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Synthesis, characterization and application of cerium phosphate as an ion exchanger

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ABSTRACT

In the present endeavour, cerium phosphate (CP), an ion exchanger of the class of tetravalent metal acid (TMA) salt has been synthesized by soft chemistry route, sol gel method. Physical and ion exchange characteristics as well as chemical stability of the material in various acids, bases and organic solvent media has been studied. CP has been characterized using instrumental methods (FTIR, TGA/DSC, XRD and SEM). Distribution coefficient (K_d) of 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 (varying temperature) of these metal ions with H^+ ions contained in CP has been studied and thermodynamic parameters equilibrium constant (K), standard Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) have been evaluated.

Keywords: Tetravalent metal acid salt; Inorganic ion exchanger; Cerium phosphate; Distribution coefficient (K_d); Thermodynamics of ion exchange; Cation exchanger

1. Introduction

Tetravalent metal acid (TMA) salts are inorganic cation exchangers in which protons present in the structural hydroxyl groups are responsible for cation exchange behaviour [1]. When a tetravalent metal is treated with phosphoric acid, M–O–P bonds are formed. In this process, a number of hydroxyl groups do not participate in the condensations which are referred to as pendant hydroxyl groups or defective P – OH, H of the P – OH contributing to cation exchange capacity (CEC) [2]. TMA salts are prepared by sol-gel routes and can be obtained both in amorphous and crystalline forms. TMA salts with varying water content, composition and crystallinity can be obtained varying several parameters such as mole ratio of reactants M:X (M = tetravalent metal, X = polyvalent anion), temperature of mixing, mode of mixing (metal salt solution to anion salt solution or vice versa), pH, rate of mixing, aging period etc. Variation in any of these parameters affects the structural hydroxyl groups, which in turn is reflected in their CEC and performance as a cation exchanger. Several studies have shown that cerium (IV) phosphates (CPs) are interesting inorganic materials for cation exchange [3]. Compared to zirconium, titanium and tin phosphates, which are well established ion exchangers, literature survey reveals that the cation exchange behaviour of cerium phosphate (CP) is not much explored [4]. Fibrous Cerium phosphate has received much attention as cation exchangers, used in the form of staples, cloths, ion exchange papers etc. [5–8]. However, for efficient metal separations column operations are preferred. In the several studies using

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TMA salts as cation exchangers it is found that the amorphous materials are preferred to crystalline materials as they can be obtained in a range of mesh sizes suitable for column operations. Crystalline materials have shown the disadvantage of small grain size, restricting their application in column operation [1,9,10].

In the present endeavour, amorphous CP has been synthesized by soft chemistry route sol-gel method and characterized for spectral analysis (FTIR), thermal analysis (TGA and DSC), X-ray diffraction studies and SEM. Physical and ion exchange characteristics as well as chemical stability of the material in various acids, bases and organic solvent media has been assessed. Distribution coefficient (K_d) for metal ions Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} has been determined in different electrolyte media/concentrations. Further, the equilibrium exchange (varying temperature) of these metal ions with H^+ ions contained in CP has been studied and thermodynamic parameters equilibrium constant (K), standard Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) have been evaluated.

2. Experimental

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

2.1. Synthesis of CP

CP has been synthesized by sol gel method. A solution containing $Ce(SO_4)_2\ 4H_2O$ [0.1 M, 50 ml in 10% (w/v) H_2SO_4] was prepared, to which $NaH_2PO_4\ 2H_2O$ [0.3 M, 50 ml] was added dropwise (flow rate 1 ml·min^{-1}) with continuous stirring for an hour at room temperature, when gelatinous precipitates were obtained. The resulting gelatinous precipitate was allowed to stand for 3 h at room temperature, then filtered, washed with conductivity water to remove adhering ions and dried at room temperature. The material was then broken down to the desired particle size [30–60 mesh (ASTM)] by grinding and sieving. 5 g of this material was treated with 50 ml of 1 M HNO_3 for 30 min with occasional shaking. The material was then separated from acid by decantation and treated with conductivity water to remove adhering acid. This process (acid treatment) was repeated at least 5 times. After final washing, the material was dried at room temperature. This material was used for all studies.

2.1.1. Physical and ion exchange characteristics

Physical characteristics such as appearance, percentage moisture content, apparent density, true density and ion exchange characteristics such as void volume fraction, concentration of fixed ionogenic groups and volume capacity for CP were studied according to known methods [11–13].

The synthesized material CP was observed for physical appearance such as colour, opacity/transparency, hardness etc. The percentage moisture content is calculated using the formula, *% moisture content* = 100 – *% solid* [where *% solid* = (*weight of dried material/weight of material before drying)* × 100)]. Apparent density is determined using the equation, *apparent density = weight of ion exchanger/volume of ion exchange bed*. The true density was determined by taking a definite amount of CP in previously weighed specific gravity bottle (W). The bottle was again weighed along with the ion exchanger (W_i). The bottle was now filled with water along with ion exchange material and weighed (W_{is}). The weight of the specific gravity bottle containing water is also noted (W_w). The true density is calculated by using equation, $D_{ie} = (W_i - W)/(W_w - W_{iw}) + (W_i - W)$. Void volume fraction is calculated using equation, *void volume fraction* = $1 - D_{col}/D_{ie}$. Concentration of fixed ionogenic group is calculated using the equation, $C_r = D_{ie} \times (100 - \%\ moisture) \times IEC/100$. Volume capacity of exchanger is evaluated using formula, $Q = (1 - \text{void volume fraction}) \times C_r$.

2.1.2. Chemical stability

The chemical stability of the material in various media - acids (HCl, H_2SO_4, HNO_3), bases (NaOH and KOH) and organic solvents (ethanol, benzene, acetone and acetic acid) was studied by taking 0.5 g of CP in 50 ml of the particular medium and allowing to stand for 24 h. The change in colour, nature, weight as well as solubility was observed. Further, to confirm the stability/solubility of exchanger in particular media, supernatant liquid was checked qualitatively for respective elements of exchanger.

2.1.3. pH titration curve

"pH titration curve" or the "potentiometric curve", a plot of pH versus number of milliequivalents of OH^- ions, gives an idea regarding the acidic nature of exchanger, weak or strong [11]. For cation exchangers, the acid sites can be titrated against an alkali hydroxide (used for neutralization) and a salt solution of same alkali metal (used as a supporting electrolyte). In the present case, 0.5 g of CP was placed in NaCl (0.1 M, 100 ml) solution. This solution mixture was titrated against NaOH (0.1 M) solution. After addition of every 0.5 ml of titrant, sufficient time was provided for establishment of equilibrium, till the pH is constant. A pH titration curve is obtained by plotting pH versus volume of NaOH (Fig. 1).

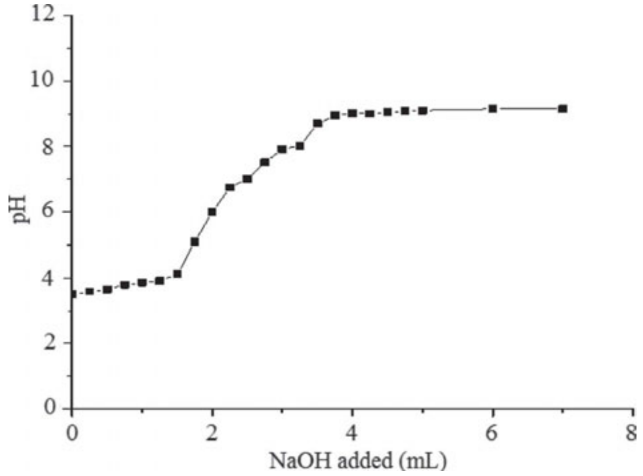

Fig. 1. pH Titration curve.

2.1.4. Cation exchange capacity (CEC) and effect of calcination on CEC

The Na^+ ion exchange capacity (CEC) of CP was determined by the column method by optimizing volume and concentration of sodium acetate solution [14]. In the first case, a fixed volume (250 ml) of sodium acetate solution of varying concentration (0.1 M, 0.2 M, 0.3 M, 0.4 M, 0.5 M, 0.6 M, 0.7 M) was passed through a glass column [30 cm × 1 cm (internal diameter)] containing 0.5 g of the exchanger, maintaining a flow rate of 0.5 $ml·min^{-1}$ and effluent (containing H^+ ions eluted out) titrated against 0.1 M NaOH solution. The optimum concentration of eluant is thus determined. In the second case the eluant of optimum concentration was used and 10 ml fractions passed through the column keeping a flow rate 0.5 $ml·min^{-1}$. This experiment was conducted to find out the minimum volume necessary for a complete elution of the H^+ ions, which reflects the efficiency of the column. Using these optimized parameters Na^+ CEC was determined, using the formula aV/W, where a is molarity and V the amount of alkali used during titration, and W is the weight of the exchanger.

The effect of calcination on CEC was studied by heating several 1 g portions of the material for 2 h at different temperatures in the range 100°C to 500°C with 100°C intervals in a muffle furnace and Na^+ exchange capacity determined by the column method at room temperature.

2.2. Instrumentation

FTIR spectra was recorded using KBr pellet on Shimadzu (Model 8400S). Thermal analysis (TGA) was carried out on a Shimadzu (Model TGA 50) thermal analyzer at a heating rate of 10°C min^{-1} and DSC was analyzed on Shimadzu (Model DSC-50). X-ray diffractogram ($2\theta = 10-80°$) was obtained on X-ray diffractometer (Brucker AXS D8) with Cu-K_α radiation with nickel filter. SEM of the sample was scanned on Jeol JSM-5610-SLV scanning electron microscope.

2.3. Distribution studies

Distribution coefficient (K_d) is a measure of the fractional uptake of metal ions in solution, competing for H^+ ions, in case of a cation exchange material. Almost, all ion exchange reactions being 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.

The distribution coefficient (K_d) for Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} was evaluated by batch method, in which 0.1 g of CP in the H^+ form was equilibrated with 20 ml of 0.001 M metal solution for 24 h at room temperature. The metal ion concentration before and after exchange was determined by EDTA titration.

Distribution studies have been carried out in aqueous as well as various electrolyte media like NH_4NO_3, HNO_3, $HClO_4$ and CH_3COOH of 0.02 and 0.20 M concentration. K_d was evaluated using the expression, $K_d = [(I-F)/F] \times V/W$ ($ml·g^{-1}$) 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; W = weight of the exchanger.

K_d was also evaluated varying temperatures (30°C to 60°C with 10°C interval). 20 ml, 0.002 M metal ion solution was equilibrated with 0.2 g of exchanger in stoppered conical flasks at a particular temperature for 6 h (maximum equilibrium time). The supernatant liquid was removed in each case after 6 h and the metal ion concentration evaluated by EDTA titration. From these experiments equilibrium values have also been determined.

2.4. Thermodynamics of ion exchange

2.4.1. Equilibrium time determination

0.1 g 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 time interval at a particular temperature. A plot of the fractional attainment of equilibrium $U(\tau)$ versus time (t) gives an idea about maximum equilibrium time (Fig. 2).

2.4.2. Equilibrium experiments

The equilibrium experiments were performed by shaking 0.2 g of the exchanger particles at the desired temperature (30°C, 40°C, 50°C and 60°C) in a shaker

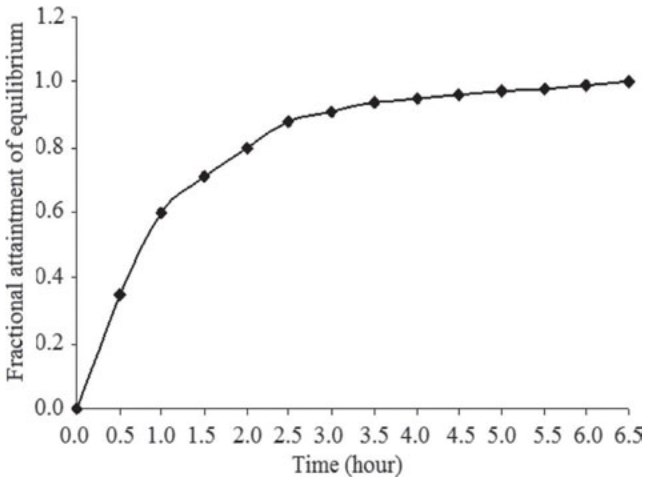

Fig. 2. Plot of $U(\tau)$ versus time (t).

bath for 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 equilibrium, the supernatant liquid was removed and metal ion estimated by EDTA titration.

3. Results and discussion

3.1. Characterization of CP

Physical and ion exchange characteristics of CP have been presented in Table 1. CP was obtained as yellow hard granules.

The Na^+ ion exchange capacity (CEC) in meq·g^{-1} evaluated by column method at room temperature is 2.48 meq·g^{-1} (using 220 ml 0.5 M of CH_3COONa solution). The Na^+ CEC of the calcined samples (Table 1) shows that CEC values decrease with increasing temperature, attributed to loss of moisture and condensation of structural hydroxyl groups.

A study on the chemical stability shows that CP is stable in acids and organic solvent media but not so stable in base medium (Table 1).

The FTIR spectra (Fig. 3) of CP exhibits a broad band in the region ~3400 cm^{-1} which is attributed to asymmetric and symmetric $^-$OH stretching vibration due to residual water and presence of structural hydroxyl groups, H^+ of the $^-$OH being cation exchange sites. These sites are also referred to as defective P-OH groups [2]. A sharp medium band at ~1630 cm^{-1} is attributed to aquo H–O–H bending [15]. The band at 1050 cm^{-1} is attributed to P=O stretching while the bands at 620 cm^{-1} and 500 cm^{-1} is attributed to Ce-O stretching [16].

Table 1
Physical and ion exchange characteristics of CP

Characteristics	Observation
Appearance	Yellow hard granules
Particle size	250–590 μ
% Moisture content	10.26%
True density	2.86 g·ml^{-1}
Apparent density	0.60 g·ml^{-1}
Void volume fraction	0.79
Concentration of fixed ionogenic groups	6.28 mmol·g^{-1}
Volume capacity of resin	1.31 meq·ml^{-1}
Nature of exchanger	Weak cation exchanger
CEC (Room Temperature)	2.45 meq g^{-1}
100°C	2.24 meq g^{-1}
200°C	1.89 meq g^{-1}
300°C	0.99 meq g^{-1}
400°C	0.20 meq g^{-1}
500°C	0.07 meq g^{-1}
Chemical stability	Maximum tolerable limits
i) Acids	1 N H_2SO_4, 2 N HNO_3, 5 N HCl
ii) Bases	0.5 N NaOH, 0.5 N KOH
iii) Organic solvents	Ethanol, Benzene, Acetone, Acetic acid

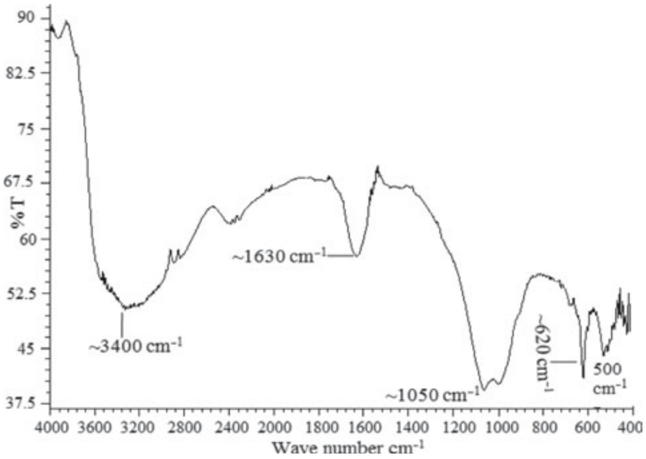

Fig. 3. FTIR of CP.

TGA (Fig. 4) exhibits two regions of weight loss. The first weight loss ~13% up to 120°C is attributed to loss of moisture/hydrated water, while the second weight loss ~8% in the range of 120–500°C is attributed to the condensation of structural hydroxyl groups.

DSC (Fig. 5) exhibits an endothermic peak at ~128°C, attributed to loss of moisture/hydrated water. Beyond this temperature no peaks are observed indicating absence of any phase change in the material upon thermal treatment in the range studied.

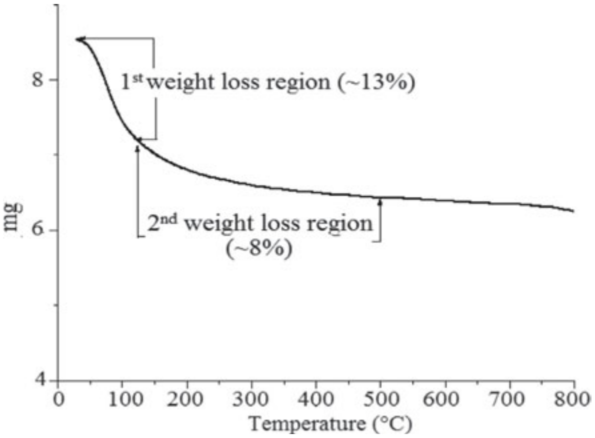

Fig. 4. TGA of CP.

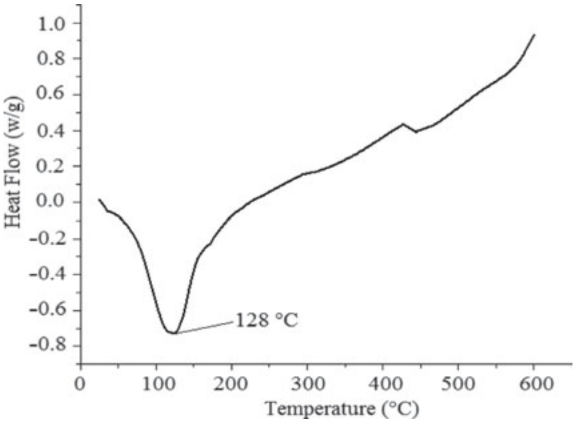

Fig. 5. DSC of CP.

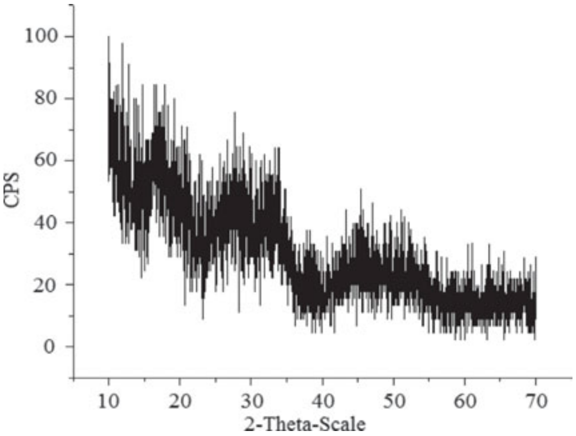

Fig. 6. XRD of CP.

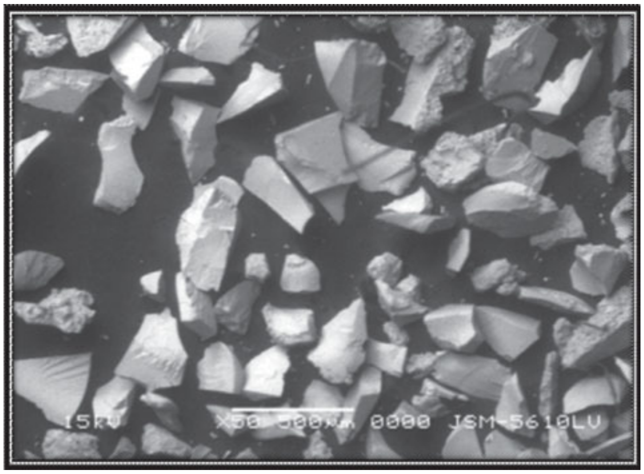

Fig. 7. SEM of CP.

Absence of sharp peaks in X-ray diffractogram (Fig. 6) of CP, indicates amorphous nature of the material. SEM (Fig. 7) of CP at room temperature, exhibits irregular particle size which indicates amorphous nature of the material which is also supported by XRD of the material.

3.2. Distribution studies

Selectivity/affinity of a particular metal ion towards an ion exchanger depends on (1) **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, (2) **the exchange media**, the factors responsible being concentration, pH, and the nature of the electrolyte, weak or strong, as well as the temperature, and (3) **the exchanging metal ion**, the factors responsible being ionic radius and ionic charge on the metal ion, with higher valent ions having more affinity for the exchanger [13,17]. 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 metal ion and the grain/particle size of the exchanger. Smaller cations have a greater tendency to be hydrated as a consequence of which the hydrated ionic radius is large. Larger ions being less hydrated, less energy is utilized for dehydration of the metal ions while occupying a site on the exchanger, plays a prominent role in determining the selectivity of metal ions [13,17].

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.

Separation factor, $\alpha = K_{d1} / K_{d2}$, where K_{d1} and K_{d2} are the distribution coefficients of the two constituent metal ions being separated on an ion exchange material in a particular electrolyte medium. 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 favourable to separation. For a given metal ion pair, the electrolyte media in which the separation factor is the highest, is selected as the eluant. Thus, a study on distribution behaviour of metal ions in various electrolyte media gives an idea about the eluants that can be used for separation [13,17].

The distribution coefficient (K_d) values evaluated for the the metal ions under study towards CP have been presented in Table 2. In general it is observed that the K_d values are lower in high concentration of electrolyte and vice versa. Further, the K_d values in strong electrolyte media 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.

The most promising property of CP is the very high K_d value observed for Pb^{2+} in aqueous medium suggesting its separation from other metals/pollutants. No sorption is observed in case of Cu^{2+} (0.2 M HNO_3 and 0.2 M $HClO_4$), $Ni^{2+}$and Hg^{2+} (0.2 M $HClO_4$). Co^{2+}, Ni^{2+} and Zn^{2+} exhibit very low K_d values (0.2 M HNO_3) while Mn^{2+} and Co^{2+} exhibit very low K_d values (0.2 M $HClO_4$). Hg^{2+} exhibits very low K_d value in aqueous medium.

The observed selectivity order (Table 2) in aqueous medium is Zn^{2+} (0.74Å) > Ni^{2+} (0.72Å) > Mn^{2+} (0.80Å) > Co^{2+} (0.72Å) > Cu^{2+} (0.74Å) amongst the transition metal ions and Pb^{2+} (1.44Å) > Cd^{2+} (0.97Å) > Hg^{2+} (1.10Å) amongst the heavy metal ions, values in parenthesis being ionic radii of respective metal ions. The ionic radii being almost equivalent in case of transition metal ions, the selectivity order is probably dependant on rate of exchange/equilibrium and dissociation of salt, while selectivity order in case of heavy metal ions can be explained on the basis of size of ions and hence hydrated ionic radii. As explained earlier, larger ions being less hydrated, less energy is utilized for dehydration of the metal ions to occupy a site on the exchanger.

The effect of temperature on K_d and equilibrium values have been presented in Table 2. It is observed that both K_d and equilibrium values increase with increase in temperature. This could be attributed to increase in mobility of the ions with increasing temperature and higher affinity of metal ions towards the exchanger, compared to H^+ ions.

3.3. Thermodynamics of ion exchange

Thermodynamic parameters such as equilibrium constant (K), standard Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) have been evaluated using standard equations [11–13]. Results are summarized in Table 3. A plot of the fractional attainment of equilibrium $U(\tau)$ versus time (t) (Fig. 2) shows that the exchange equilibrium for CP appears to have attained within 4 h and hence all the equilibrium studies were performed after shaking for 6 h.

Equilibrium constant (K) values increase with increase in temperature for all metal ions under study (Table 3), indicating that the metal ions have higher affinity for the exchanger and that the mechanism is ion exchange [14].

Negative $\Delta G°$ values indicate that the exchange process is feasible and spontaneous in nature. In the present study, the free energy change 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. The $\Delta G°$ values become more negative with increasing temperature, confirming that the exchange is favoured with increasing temperature. As dehydration is essential for ion exchange to occur [18], less negative $\Delta G°$ values observed may be attributed to metal ions that are heavily hydrated. In case of Pb^{2+} more negative $\Delta G°$ values are observed indicating that exchange takes place more readily in case of Pb^{2+}, being the least hydrated.

The enthalpy change ($\Delta H°$) for an ion exchange reaction can be either of the five reasons or a net effect of these factors: (1) the heat consumed in bond breaking, as H^+ is released from the resin (2) the heat released in the formation of bonds with the incoming cation (3) the heat corresponding to the energy required for crossing the barrier (distance between exchange phase and solution phase) (4) the enthalpy change accompanying hydration and dehydration of exchanging ion in the solution (5) 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.

In the present study, enthalpy change is positive in all cases, except Mn^{2+} and Ni^{2+}. 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 [18]. The observed order of $\Delta H°$ is: $Pb^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Cd^{2+} > Hg^{2+} > Ni^{2+} > Mn^{2+}$. Higher/positive values of enthalpy change indicate more endothermicity of the process and requirement of more energy for dehydration to occur. The $\Delta H°$ values indicate that probably complete dehydration occurs in case of Pb^{2+}. These observations are in keeping with high negative $\Delta G°$ values in case of Pb^{2+}.

Table 2
Distribution coefficient (K_d) (ml·g^{-1}) and equilibrium values (meq·g^{-1}) of metal ions

Metal ion	Ionic radius (A°)	K_d values in aqueous and various electrolyte media/concentration									K_d and Equilibrium values at different temperatures							
		Aqueous media	NH_4NO_3		HNO_3		$HClO_4$		CH_3COOH		30°C		40°C		50°C		60°C	
			0.02 M	0.2 M	0.02 M	0.2 M	0.02 M	0.2 M	0.02 M	0.2 M	K_d	EV	K_d	EV	K_d	EV	K_d	EV
Mn^{2+}	0.80	200.12	359.53	312.65	219.35	199.63	20.25	4.90	942.85	1032.00	336.36	0.370	468.75	0.375	480.00	0.443	685.00	0.475
Co^{2+}	0.72	180.00	105.85	27.14	13.05	2.78	16.29	7.95	211.45	184.00	61.00	0.150	68.00	0.161	83.00	0.170	97.00	0.200
Ni^{2+}	0.72	217.00	114.00	22.00	17.00	7.00	2.00	NS	205.00	135.00	37.10	0.144	42.12	0.164	66.00	0.178	111.00	0.024
Cu^{2+}	0.74	172.00	185.00	73.00	40.00	NS	3.00	NS	303.00	241.00	118.00	0.230	171.00	0.240	182.00	0.274	228.00	0.320
Zn^{2+}	0.74	266.00	174.00	65.01	56.00	14.00	30.00	15.00	273.00	190.00	57.00	0.213	69.00	0.242	87.00	0.268	91.00	0.276
Cd^{2+}	0.97	442.00	291.00	63.03	89.00	25.00	70.00	84.00	511.00	768.00	90.00	0.190	124.00	0.222	205.00	0.269	207.00	0.282
Hg^{2+}	1.44	19.09	50.42	28.87	56.47	35.04	18.00	NS	64.24	54.97	35.59	0.105	42.00	0.120	59.09	0.156	68.00	0.170
Pb^{2+}	1.10	3590.47	3780.00	2212.12	3418.18	279.51	1493.61	2642.85	5106.66	2141.17	568.00	0.343	601.00	0.347	3940.00	0.394	4000.00	0.402

NS = No sorption, EV = Equilibrium value.

Table 3
Thermodynamic parameters for M^{2+} - H^+ exchange at various temperatures

Exchanging system	Temperature (K)	K_a	$\Delta G°$ (k J mol^{-1})	$\Delta H°$ (k J mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})
Mn(II) – H(I)	303	3.45	–1.71	–36.47	–111.32
	313	8.83	–2.74		–91.35
	323	23.99	–4.26		–99.72
	333	428.33	–7.88		–104.38
Co(II) – H(I)	303	2.34	–1.07	12.71	45.52
	313	2.6	–1.24		44.6
	323	3.3	–1.6		44.34
	333	3.68	–1.80		43.62
Ni(II) – H(I)	303	1.45	–0.51	–5.06	–14.39
	313	1.57	–0.60		–14.21
	323	1.6	–0.61		–13.78
	333	1.74	–0.69		–13.64
Cu(II) – H(I)	303	2.70	–1.25	62.16	209.3
	313	4.32	–1.90		204.69
	323	8.02	–2.79		201.11
	333	23.89	–4.39		199.87
Zn(II) – H(I)	303	0.47	0.93	67.86	220.88
	313	7.01	–2.69		229.88
	323	10.87	–3.20		220.02
	333	23.06	–4.08		211.12
Cd(II) – H(I)	303	2.06	–0.91	9.87	35.67
	313	2.21	–1.03		34.87
	323	2.27	–1.10		34.00
	333	2.90	–1.47		34.10
Pb(II) – H(I)	303	0.41	1.10	143.97	471.50
	313	1.73	–0.71		462.25
	323	13.10	–3.45		456.40
	333	69.58	–5.87		449.99
Hg(II) – H(I)	303	3.77	–1.67	1.21	9.54
	313	3.88	–1.76		9.52
	323	3.96	–1.90		9.38
	333	4.15	–1.91		9.68

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

4. Conclusions

CP exhibits promising ion exchange characteristics - good CEC, thermal stability and chemical stability, which are characteristics of a good ion exchange material. The most promising property of CP, is its high selectivity for Pb^{2+} and very low selectivity for Hg^{2+}, suggesting their removal from other metal ions/pollutants.

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