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Sorption and separation study of heavy metal ions using cerium phosphate: a cation exchanger

Tarun Parangi[a], Bina Wani[b], Uma Chudasama[a,*]

[a]*Faculty of Technology & Engineering, Applied Chemistry Department, The M.S. University of Baroda, Vadodara 390 001, Gujarat, India, Tel. +91 9426344434; emails: juvenile34@gmail.com (T. Parangi), uvcres@gmail.com (U. Chudasama)*
[b]*Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, Maharashtra, India, email: bnwani@rediffmail.com*

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ABSTRACT

Cerium (IV) phosphate (CP), material of the class of tetravalent metal acid salts has been used as cation exchanger. The sorption/ion exchange behavior of CP toward heavy metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) has been studied using Langmuir and Freundlich adsorption isotherms. The distribution coefficient (K_d) (at optimum conditions) and breakthrough capacity for these metal ions have been determined. Elution behavior of these metal ions has been studied using acids and electrolytes. Based on the separation factor α a few binary and ternary metal ion separations have been performed.

Keywords: Cerium phosphate; Ion exchanger; Cation exchanger; Langmuir; Fruendlich; Separation

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1. Introduction

Among various processes developed to remove metal ions from wastewater, it is observed that at low concentrations, the removal is more effective by ion exchange [1–4]. Inorganic ion exchangers have played a prominent role in water processing for the chemical and nuclear industries, and also used extensively for the removal and recovery of metal ions. Further, different types of metal pollutants from chemical process industries necessitate finding new ion exchangers, that have good ion exchange capacity, stability toward temperature, and oxidizing solutions and that are capable of removing toxic substances from aqueous effluents [2–4].

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 [5]. Varshney et al. have reported kinetics of ion exchange of alkali and transition metal ions using acrylamide and acrylonitrile-based fibrous CP [6–8]. Sorption studies of strontium and uranium ions on fibrous cerium (IV) hydrogen phosphate have been reported [9]. Nilchi et al. have reported analytical applications of disodium, dipotassium, and distrontium substituted cerium phosphate and molybdate as cation exchangers for alkaline earth metal ions [10]. Varshney has reported synthesis, characterization, and adsorption behavior of triton X-100 based CP as a new Hg(II) selective, surfactant-based fibrous ion exchanger [11], and analytical applications of Pb(II) selective, surfactant-based sodium dodecyl sulfate cerium

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*Corresponding author.

phosphate [12]. Analytical applications of pyridine-based CP as fibrous ion exchangers have been reported by Varshney [13]. Suzuki et al. [14] 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 and Janardanan [15] have reported synthesis, characterization, and application of cerium zirconium phosphate as cation exchanger for metal ion separations of some transition metal ions.

In earlier publication, the authors have reported synthesis, characterization, and application of CP as an ion exchanger [16]. Distribution coefficient (K_d) of heavy metal ions (Mn^{2+},Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) has been determined in aqueous as well as various electrolyte media/concentrations. The equilibrium exchange of these metal ions with H^+ ions contained in CP has been studied and thermodynamic parameters equilibrium constant (K), standard Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) have been reported [16].

In the present endeavor, the sorption/ion exchange behavior of CP toward heavy metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) has been studied using Langmuir and Freundlich adsorption isotherms. The distribution coefficient (K_d) (at optimum conditions) and breakthrough capacity (BTC) for these metal ions have been determined. Elution behavior of these metal ions has been studied using acids and electrolytes. Based on the separation factor α and elution behavior a few binary and ternary metal ion separations have been performed.

2. Experimental

All chemicals and reagents used are of analytical grade. Double distilled water (DDW) was used for all the studies.

2.1. Adsorption studies

2.1.1. Effect of pH, contact time, and temperature on adsorption/ion exchange

Adsorption/ion exchange of metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} using CP [30-60 mesh (ASTM)] was 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 titrations [4,17]. The percentage uptake has been calculated using formula, $[(C_0 - C_e)/C_0] \times 100$ where C_0 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 percentage 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 (303–333 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. The supernatant liquid was removed immediately after each prescribed time interval and the metal ion concentration evaluated by EDTA titrations [4,17].

2.2. Distribution study and BTC

Effect of metal ion concentration on distribution coefficient (K_d) values for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} (heavy metal ions) has been determined by batch method. To 0.1 g of CP 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 (maximum equilibrium time) at room temperature. The metal ion concentration before and after exchange was determined by EDTA titration.

The K_d was also evaluated at optimum condition (optimum metal ion concentration and pH of maximum adsorption for maximum 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 K_d was evaluated using the expression, $K_d = [(I - F)/F] \times V/W$ (mL/g) 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 metal ion solution; and W = weight of the exchanger in gram [4,17].

For determination of BTC, 0.5 g of the ion exchanger, TP, was taken in a glass column [30 × 1 cm (internal diameter)] and washed thoroughly with DW, and flow rate adjusted to 0.5 mL/min. Five milliliter fractions of each individual metal ion [Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}] of 0.001 M concentration were 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_0 against the effluent volume, where C_0 and C_e are the concentrations of the initial solution and effluent, respectively. BTC is calculated using formula, $(C_0 V_{(10\%)})/W$ (mmol/g) where C_0 is concentration of metal ion in mol/L, $V_{(10\%)}$ 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 gram [4,17].

2.3. Elution and separation studies

For elution studies (single metal), the column were prepared as discussed earlier. The metal ion solution (0.001 M, 10 mL) was loaded onto the column. The metal ion loaded was eluted with eluents like HNO_3, $HClO_4$, CH_3COOH, and NH_4NO_3 of 0.02 and 0.2 M concentration. The amount of metal ion recovered was calculated in terms of percentage elution expressed as, $\% \ E = (C_e/C_0) \times 100$ where C_e is the concentration of the metal ion in the eluted solution and C_0 is the concentration of metal ion loaded onto the column.

For binary and ternary separations, mixture of metal ion solutions (0.001 M, 10 mL of each metal ion) to be separated was loaded onto the column. The separation was achieved by passing suitable eluent through the column and percentage metal eluted was calculated using above equation in each case.

3. Results and discussion

3.1. Adsorption studies

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

At pH values less than ~3, very less sorption has been observed for all metal ions (Table 1). 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. Effect of contact time and reaction temperature toward percentage uptake of metal ion is presented in Table 2. It is observed that sorption increases gradually with increase in contact time and reaches a maximum value after which randomness is observed. Increase in percentage uptake could be attributed to two different sorption processes, namely, a fast ion exchange followed by chemisorption [18]. It is observed that percentage uptake of each metal ion increases with increase in temperature, which indicates the uptake to be an ion-exchange mechanism.

Table 1
Percentage uptake of metal ions varying pH using CP

	Uptake of metal ion (%)						
pH	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*	–	–
6	4.42	–	–	–	28.00	–	–
7	2.24	–	–	–	31.00	–	–

Note: Maximum deviation in percentage uptake of metal ion = ±2%.
Italic values are indicating optimum pH value for respective metal ion.

Table 2
Effect of contact time and temperature on adsorption behavior of metal ions using CP

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

Equilibrium behavior is described in terms of equilibrium isotherms, which depend on the system temperature, concentration of the solution, contact time, and pH [19,20]. 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.

The linearized form of the Langmuir isotherm equation is given as: $C_e/(X/\mathrm{m}) = 1/(bV_m) + C_e/V_m$ where X is the amount of adsorbate, m is the amount of adsorbent, and C_e is the equilibrium concentration of the adsorbate in the solution. The constant "*b*" 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. The V_m is a constant related to the area occupied by a monolayer of sorbate, reflecting the maximum adsorption capacity [20,21]. 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 favorable adsorption, $R_L = 0$ irreversible adsorption, and $R_L = 1$ means linear adsorption while a value, $R_L > 1$ indicates an unfavorable adsorption [21].

Freundlich isotherm is expressed as, $\log(X/\mathrm{m}) = \log K + (1/n)\log C_e$ where X and m have the same

Table 3
Langmuir and Freundlich constants for heavy metal ions using CP

Metal ion	Temp. (K)	Langmuir constants				Freundlich constants		
		R^2	b (dm^3/mg)	V_m (mg/g)	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

Table 4
Distribution coefficient (K_d) values varying metal ion concentration using CP

Metal ions	Distribution coefficient (K_d) values (mL/g)				
	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+}	2,410.00	2,500.00	*2,590.00*	2,600.00	2,600.00

Note: Italic values are indicating optimum metal ion concentration for respective metal ion.

meaning as described in Langmuir isotherm, K and $1/n$ are the Fruendlich 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 [20,21].

The isotherm constants are important in understanding the adsorption mechanism and their subsequent application for prediction of some important design parameters. Plots of $C_e/(X/m)$ vs. C_e and $\log(X/m)$ vs. $\log C_e$ 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.

Langmuir constants (b and V_m) and Freundlich constants (K and $1/n$) obtained from the slopes and

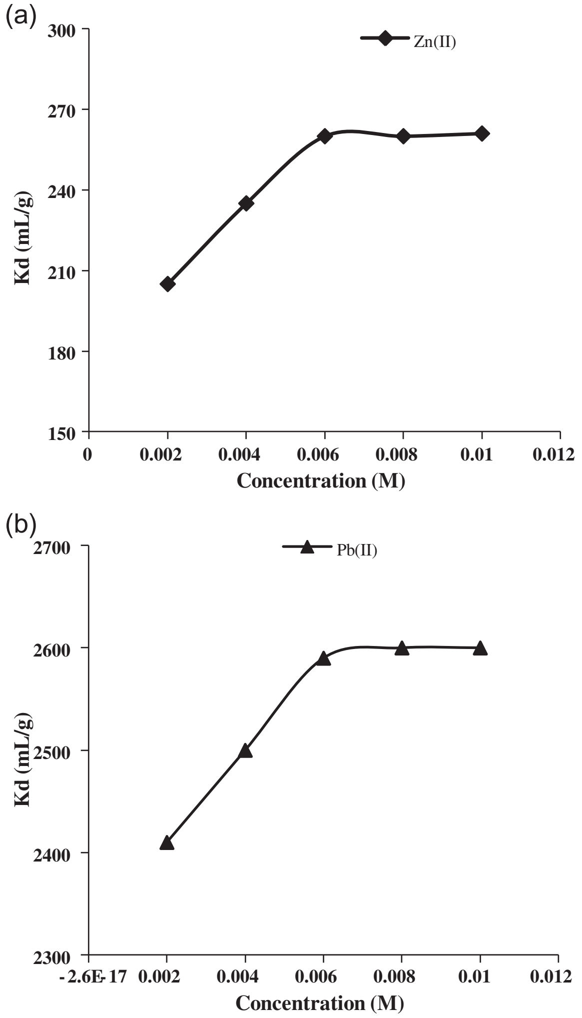

Fig. 1. (a) effect of metal ion (Zn^{2+}) concentration toward K_d and (b) effect of metal ion (Pb^{2+}) concentration toward K_d.

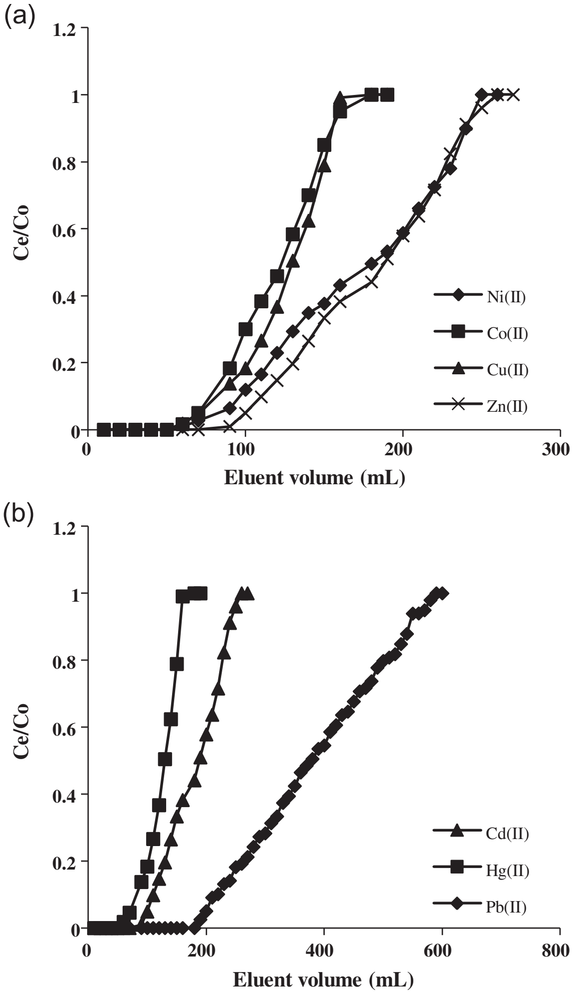

Fig. 2. BTC of heavy metal ions; (a) Ni(II), Co(II), Cu(II), Zn(II) and (b) Cd(II), Hg(II), Pb(II).

Table 5
BTC and distribution coefficient (K_d)* values for heavy metal ions using CP

			K_d*values (mL/g) in aqueous and various electrolyte media/concentration								
				NH_4NO_3		HNO_3		$HClO_4$		CH_3COOH	
Metal ion	Ionic radii (Å)	BTC (mmol/g)	DDW	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	3,640.10	3,810.00	2,235.20	3,450.0	290.50	1,528.00	2,700.00	5,180.20	2,210.20

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

NS = No sorption; Maximum deviation in K_d values = ±3.

Table 6
Percentage elution (% *E*) of metal ions in different electrolyte media using CP

	NH_4NO_3		HNO_3		$HClO_4$		CH_3COOH	
Metal 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+}	81.30	83.35	92.15	97.00	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	96.00	93.10	95.10	90.15	92.15
Cd^{2+}	85.10	89.35	94.70	95.20	91.50	93.60	89.20	95.40
Hg^{2+}	91.66	92.60	96.30	98.15	93.50	96.75	89.20	92.10
Pb^{2+}	84.20	86.50	88.45	91.35	86.55	89.40	78.80	80.35

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

Table 7
Binary separations of heavy metal ions using CP

		Metal ion (mg)		
Separation achieved	Eluent	Loaded (C_0)	Eluted (C_e)	Elution (%)
Co^{2+}-Zn^{2+}	(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
Ni^{2+}-Zn^{2+}	(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
Cu^{2+}-Zn^{2+}	(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
Hg^{2+}-Pb^{2+}	(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
Cd^{2+}-Pb^{2+}	(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
Hg^{2+}-Cd^{2+}	(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

Note: Maximum deviation in % elution = ±2.

intercepts of the linear plots are listed in Table 3. It is observed that R^2 values are found to be close to unity for both isotherms and provide a good fit to the experimental data for sorption of all the metal ions taken (except Cd^{2+} for Fruendlich 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 [18]. In the present study, low values of b indicate favorable adsorption. Based on V_m values, that reflects maximum adsorption capacity of metal ions toward exchanger follows the order $Pb^{2+} > Cd^{2+} > Co^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+} > Hg^{2+}$ at 303 K. The values of $1/n$ and R_L are obtained between 0 and 1, which indicate normal isotherm and favorable adsorption, respectively, and agree with reported results [19,20].

3.2. Distribution studies and BTC

The effect of metal ion concentration on K_d values (Table 4) show that 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. A plot of K_d values vs. metal ion concentration for Zn^{2+} and Pb^{2+} are presented in Fig. 1(a) and (b) showing optimum concentration for both metal ions, respectively.

The K_d values evaluated for the metal ions under study at optimum conditions (optimum metal ion concentration, optimum pH of solution, and maximum equilibrium time) toward CP have been presented in Table 5. In general, it is observed that the K_d values

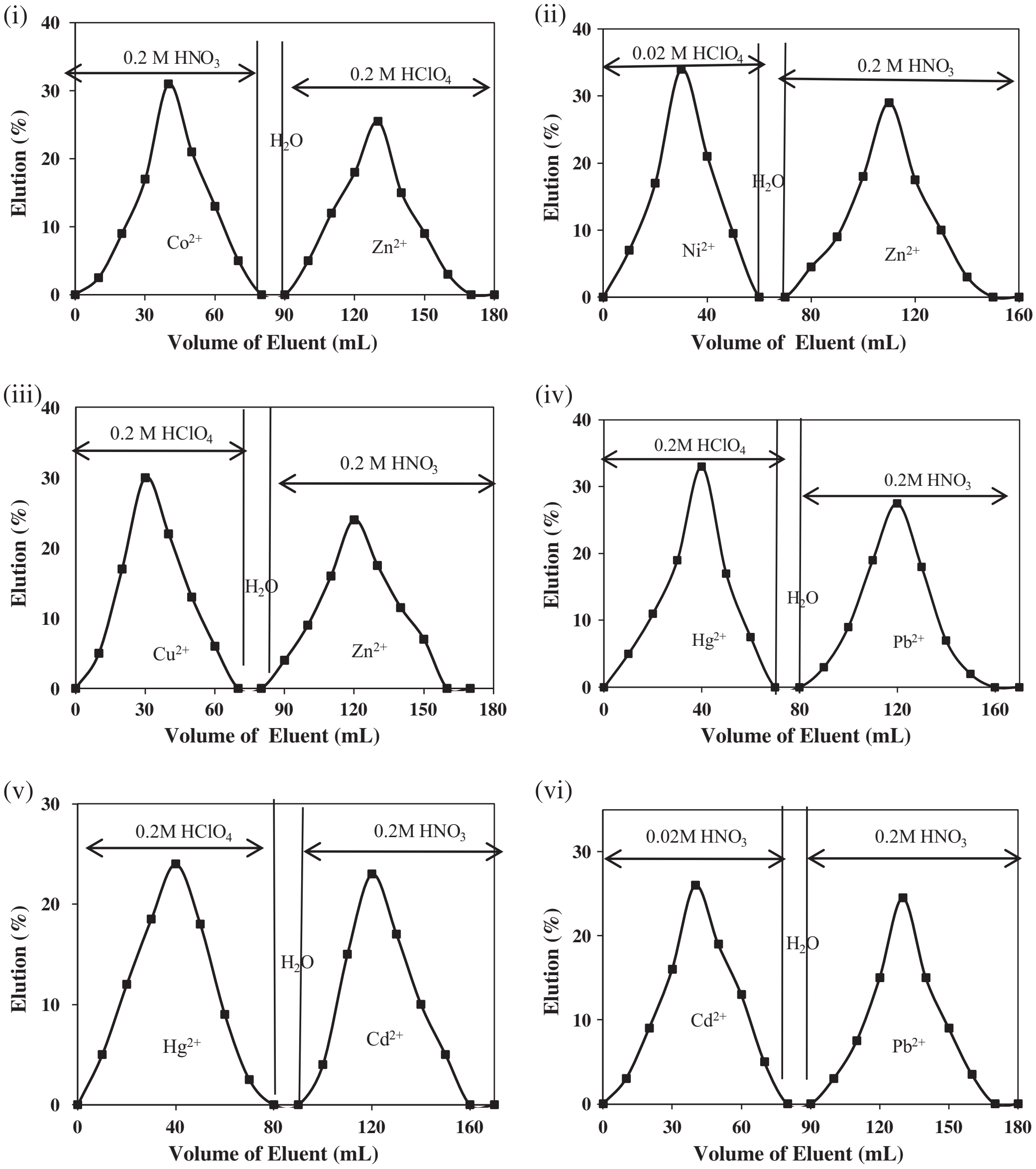

Fig. 3. Binary separation of (i) Co^{2+}-Zn^{2+}, (ii) Ni^{2+}-Zn^{2+}, (iii) Cu^{2+}-Zn^{2+}, (iv) Hg^{2+}-Pb^{2+}, (v) Hg^{2+}-Cd^{2+}, and (vi) Cd^{2+}-Pb^{2+}.

Table 8
Ternary separations of heavy metal ions using CP

		Metal ion (mg)		
Separations achieved	Eluent	Loaded (C_0)	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 HNO_3 (Cd^{2+})	1.1241	0.5732	51.00
	(c) 0.2 M HNO_3 (Pb^{2+})	2.072	0.8598	41.50

Note: Maximum deviation in percentage elution = ±2.

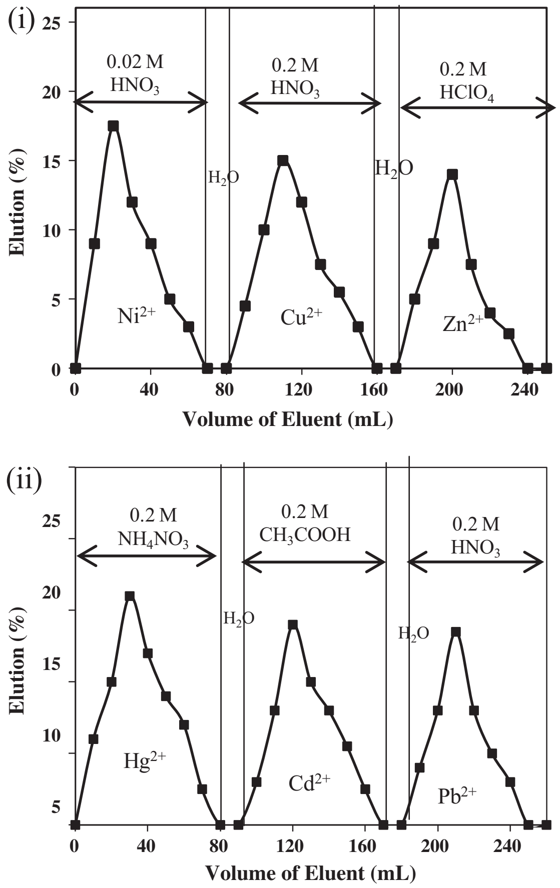

Fig. 4. Ternary separation of (i) Ni^{2+}-Cu^{2+}-Zn^{2+} and (ii) Hg^{2+}-Cd^{2+}-Pb^{2+}.

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.

Breakthrough curves (a plot of C_e/C_0 vs. effluent volume) are presented in Fig. 2(a) and (b). BTC is the dynamic capacity or operating capacity of a known amount of ion-exchange material toward metal ion in column operation. In dynamic process, exchange of a particular metal ion depends mainly on the rate of exchange, contact time, flow rate of feed solution through the column, bed depth, selectivity coefficient, particle size, and temperature. The K_d values also give an idea of affinity of metal ion toward ion exchanger. However, K_d is determined by a batch process. It is expected that the metal ion affinity toward CP, based on K_d and BTC values should be the same, which is observed (Table 5) in the present study confirming the metal ion affinity toward CP.

3.3. Elution and separation studies

The elution behavior 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 are presented in Table 6. The percentage metal eluted in all cases, is in the range 80–97%. 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. To 0.2 M HNO_3 is the best eluent for most metal ions. Using 0.2 M HNO_3, order of percentage metal eluted is Hg^{2+} (98.14) > Cu^{2+} (97.22) > Co^{2+} (97. 05) > Ni^{2+} (97.00) > Zn^{2+} (96.03) > 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 [4,17,22]. All elution curves are symmetrical bell shaped indicating elution efficiency.

Separation factor α, at which two constituents separate on a column, given by, $\alpha = K_{d1}/\ K_{d2}$ where K_{d1} and K_{d2} are the distribution coefficients of the two constituents being separated, provides a guideline for metal separation. The greater the deviation of α from unity, better is the separation. The efficiency of an ion-exchange separation depends on the condition under which α has a useful value, or influencing in a direction favorable to separation. For a given metal ion pair, the electrolyte media in which the separation factor is the highest, is selected as the eluent. Thus, a study on distribution behavior of metal ions in various electrolyte media gives an idea about the eluents that can be used for separation [4,17,22].

Binary separations for following metal ion pairs, Co^{2+}-Zn^{2+}, Ni^{2+}-Zn^{2+}, Cu^{2+}-Zn^{2+}, Hg^{2+}-Pb^{2+}, Cd^{2+}-Pb^{2+}, and Hg^{2+}-Cd^{2+} have been performed using concept of high separation factor in a particular medium as discussed earlier in the text. In binary separations, separation efficiency is in the range 80–92% (Table 7). In all cases of binary separations, irrespective of metal ion pair, maximum percentage metal eluted is Hg^{2+} (92.50), Cd^{2+} (91.00), Ni^{2+} (87.35), Cu^{2+} (86.20), Pb^{2+} (85.50), Co^{2+} (84.51), and Zn^{2+} (80.97). This observation is in keeping with separation factor (α) and K_d values of metal ions. The % 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 separation in terms of % metal eluted is observed in case of Co^{2+}-Zn^{2+}, Ni^{2+}-Zn^{2+}, Cu^{2+}-Zn^{2+}, Hg^{2+}-Pb^{2+}, Cd^{2+}-Pb^{2+}, and Hg^{2+}-Cd^{2+} where α values are high, which is also supported by symmetrical bell-shaped curves (Fig. 3).

In ternary separations for Ni^{2+}-Cu^{2+}-Zn^{2+} and Hg^{2+}-Cd^{2+}-Pb^{2+}, the percentage metal eluted is in the range 47–55% and 41–62%, respectively (Table 8). In all cases, three distinct peaks are observed (Fig. 4), however, with tailing effects for every metal ion eluted. The percentage 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 change-over 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 [4,17,22].

4. Conclusions

The most promising property of CP, is its high selectivity for 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 toward Pb^{2+} suggests the possibility of their application for lead separation from other pollutants.

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