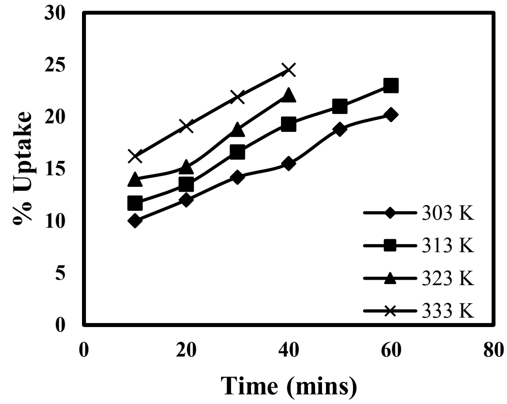


Figure 3.20 *% Uptake of Ni^{2+} on TP*

Reaction conditions: *Amount of TP=100 mg; metal ion concentration=0.001M; total volume of metal ion=10 mL; pH=4*

Table 3.22 *% Uptake of Cu^{2+} on TP*

Time	% Uptake of Cu^{2+}			
mins	303K	313 K	323 K	333K
10	14.5	15.7	17.0	18.7
20	16.2	18.3	19.5	21.4
30	18.0	20.8	22.6	25.2
40	20.1	23.4	25.8	29.6
50	23.5	25.8	29.1	35.4
60	26.0	28.2		

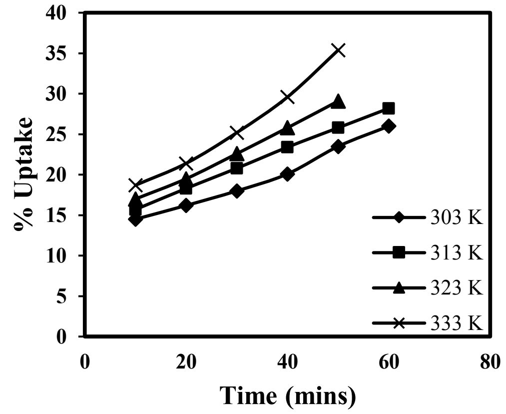


Figure 3.21 *% Uptake of Cu^{2+} on TP*

Reaction conditions: *Amount of TP=100 mg; metal ion concentration=0.001M; total volume of metal ion=10 mL; pH= 3*

Table 3.23 *% Uptake of Zn^{2+} on TP*

Time mins	% Uptake of Zn^{2+}			
	303K	313 K	323 K	333K
10	8.2	10.1	11.5	13.1
20	10.2	11.4	14.0	15.3
30	12.2	13.1	16.5	17.4
40	13.4	14.8	18.3	21.0
50	15.1	17.3		
60	17.0			

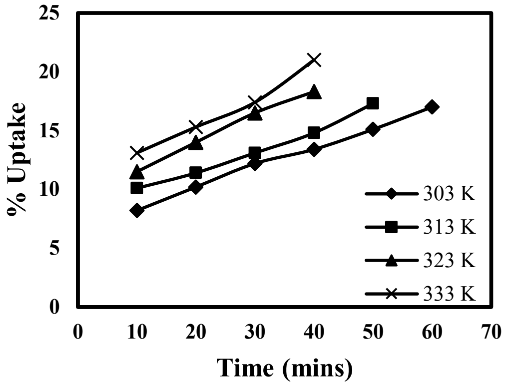


Figure 3.22 *% Uptake of Zn^{2+} on TP*

Reaction conditions: *Amount of TP=100 mg; metal ion concentration=0.001M; total volume of metal ion=10 mL; pH= 3*

Table 3.24 *% Uptake of Cd^{2+} on TP*

Time mins	% Uptake of Cd^{2+}			
	303 K	313 K	323 K	333 K
10	13.2	14.7	16.0	18.1
20	14.1	16.2	18.5	21.5
30	15.0	18.7	20.3	24.0
40	15.9	20.3	21.7	26.3
50	16.7	21.8	24.9	28.6
60	17.9	24.6	28.2	35.0
70	19.5	25.3	30.0	
80	21.6	27.0		
90	23.0	28.3		

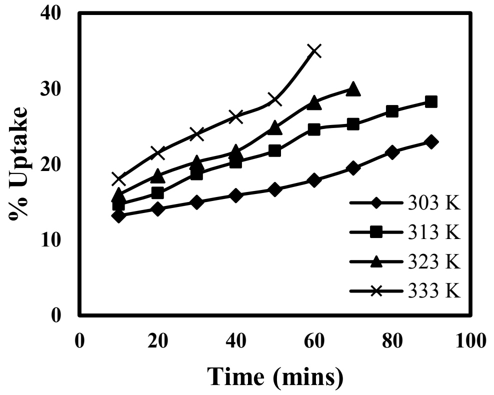


Figure 3.23 *% Uptake of Cd^{2+} on TP*

Reaction conditions: *Amount of TP =100 mg; metal ion concentration=0.001M; total volume of metal ion=10 mL; pH= 5*

Table 3.25 *% Uptake of Hg^{2+} on TP*

Time mins	% Uptake of Hg^{2+}			
	303 K	313 K	323 K	333 K
10	1.7	2.3	3.0	3.9
20	2.2	3.6	4.1	4.8
30	3.0	4.2	5.3	5.9
40	4.2	5.0	6.3	7.5

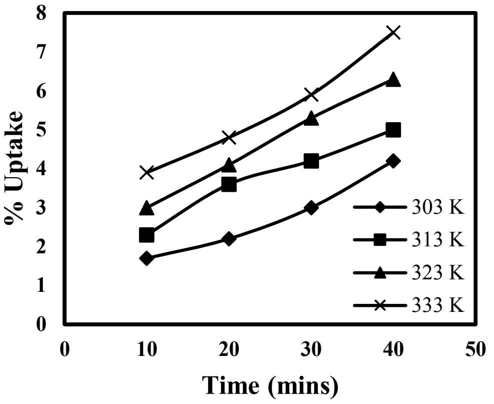


Figure 3.24 *% Uptake of Hg^{2+} on TP*

Reaction conditions: *Amount of TP=100 mg; metal ion concentration=0.001M; total volume of metal ion=10 mL; pH= 4*

Table 3.26 *% Uptake of Pb^{2+} on TP*

Time mins	% Uptake of Pb^{2+}			
	303 K	313 K	323 K	333 K
10	16.2	18.0	22.0	28.2
20	19.2	19.7	23.8	30.5
30	21.1	23.0	26.1	34.5
40	23.5	25.1	28.4	37.1
50	25.1	27.6	31.2	39.7
60	26.6	29.3	34.0	42.2
70	27.9	32.0	37.1	45.0
80	29.5	34.3	39.9	48.0
90	32.0	36.7	42.2	50.6
100	33.7	39.8	44.6	53.8
110	35.8	41.3	48.0	55.5
120	37.6	43.8	50.3	58.0
130	39.2	45.7		
140	41.2	48.0		
150	43.0	50.1		
160	45.2	52.2		
170	47.0	53.4		

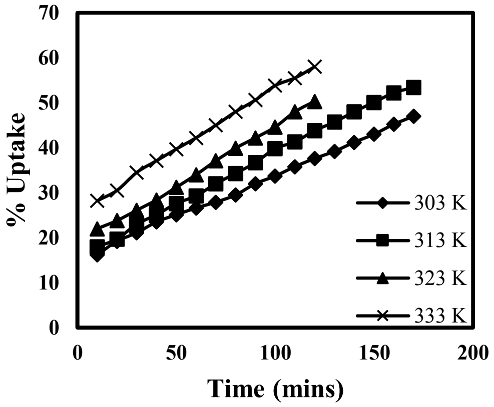
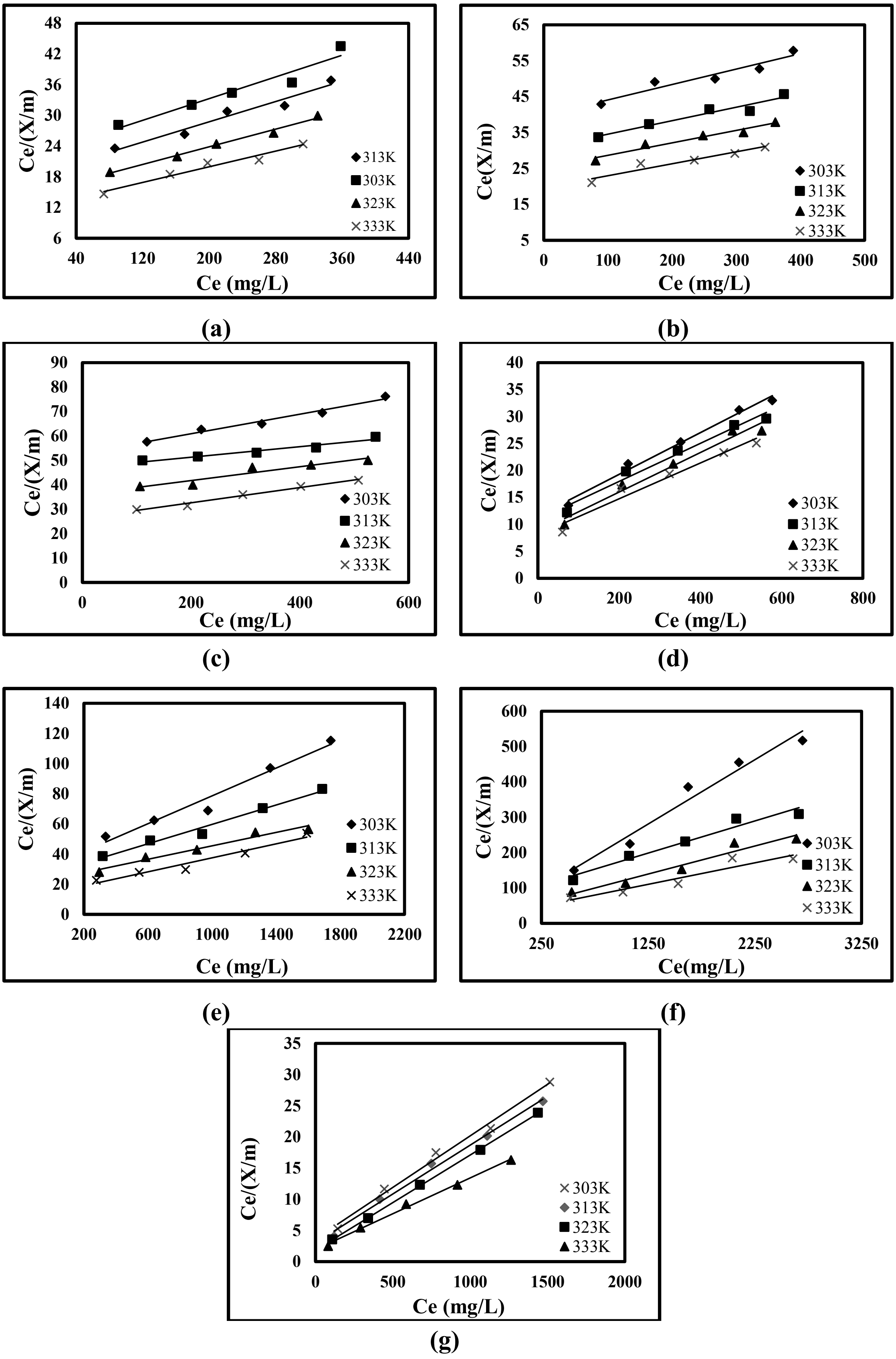


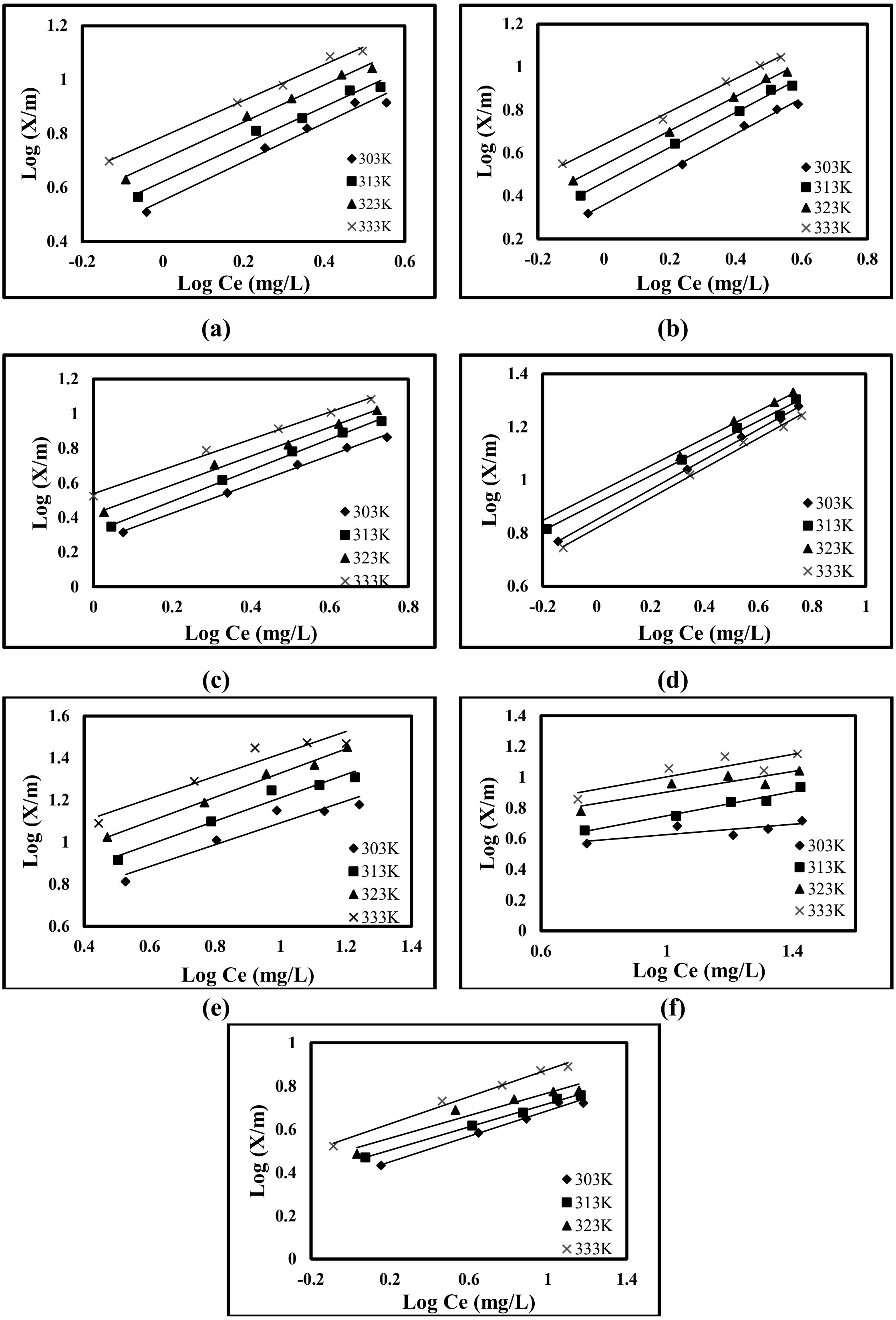
Figure 3.25 *% Uptake of Pb^{2+} on TP*

Reaction conditions: *Amount of TP=100 mg; metal ion concentration=0.001M; total volume of metal ion=10 mL; pH= 4*



Reaction conditions: *Amount of TP = 100 mg; total volume of metal ion solution = 10 mL*
pH of metal ion solution: pH 3 for Co^{2+}, Cu^{2+}, Zn^{2+}; pH 4 for Ni^{2+}, Hg^{2+}, Pb^{2+} and pH 5 for Cd^{2+}

Figure 3.26 (a-g)*Langmuir plots for (a) Co^{2+}; (b) Ni^{2+}; (c) Cu^{2+}; (d) Zn^{2+}; (e) Cd^{2+}; (f) Hg^{2+} and (g) Pb^{2+}using TP*



Reaction conditions: *Amount of TP = 100 mg; total volume of metal ion solution = 10 mL*
pH of metal ion solution: pH 3 for Co^{2+}, Cu^{2+}, Zn^{2+}; pH 4 for Ni^{2+}, Hg^{2+}, Pb^{2+} and pH 5 for Cd^{2+}

Figure 3.27 (a-g)*Freundlichplots for (a) Co^{2+}; (b) Ni^{2+}; (c) Cu^{2+}; (d) Zn^{2+}; (e) Cd^{2+}; (f) Hg^{2+} and (g) Pb^{2+}using TP*

Table 3.27*Langmuir and Freundlichconstants for transition and heavy metal ions using TP*

Metal Ion	Temp. (*K*)		Langmuir Constants			Freundlich Constants		
		R^2	b (dm^3 mg^{-1})	V_m (mg g^{-1})	R_L	R^2	*K*	*1/n*
Co^{2+}	303	0.933	0.0023	18.86	0.997	0.981	5.18	0.715
	313	0.957	0.0026	20.40	0.993	0.980	4.93	0.693
	323	0.989	0.0028	23.25	0.991	0.994	4.86	0.687
	333	0.961	0.0031	26.31	0.988	0.991	4.64	0.667
Ni^{2+}	303	0.917	0.0011	23.25	0.999	0.996	5.80	0.764
	313	0.934	0.0012	27.02	0.998	0.998	6.22	0.794
	323	0.957	0.0014	29.41	0.996	0.996	6.50	0.813
	333	0.925	0.0017	30.30	0.993	0.995	6.09	0.825
Cu^{2+}	303	0.976	0.0008	25.00	0.999	0.993	6.80	0.833
	313	0.948	0.0004	47.61	0.999	0.994	7.92	0.899
	323	0.908	0.0008	35.71	0.997	0.999	6.66	0.824
	333	0.983	0.0012	32.25	0.994	0.994	6.08	0.784
Zn^{2+}	303	0.987	0.0033	26.31	0.992	0.995	3.25	0.513
	313	0.972	0.0033	27.77	0.978	0.995	3.27	0.515
	323	0.975	0.0040	28.57	0.959	0.999	3.67	0.565
	333	0.961	0.0041	30.30	0.943	0.997	3.64	0.562
Cd^{2+}	303	0.964	0.0014	21.73	0.994	0.921	1.65	0.219
	313	0.979	0.0012	31.25	0.991	0.963	3.58	0.555
	323	0.963	0.0009	45.45	0.989	0.991	3.75	0.575
	333	0.950	0.0016	43.47	0.976	0.912	3.39	0.531
Hg^{2+}	303	0.967	0.0034	5.52	0.980	0.744	2.32	0.366
	313	0.955	0.0011	10.98	0.987	0.801	2.15	0.333
	323	0.947	0.0019	12.65	0.968	0.968	2.46	0.391
	333	0.899	0.0018	16.66	0.963	0.631	1.46	0.167
Pb^{2+}	303	0.991	0.0043	62.50	0.982	0.984	2.45	0.295
	313	0.992	0.0050	65.78	0.959	0.996	2.81	0.268
	323	0.912	0.0057	90.90	0.934	0.935	3.20	0.261
	333	0.999	0.0081	66.66	0.880	0.987	3.64	0.313

3.9.3 Distribution Studies using TP

The effect of metal ion concentration ondistribution coefficient (K_d) was studied in aqueous medium(**Table 3.28**).With increase in concentration,K_d values increase. Above a particular concentration,K_d values are constant which could be explained to be due to the fact that at lower concentrations, almost all the ions are exchanged due to availability of exchangeable sites, which are not available at higher concentrations.

K_d values were also evaluated in aqueous and various electrolyte media {HNO_3, NH_4NO_3,$HClO_4$and CH_3COOH of 0.2 M and 0.02 M} at optimum conditions (optimum metal ion concentration, optimum pH and optimum equilibrium time) (**Table 3.29).** In general, it is observed that K_d values are lower in high concentration of electrolyte and vice versa. In strong electrolyte media,K_d values are lower as compared to weak electrolyte and aqueous media. This may be attributed to the high competition amongst ions for exchange in strong electrolyte media.K_d values in aqueous medium follows the order: Cu^{2+}> Zn^{2+}> Ni^{2+} > Co^{2+} amongst the transition metal ions, Pb^{2+}> Cd^{2+} > Hg^{2+} amongst the heavy metal ions. The most promising features of TP are, high K_d values observed in case of Cu^{2+} andPb^{2+} (aqueous medium), no sorption observed in case of Cu^{2+} (0.2 M HNO_3 and 0.2 M $HClO_4$), Ni^{2+} (0.2 M HNO_3), Cd^{2+} (0.2 M HNO_3 and 0.2 M $HClO_4$) and Zn^{2+} (0.2 M $HClO_4$) while Co^{2+}(0.2 M $HClO_4$) and Ni^{2+}(0.2 M $HClO_4$) exhibit very low $K_d$values.

Breakthrough curves (a plot of C_e/C_0 versus effluent volume) are presented in **Figure 3.28(a-g)**. Breakthrough capacity (BTC) is the dynamic capacity or operating capacity of a known amount of ion exchange material towards metal ion in column operation. K_d, however is determined by a batch process. Thus, the metal ion affinity towards TP, based on K_d and BTC values should be the same, which is observed (**Table 3.29**) in the present study confirming the order of metal ion affinity towards TP.

3.9.4 Elution and Separation Studies using TP

The elution behaviour of single metal ions (under study) have been carried out using different eluents such as HNO_3, $HClO_4$, CH_3COOH and NH_4NO_3 of 0.2 and 0.02 M concentration, and resultspresented in **Table 3.30.** The % metal eluted in all cases, is in the range 86 to 97 % (transition metal ions) and 79 to 95 % (heavy metal ions). Good elution is observed due to presence of single metal ion and non interference of elements. Higher concentration of eluent and acids in general, are better eluents. 0.2 M HNO_3 is the best eluent for most metal ions.Order of % metal eluted amongst the transition metal ions using 0.2 M $HNO_3$is Ni^{2+} (97.95) > Cu^{2+} (97. 05) > Co^{2+} (96.10) > Zn^{2+} (95.09) and amongst the heavy metal ions is Cd^{2+}(95.71) > Pb^{2+} (95.05) > Hg^{2+} (88.14). This observation is in keeping with the fact that metal ions with high K_d values are less eluted and vice-versa **[39,40]**. All elution curves are symmetrical bell shaped indicating elution efficiency **{Figure 3.29{a-g)}**.

Binary separations for following metal ion pairs, Ni^{+2}-Cu^{+2}, Co^{+2}-Cu^{+2}, Ni^{+2}-Zn^{+2} (transition metal ions) and Hg^{+2}-Pb^{+2}, Cd^{+2}-Hg^{+2}, Cd^{+2}-Pb^{+2} (heavy metal ions) have been performed using concept of high separation factor in a particular medium as discussed earlier in the text (**Section 3.4**). In binary separations, separation efficiency is in the range 84-92 % amongst the transition metal ions and 80-92% amongst the heavy metal ions (**Table 3.31**). In all cases of binary separations, irrespective of metal ion pair, maximum % metal eluted is Co^{2+} (92.50), Ni^{2+} (90.50), Zn^{2+} (87.50), Cu^{2+} (86.00) amongst the transition metal ions and Cd^{2+}(92.50), Hg^{2+} (90.00), Pb^{2+} (86.50) amongst the heavy metal ions. This observation is in keeping with separation factor (α) and K_d values of metal ions. % metal eluted decreases with decreasing separation factor and increases with increasing separation factor and as explained earlier, metal ions with high K_d values are less eluted and vice-versa. Efficient separations for all metal ion pairs under studycould be attributed to high α values and symmetrical bell shaped curves {**Figure 3.30(a-f**)}.

In ternary separations for Co^{2+}- Ni^{2+}- Cu^{2+} (transition metal ions) and Hg^{2+}-Cd^{2+}- Pb^{2+} (heavy metal ions) % metal eluted is in the range 48-52% and 44-50% respectively (**Table 3.32**). In all cases, three distinct peaks are observed {**Figure 3.31 (a-b)**}, however, with tailing effects for every metal ion eluted. % metal eluted is also lower as compared to single and binary metal ion separations. Probably the separation process becomes complex, attributed to the loss of metal ions during the changeover of the eluent, interference of metal ions, pH, simultaneous elution of two or more metal ions with the same eluent, and lastly, experimental errors involved in the determination of metal ions in the presence of other ions, etc.**[39,40]**.

3.9.5 Regeneration and Reusability Studies usingTP

A study on regeneration and reuse was performed as described in experimental section. It is observed that the exchanger, once used, can be converted back to its original form by desorption of the metal ions with 1 M HNO_3. A plot of % retention in $K_d$values versus number of cycles is presented in **Figure 3.32** which shows that % retention in K_d values is almost the same ~100 % upto 4 cycles, indicating that TP could be regenerated and reused without much decline in performance.

Table 3.28 *Distribution coefficient (K_d) values ($mL\cdot g^{-1}$) varying metal ion concentration using TP*

Metal Ions	**Distribution coefficient (K_d) values ($mL\cdot g^{-1}$)**				
	0.002 M	**0.004 M**	**0.006 M**	**0.008 M**	**0.010 M**
Co^{2+}	95.26	**125.14**	127.00	128.40	130.00
Ni^{2+}	138.10	**161.20**	164.00	166.10	168.00
Cu^{2+}	230.15	**254.10**	258.00	258.62	259.24
Zn^{2+}	172.40	199.00	**210.50**	214.00	214.40
Cd^{2+}	245.50	299.32	**312.25**	315.00	318.0
Hg^{2+}	72.80	85.20	**99.56**	100.00	100.00
Pb^{2+}	2300.10	2360.00	**2410.00**	2410.00	2415.00

Table 3.29 *BTC ($mmol\cdot g^{-1}$) and K_d ($mL\cdot g^{-1}$) values in aqueous and various electrolyte media using TP*

Metal Ions	**Ionic Radii (Å)**	**BTC**	**K_d*values in aqueous and various electrolyte media/concentration**								
			DIW	**NH_4NO_3**		**HNO_3**		**$HClO_4$**		**CH_3COOH**	
				0.02 M	**0.2 M**	**0.02 M**	**0.2 M**	**0.02 M**	**0.2 M**	**0.02 M**	**0.2 M**
Co^{2+}	0.72	0.24	87.94	72.94	18.86	18.99	5.56	9.27	3.00	124.80	69.30
Ni^{2+}	0.72	0.32	167.78	151.21	144.30	27.60	NS	24.17	19.00	88.20	73.31
Cu^{2+}	0.74	0.45	270.43	207.00	74.19	49.66	NS	17.37	NS	287.32	118.80
Zn^{2+}	0.74	0.34	180.36	134.40	94.15	48.31	24.12	86.47	NS	181.42	140.26
Cd^{2+}	0.97	0.47	245.00	179.20	65.10	20.00	NS	23.75	NS	235.42	180.90
Hg^{2+}	1.44	0.22	80.18	143.00	136.50	150.40	118.10	186.20	178.21	140.40	128.30
Pb^{2+}	1.10	0.96	2390.16	1400.00	978.20	560.76	78.72	526.77	89.26	2980.42	1788.58

*K_d*Values obtained at optimum condition (Optimum metal ion concentration, Optimum pH of solution and maximum equilibrium time); DIW = Deionized water, NS = No sorption*

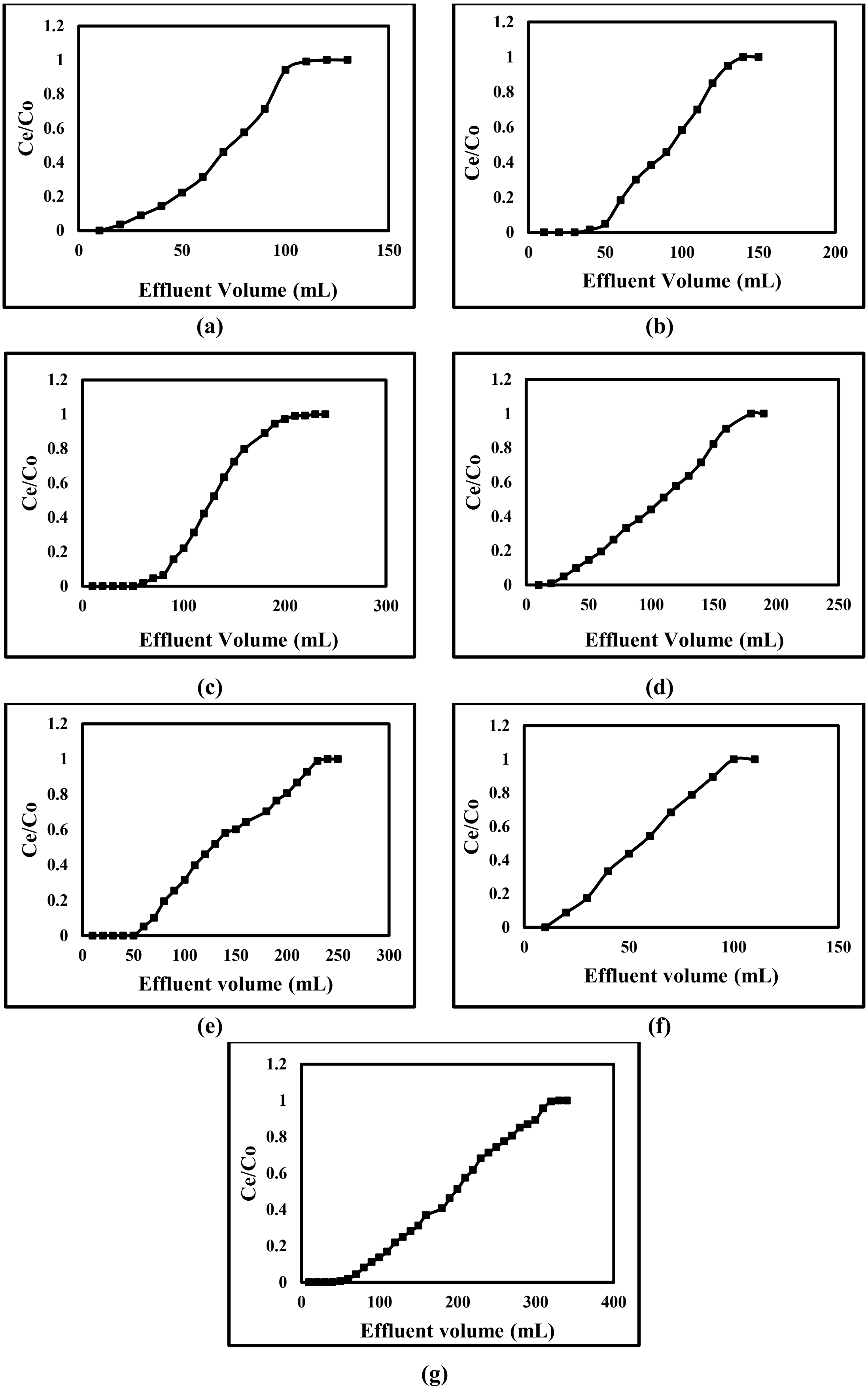
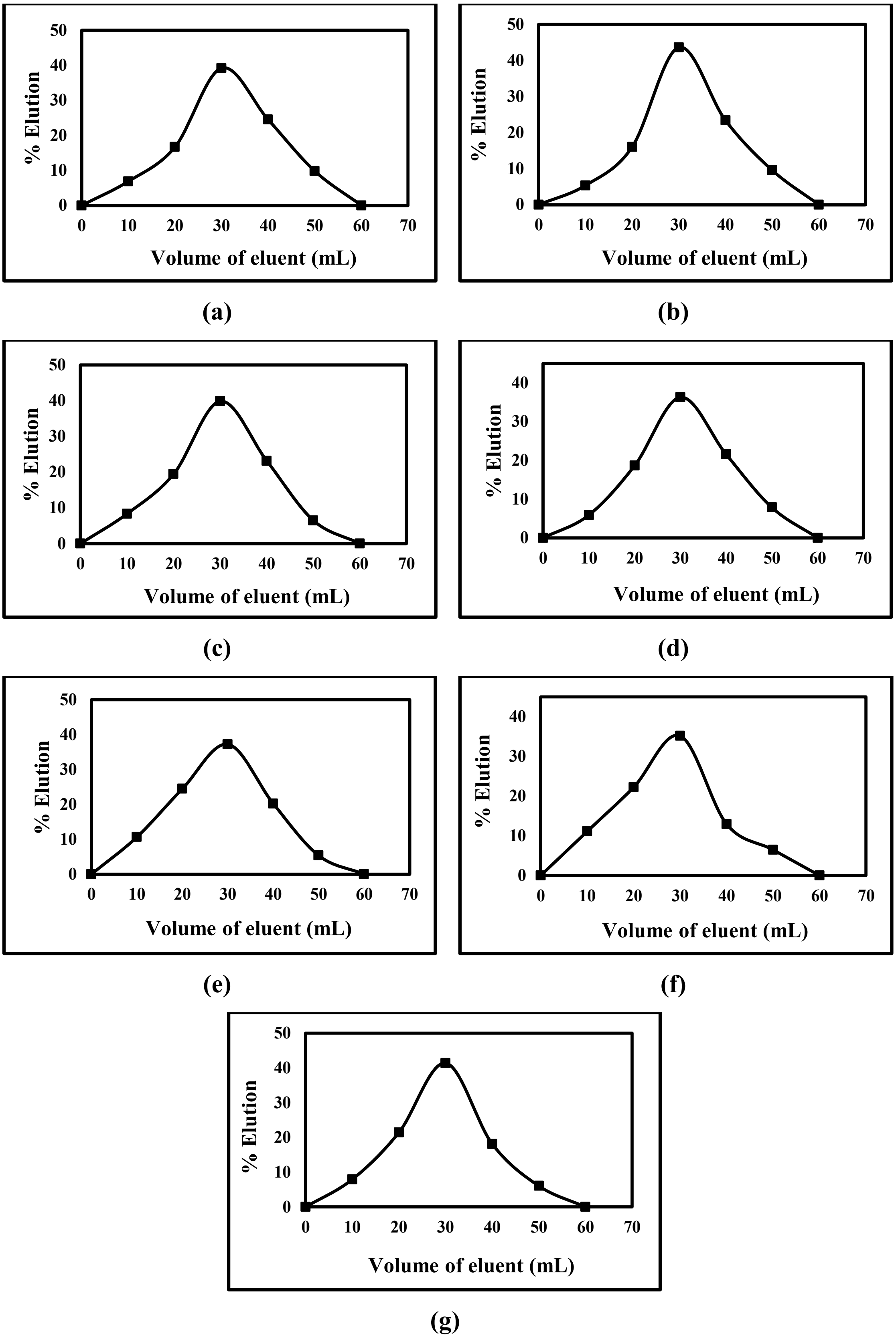


Figure 3.28(a-g)*Breakthrough curves for, (a) Co^{2+}; (b) Ni^{2+}; (c) Cu^{2+}; (d) Zn^{2+}; (e) Cd^{2+}; (f) Hg^{2+} and (g) Pb^{2+}usingTP*



(a) (b) (c) (d) (e) (f) (g)

Figure 3.29*Elution behaviour oftransition and heavy metal ions with 0.2 M HNO_3, (a) Co^{2+}; (b) Ni^{2+}; (c) Cu^{2+};(d) Zn^{2+};(e) Cd^{2+}; (f) $Hg^{2+}$and (g) Pb^{2+}using TP*

Table 3.30 *%Elution (% E) of metal ions in different electrolyte media using TP*

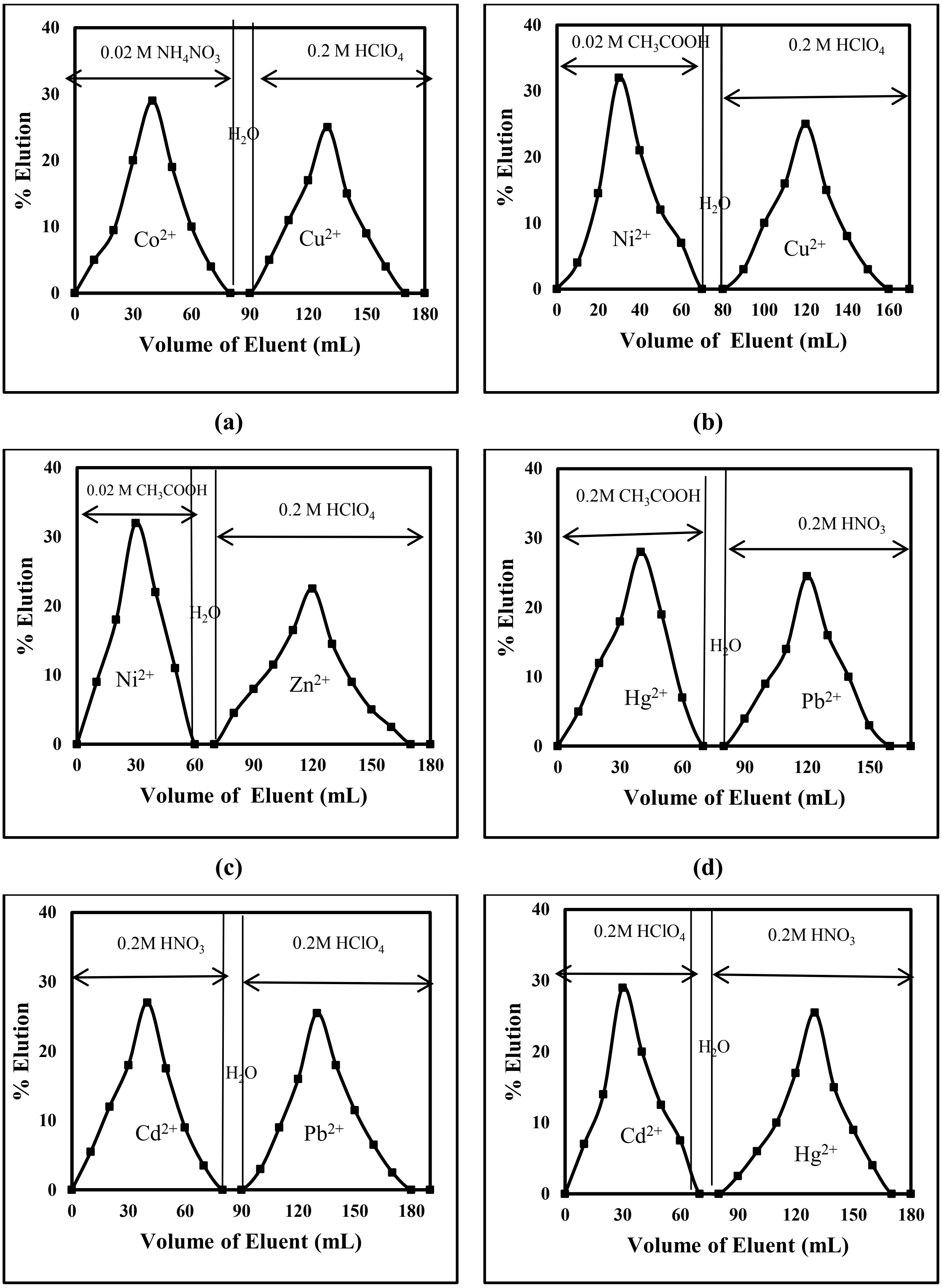
Metal	**NH_4NO_3**		**HNO_3**		**$HClO_4$**		**CH_3COOH**	
Ions	**0.02 M**	**0.2 M**	**0.02 M**	**0.2 M**	**0.02 M**	**0.2 M**	**0.02 M**	**0.2 M**
Co^{2+}	90.19	92.15	94.60	96.10	93.13	94.11	90.19	92.15
Ni^{2+}	92.15	93.36	96.93	97.95	93.50	94.89	91.83	93.33
Cu^{2+}	91.17	93.13	94.10	97.05	95.05	96.00	90.40	91.17
Zn^{2+}	88.27	90.23	94.00	95.09	91.21	95.00	86.27	92.15
Cd^{2+}	88.51	91.68	93.06	95.71	92.00	94.00	90.00	91.09
Hg^{2+}	91.42	92.38	94.28	88.14	94.26	94.76	89.52	91.42
Pb^{2+}	80.31	84.22	84.69	95.05	85.57	87.75	79.59	82.26

**Eluent volume = 70 mL and 60 mL for 0.02 M and 0.2 M electrolytes respectively*
Maximum deviation in % elution of metal ions =±2

Table 3.31*Binary separations of transition and heavy metal ions using TP*

Separation achieved	**Separation Factor (α)**	**Eluent**	**Metal Ion [mg]**		**Elution [%]**
			Loaded (C_o)	**Eluted (C_e)**	
Co^{2+}-Cu^{2+}	3.1	a) 0.02 M NH_4NO_3 (Co^{2+})	0.5893	0.5877	92.50
		b) 0.2 M $HClO_4$ (Cu^{2+})	0.6354	0.5464	86.00
Ni^{2+}-Cu^{2+}	1.6	a) 0.02 M CH_3COOH (Ni^{2+})	0.5893	0.5333	90.50
		b) 0.2 M $HClO_4$ (Cu^{2+})	0.6354	0.5350	84.20
Ni^{2+}-Zn^{2+}	1.1	a) 0.02 M CH_3COOH (Ni^{2+})	0.5893	0.5421	92.00
		b) 0.2 M $HClO_4$ (Zn^{2+})	0.6540	0.5722	87.50
Hg^{2+}-Pb^{2+}	29.8	a) 0.2 M CH_3COOH (Hg^{2+})	2.0059	1.7852	89.00
		b) 0.2 M HNO_3 (Pb^{2+})	2.0720	1.6679	80.50
Cd^{2+}-Pb^{2+}	9.7	a) 0.2 M HNO_3 (Cd^{2+})	1.1241	1.0397	92.50
		b) 0.2 M $HClO_4$ (Pb^{2+})	2.0720	1.7922	86.50
Cd^{2+}-Hg^{2+}	3.0	a) 0.2 M $HClO_4$ (Cd^{2+})	2.0059	1.0116	90.00
		b) 0.2 M HNO_3 (Hg^{2+})	1.1241	1.7351	86.50

Maximum deviation in %elution =±2



(a) **(b)**

(c) **(d)**

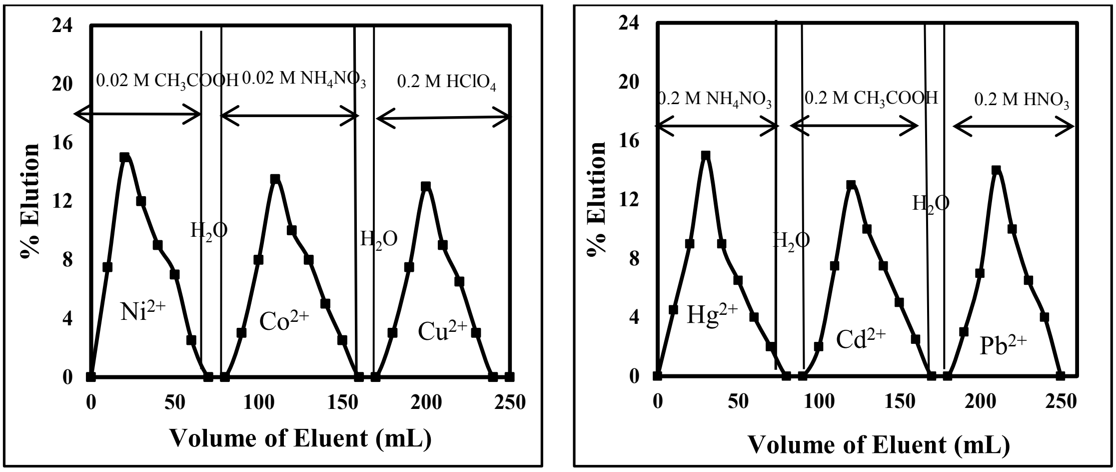
(e) **(f)**

Figure 3.30(a-f)*Binary separations of transition and heavy metal ions using TP,(a) Co^{2+}-Cu^{2+}, (b) Ni^{+2}-Cu^{+2}, (c) Ni^{2+}-Zn^{2+}, (d) Hg^{2+}-Pb^{2+}, (e) Cd^{2+}-Hg^{2+} and (f) Cd^{2+}-Pb^{2+}*

Table 3.32*Ternary separations of transition and heavy metal ions using TP*

Separations achieved	Eluent	Metal ion [mg] Loaded (C_o)	Metal ion [mg] Eluted (C_e)	Elution [%]
Ni^{2+}-Co^{2+}-Cu^{2+}	a) 0.02 M CH_3COOH (Ni^{2+})	0.5869	0.3094	52.72
	b) 0.02 M NH_4NO_3 (Co^{2+})	0.5893	0.2958	50.20
	c) 0.2 M $HClO_4$ (Cu^{2+})	0.6354	0.3086	48.58
Hg^{2+}-Cd^{2+}-Pb^{2+}	a) 0.2 M NH_4NO_3 (Hg^{2+})	2.0059	1.0029	50.00
	b) 0.2 M CH_3COOH (Cd^{2+})	1.1241	0.5339	47.50
	c) 0.2 M HNO_3 (Pb^{2+})	2.0720	0.9220	44.50

Maximum deviation in % elution =±2



(a) (b)

Figure 3.31(a-b)*Ternary separation of transition and heavy metal ions using TP, (a) Ni^{2+}-Co^{2+}-Cu^{2+} and (b) Hg^{2+}-Cd^{2+}-Pb^{2+}*

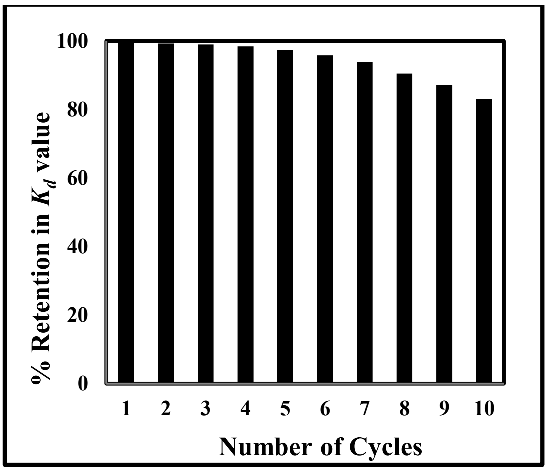


Figure 3.32*A plot of % retention in K_d values versus number of cycles using TP*

3.10 CONCLUSIONS

- ✓ The synthesized materials CP and TP exhibit promising ion exchange characteristics - good CEC value (retained upto 150 ºC), granular nature (30-60 mesh size) suitable for column operation,good chemical(insoluble in aqueous, acid and organic solvent media) and thermal stability.
- ✓ For both CP and TP,(thermodynamic studies) equilibrium constant (K) values increase with increase in temperature for all metal ions under study, indicating that the metal ions have higher affinity for the exchanger and that the mechanism is ion exchange. $\Delta G°$values for all the exchange reactions are negative and become more negative with increasing temperature indicating increase in feasibility and spontaneity of the exchange process.$\Delta H°$ is positive in all cases indicating complete dehydration ofions for exchange to take place.
- ✓ For both CP and TP, R^2 values are found to be close to unity(for both Langmuir and Freundlichisotherms) providing a good fit to the experimental data for sorption of all the metal ions studied.
- ✓ The most promising property of the materialsCP and TP is their high selectivity for lead (Pb^{2+}). Lead is a toxic metal requiring stringent regulations to be applied to its content in wastes and water streams. An extremely high affinity of CP and TP towards Pb^{2+} suggests the possibility of their application for lead separation from other pollutants.
- ✓ Efficient binary metal separations carried out using CP and TP indicate good potential for these materials to be used as cation exchangers.

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