

# Synthesis and Characterization of a Novel Metal Phosphonate, Zirconium (IV)-Hydroxy Ethylidene Diphosphonate, and Its Application as an Ion Exchanger

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A novel hybrid ion exchange material, Zirconium-hydroxy ethylidene diphosphonate [ZrHEDP], of the class of tetravalent metal acid (TMA) salts has been synthesized by the sol-gel technique. The material was characterized with elemental analysis (ICP-AES), thermal analysis (TGA, DSC), and FT-IR and X-ray diffraction studies. The chemical resistivity of the material in various media was evaluated. ZrHEDP was further investigated for its possible use as an ion exchanger. The Na<sup>+</sup> ion-exchange capacity (IEC) of the material was determined, and kinetics and thermodynamics of exchange for the metal ions Cu(II), Ni(II), Zn(II), and Mn(II) towards ZrHEDP were studied. The sorption of the metal ions follow the order Zn(II) > Cu(II) > Mn(II) ≈ Ni(II).

**Key Words:** Inorganic ion exchanger, metal phosphonate, tetravalent metal acid salt, zirconium-hydroxy ethylidene diphosphonate, Zr(IV) phosphonate.

## Introduction

Ion exchange materials have found extensive application in analytical and industrial chemistry, and play a vital role in the treatment of environmental pollutants. Ion exchange materials with higher selectivities are continuously being investigated.<sup>1</sup> Amongst the most important inorganic ion exchangers studied are synthetic clay minerals, heteropoly acid salts, hexacyanoferrates, zeolites, hydrous oxides, and tetravalent metal acid (TMA) salts. Amongst these, TMA salts have been the most widely studied due to their excellent thermal stability and chemical resistivity. In this respect, TMA salts have proved to be superior to many organic resins.<sup>2-6</sup> TMA salts have the general formula, M(IV) (HXO<sub>4</sub>)<sub>2</sub> · nH<sub>2</sub>O, where M(IV) = Zr, Ti,

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Ce, Th, Sn, etc., and X = P, Mo, W, As, Sb, etc. The protons present in the structural hydroxyl groups of these materials can be exchanged for several cations and thus, they act as cation exchangers.

There is currently great interest in engineering mixed materials (organic/inorganic) in which features of the organic and inorganic components complement each other, leading to the formation of new solid-state structures and materials with new composite properties.<sup>7</sup> Zr(IV) phosphate has been widely used as a cation exchanger. In the tetrahedral moiety of phosphoric acid, PO(OH)<sub>3</sub>, if H or OH is replaced by R (where R = alkyl or aryl), phosphonic acids are obtained, which when treated with tetravalent metals, such as Zr, Ti, Sn, Th, Ce, etc., give rise to metal phosphonates.<sup>8–10</sup> Depending on the complexity of the phosphonate used, the material gives rise to 2- or 3-dimensional hybrid polymeric structures. Though several metal phosphonates have been synthesized and characterized, the focus has been on structural elucidation.<sup>8–10</sup> These materials are interesting because of their potential utility as sorbents and supports<sup>11</sup> in the area of catalysis,<sup>12</sup> as ion exchangers,<sup>13</sup> and for proton conduction,<sup>14</sup> intercalation chemistry,<sup>15</sup> photochemistry,<sup>16</sup> and materials chemistry.<sup>17</sup>

Several phosphonic acids, such as hydroxy ethylidene di-phosphonic acid (HEDP), amino tris (methylene phosphonic acid) (ATMP), and diethylene triamine pentakis (methylene phosphonic acid) (DETPMP), have been widely used as sequestering agents, dispersants, scale and corrosion inhibitors, and therapeutic agents.<sup>18</sup>

In the present endeavor a novel metal phosphonate (ZrHEDP), which is a hybrid ion exchange material of the TMA salt class, has been synthesized by the sol-gel method using tetravalent zirconium (as ZrOCl<sub>2</sub>.8H<sub>2</sub>O) and HEDP. The material was characterized by elemental analysis (ICP-AES), thermal analysis (TGA, DSC), and FT-IR and X-ray diffraction studies. Chemical resistivity of the material in various media, including acids, bases, and organic solvents, was evaluated. Though the potential use of metal phosphonate as an ion exchanger has been suggested, a literature survey revealed that no systematic studies have been published on the ion exchange characteristics of these materials. ZrHEDP has been further investigated for its possible use as an ion exchanger. The Na<sup>+</sup> ion-exchange capacity (IEC) of the material was determined and the effect of heating on IEC studied. In order to understand the mechanism of the ion-exchange process taking place on the surface of an ion exchange material, a kinetic (rate of exchange) and thermodynamic (uptake/equilibrium) study is of great importance in evaluating the exchange process. In the present study, the sorption/ion exchange behavior of metal ions Cu(II), Ni(II), Zn(II), and Mn(II) towards ZrHEDP was studied at 313 K, 323 K, and 333 K. Kinetic parameters (overall rate constant: *k*; equilibrium constant: *k<sub>c</sub>*; forward and reverse reaction rate constant; *k*<sub>1</sub> and *k*<sub>2</sub>, respectively), thermodynamic parameters (standard free energy: Δ*G*<sup>o</sup>; enthalpy: Δ*H*<sup>o</sup>; entropy: Δ*S*<sup>o</sup>), and adsorption isotherms (Langmuir and Freundlich) were studied. Based on these studies the order of metal ion affinity towards ZrHEDP is evaluated and discussed.

## Experimental

### Synthesis of ZrHEDP

ZrHEDP was prepared by mixing aqueous solutions of (0.1 M, 250 mL) ZrOCl<sub>2</sub>.8H<sub>2</sub>O and (0.2 M, 250 mL) sodium salt of HEDP, dropwise and with constant stirring at 70 °C. The gelatinous precipitates obtained were digested for 1 h at 70 °C, filtered, and washed with conductivity water until chloride ions were removed, followed by drying at room temperature. The material was then broken down to the desired particle size

[30-60 mesh (ASTM)] by grinding and sieving. The material was converted to the acid form by taking 5 g of the material and treating with 50 mL of 1 M HNO<sub>3</sub> for 30 min with occasional shaking. The sample was then separated from acid by decantation and treated with conductivity water for the removal of 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. The Na<sup>+</sup> IEC of the material was determined by the column method.<sup>19</sup>

### Calcination studies

The effect of heating on IEC was studied by heating a 1-g portion of the material for 2 h at temperatures between 100 °C and 500 °C, with 100 °C intervals in a muffle furnace. Na<sup>+</sup> IEC was determined with the column method<sup>19</sup> at room temperature.

### Chemical Resistivity

The chemical resistivity of the material in various media, including acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and HCl), bases (NaOH and KOH), and organic solvents (ethanol, benzene, and acetone) was studied by taking 500 mg of sample in 50 mL of the particular medium and allowing it to stand for 24 h. The change in nature, weight, and color was observed.

### Instrumentation

ZrHEDP was analyzed for zirconium and phosphorus by ICP-AES. Carbon and hydrogen were determined using a Coleman model 33 CHN analyzer. Thermal analysis (TGA) was carried out on a Shimadzu DT-30 thermal analyzer at a heating rate of 10 °C min<sup>-1</sup>. DSC was performed on a Mettler TA 4000 system at a heating rate of 20 °C min<sup>-1</sup>. FTIR spectra were obtained using KBr wafers on BOMEM MB series with an Epson Hi 80 printer/plotter. X-ray diffractograms were obtained on a Bruker AXS D8 X-ray diffractometer using Cu-K<sub>α</sub> radiation with a nickel filter. A temperature-controlled shaker bath with a temperature variation of ± 0.5 °C was used for the equilibrium studies.

### Sorption studies

#### Effect of pH

Sorption of various metal ions (Cu(II), Ni(II), Zn(II), and Mn(II)) on ZrHEDP was performed in the pH range of 1-9. Then, 100 mg of ZrHEDP and 10 mL of 0.002 M metal ion solution was added, and the pH was adjusted with HNO<sub>3</sub> and NaOH, followed by shaking the mixture for 30 min. Metal ion concentration was determined using the supernatant liquid and EDTA titration.<sup>20</sup>

### Sorption Kinetics and Thermodynamics

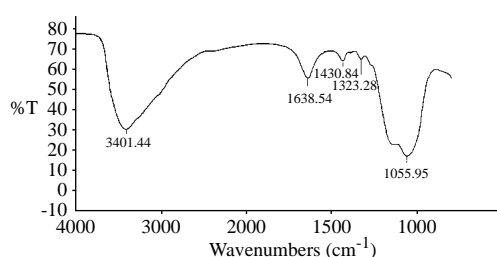
ZrHEDP particles of definite mesh size [30-60 mesh (ASTM)] were used to evaluate various kinetic and thermodynamic parameters. In stoppered conical flasks, 10 mL of 0.002 M metal ion solution was shaken with 100 mg of exchanger at the desired temperatures [313 K, 323 K, and 333 K] for different time intervals, with increments of 10 min (range: 10-120 min). pH of the solution was adjusted to the value at which maximum sorption of each respective metal ion took place.

## Adsorption isotherm studies

For adsorption isotherm studies, 10 mL of metal ion solution of different concentrations, with increments of 0.002 M (range: 0.002-0.01 M) were equilibrated for a specific period of time with 100 mg of exchanger in stoppered conical flasks at desired temperatures [313, 323, and 333 K]. After equilibrium, the supernatant liquid was immediately removed and the metal concentration was evaluated by EDTA titration.<sup>20</sup>

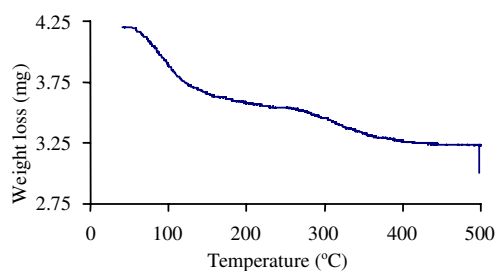
## Results and Discussion

ZrHEDP was obtained as transparent granules. Elemental analysis with ICP-AES showed a zirconium to phosphorus ratio of 1:2. The carbon and hydrogen content in ZrHEDP were 7.01% and 3.21%, respectively.



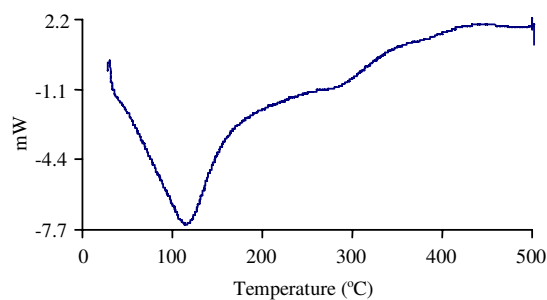
**Figure 1.** FT-IR spectra of ZrHEDP.

FTIR spectra of Zr-HEDP (Figure 1) showed a broad band in the 3400 cm<sup>-1</sup> region, which is attributed to symmetric and asymmetric -OH stretching, while the band at 1642 cm<sup>-1</sup> is attributed to H-O-H bending. This indicates that the presence of structural hydroxyl protons in ZrHEDP is responsible for cation exchange, which is supported by the Na<sup>+</sup> IEC value that was determined. A broad shoulder at 1058 cm<sup>-1</sup> is attributed to the presence of P=O stretching and bands at 1452 and 1380 cm<sup>-1</sup> are attributed to symmetric and asymmetric C-CH<sub>3</sub> bending.<sup>21</sup> The Na<sup>+</sup> IEC, as determined by the column method,<sup>19</sup> was 3.18 meq g<sup>-1</sup>. The effect of calcination on IEC was studied in the temperature range of 100-500 °C, at intervals of 100 °C and was 3.20, 3.00, 3.22, 1.96, and 1.55 meq g<sup>-1</sup>, respectively. The initial increase in the IEC value at 100 °C could be attributed to loss of moisture that adhered to it, thereby increasing the active exchanger content for the same weight of material taken for IEC determination. However, at 300 °C an increase in IEC value was observed, which is attributed to the decomposition of organic moiety, leading to the formation of active carbon, as evidenced by the color of the heated samples changing to black. Furthermore, the decrease in IEC was great beyond 300 °C, which is attributed to the complete decomposition of organic moiety/active carbon in the form of CO<sub>2</sub>.



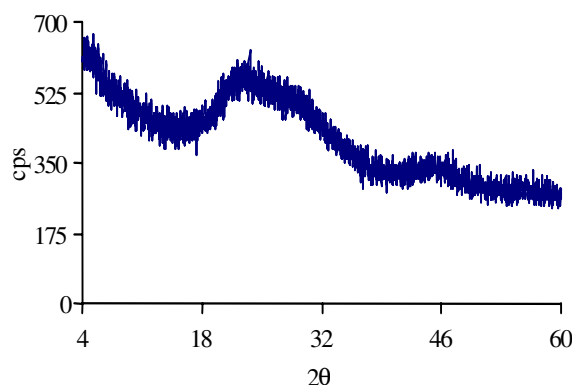
**Figure 2.** TG curve of ZrHEDP.

TGA of Zr-HEDP (Figure 2) showed a sharp change within the temperature range of 52-224 °C, corresponding to the loss of moisture/hydrated water after which weight loss is observed in the range of 255-479 °C, which may have been due to the condensation of structural hydroxyl groups, as well as decomposition and dissociation of the organic moieties.



**Figure 3.** DSC curve of ZrHEDP.

DSC of ZrHEDP (Figure 3) exhibited an endothermic peak at 120 °C, which is attributed to loss of moisture/hydrated water. However, an exothermic process started at 300 °C, which is attributed to both decomposition of the organic moiety present in the framework as well as the condensation of structural hydroxyl groups. The decomposition of the organic moiety dominated the condensation of structural hydroxyl groups, which were observed to exotherms. Based on the zirconium and phosphorous content determined by ICP-AES, % carbon and % hydrogen, as well as thermal analysis (TGA) data, ZrHEDP was formulated as  $\text{Zr}(\text{C}_2\text{H}_8\text{P}_2\text{O}_7) \cdot 2\text{H}_2\text{O}$ , using the Alberti & Torracca formula.<sup>22</sup>



**Figure 4.** XRD of ZrHEDP.

No characteristic peak in the X-ray diffractogram of ZrHEDP (Figure 4) indicated that the material was amorphous in nature. ZrHEDP was stable in acid medium (maximum tolerable limits being 36 N  $\text{H}_2\text{SO}_4$ , 16 N  $\text{HNO}_3$ , and 11.3 N  $\text{HCl}$ ) and in organic solvent media (ethanol, benzene, and acetone). It was, however, not so stable in base medium, the maximum tolerable limits being 3 N  $\text{NaOH}$  and 0.1 N  $\text{KOH}$ .

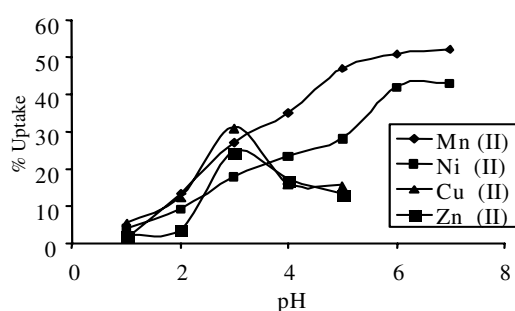
Material characteristics are presented in Table 1. ZrHEDP, a novel hybrid material of the TMA salt class, is an amorphous material that possesses structural hydroxyl groups, the  $\text{H}^+$  of the OH groups being the cation exchange sites.

**Table 1.** Material characteristics.

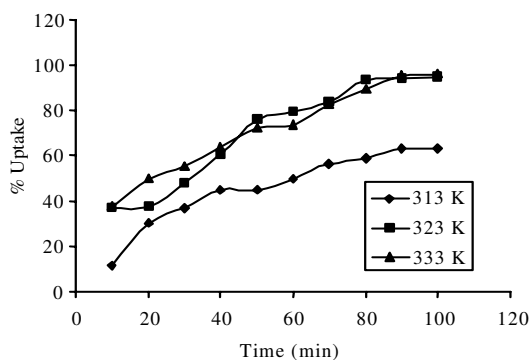
Characteristics	ZrHEDP
Color	White, Transparent
Nature	Hard, Amorphous
Ion exchange capacity	3.18 meq g <sup>-1</sup> (retained up to 300 °C)
Chemical resistivity	Acids were stable (18 N H <sub>2</sub> SO <sub>4</sub> , 16 N HNO <sub>3</sub> , and 11.3 N HCl) Bases were not stable (3 N NaOH and 0.1 M KOH) Organic solvents were stable (ethanol, benzene, and acetone)
Thermal stability	Up to 300 °C

## Sorption studies

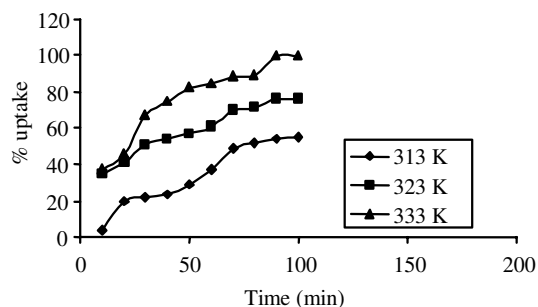
Ion exchange of metal ions from the liquid phase onto the solid phase can be considered a reversible reaction with 2 phases, which can be expressed as  $RA + B = RB + A$ , where R is the exchanger matrix, and A and B are the exchanging ions. The exchange is, as a rule, reversible. At equilibrium the 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 the electrostatic interactions between the charged framework and the counter ions that depend on the size and, in particular, on the valence of the counter ion. In addition to the electrostatic forces, other interactions between the ions and their environment are effective. Large counter ions may be sterically excluded from the narrow pores of the ion exchanger.

**Figure 5.** Effect of pH on percent uptake of metal ions.

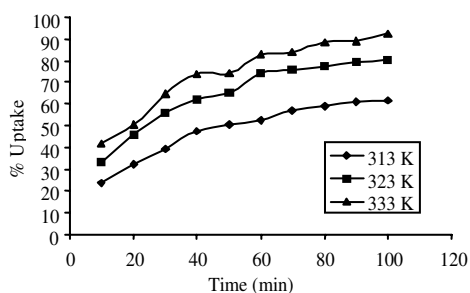
In Figure 5 the maximum sorption is observed at pH 3 in the case of Cu(II) and Zn(II), % uptake being 31.13 and 24.95, respectively. In the case of Mn(II) and Ni(II), maximum sorption is observed at pH 7, % uptake being 52.17 and 43.21, respectively.



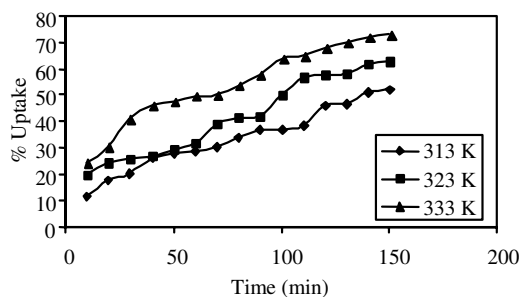
**Figure 6a.** Percent uptake of Mn(II) towards ZrHEDP at pH 7.



**Figure 6b.** Percent uptake of Ni(II) towards ZrHEDP at pH 7.



**Figure 6c.** Percent uptake of Cu(II) towards ZrHEDP at pH 3.



**Figure 6d.** Percent uptake of Zn(II) towards ZrHEDP at pH 3.

The effect of contact time, reaction temperature, and % uptake of the metal ions under study are presented in Figure 6a-d. Equilibrium time for Mn(II), Ni(II), and Cu(II) was 100 min; while for Zn(II) it was 150 min. It was observed that sorption increased with an increase in contact time and temperature, reaching a maximum value. The increase in uptake (%) of metal ions could be attributed to an endothermic nature of the sorption process,<sup>23–25</sup> which could be attributed to 2 different sorption processes, namely a fast ion exchange followed by chemisorption.<sup>26</sup> It was observed that uptake of cations increased with an increase in temperature, which indicates that the uptake is an ion exchange mechanism. Percent uptake was calculated using the formula,  $[(C_o - C_e)/C_o] \times 100$ , where  $C_o$  = initial concentration of metal ion (mg/L) and  $C_e$  = final concentration of metal ion (mg/L).

Equilibrium behavior is usually described in terms of equilibrium isotherms, which depend on the system temperature, concentration of the solution, contact time, and pH.<sup>27</sup> Sorption is a process in which both adsorption and absorption take place simultaneously. It may be a process involving physical phenomena or chemical interaction. Variation in sorption with concentration and temperature is generally expressed in terms of 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.

The Freundlich adsorption isotherm is represented by,  $\text{Log}(X/m) = \text{Log} K + (1/n) \text{Log} C_e$  (1), where  $X$  is the amount of adsorbate,  $m$  is the amount of adsorbent,  $C_e$  is the equilibrium concentration of the adsorbate in the solution, and  $K$  and  $1/n$  are Freundlich constants. If the adsorption process follows the

Freundlich pattern, the plot of  $\text{Log}(X/m)$  versus  $\text{Log Ce}$  is a straight line. Furthermore, from the above plot,  $1/n$  and  $K$  are calculated from the slope and intercept, respectively.

The Langmuir adsorption isotherm is represented by  $Ce/(X/m) = 1/(bV_m) + Ce/V_m$  (2), where  $Ce$ ,  $X$ , and  $m$  have the same meaning as described for the Freundlich isotherm;  $b$  is a constant that represents adsorption bond energy and  $V_m$  is a constant that represents maximum adsorption capacity corresponding to a monolayer covering the surface of the adsorbent. If the adsorption process follows the Langmuir pattern, the plot of  $Ce/(X/m)$  versus  $Ce$  is a straight line. Furthermore, from the above plot,  $b$  and  $V_m$  are calculated from the slope and intercept. The isotherm constants are important in understanding the sorption mechanism.

**Table 2.** Langmuir and Freundlich constants for sorption of Cu(II), Ni(II), Zn(II), and Mn(II) towards ZrHEDP.

Metal ion	Temperature K	Langmuir parameter			Freundlich parameter		
		$R^2$	$b \text{ dm}^3 \text{ mg}^{-1}$	$V_m \text{ mg g}^{-1}$	$R^2$	Log K	$1/n$
Copper(II)	313	0.9924	0.032	12.610	0.9052	0.785	0.107
	323	0.9877	0.050	15.898	0.8706	0.921	0.099
	333	0.9982	0.045	21.276	1.0000	0	1.000
Manganese(II)	313	0.9322	0.015	8.569	0.3012	0.586	0.100
	323	0.9877	0.169	8.920	0.2886	0.828	0.055
	333	0.9948	0.059	13.869	0.5989	0.996	0.045
Nickel(II)	313	0.9042	0.013	6.196	0.8542	0.146	0.364
	323	0.9752	0.243	8.711	0.2033	1.238	0.236
	333	0.9614	0.094	9.407	0.3303	0.719	0.072
Zinc(II)	313	0.9826	0.012	11.905	0.8670	0.429	0.214
	323	0.9964	0.013	17.094	0.9958	0.609	0.206
	333	0.9866	0.010	23.148	0.9862	0.611	0.247

Linear regression is the widely used method for fitting the transformed forms of original Langmuir and Freundlich isotherm equations. Langmuir and Freundlich constants, as well as  $R^2$  values are presented in Table 2.  $R^2$  is described as the correlation coefficient and indicates deviation from linearity or unit value. Unit value or closeness to unit value indicates that adsorption follows a particular pattern, either Langmuir or Freundlich. Based on  $R^2$  values, it is observed that the adsorption process followed the Langmuir pattern for all metal ions. Variation in  $R^2$  (Langmuir) is attributed to the fact that the surface adsorption is not a monolayer with a single site. Two or more sites with different affinities may be involved in metal ion sorption.<sup>28</sup> It was observed that with an increase in temperature,  $V_m$ , the maximum adsorption capacity, increased. At 333 K,  $V_m$ , the maximum adsorption capacity, followed the order Zn(II) (0.83 Å) > Cu(II) (0.80 Å) > Mn(II) (0.91 Å)  $\approx$  Ni(II) (0.74 Å) (values in parenthesis being ionic radii of the respective metal ion). Since sorption was carried out in aqueous medium, the most important factor responsible for selectivity order is the size of the hydrated ionic radius. The smaller the size of the cation the more heavily it is hydrated and, therefore, more difficult to exchange. Other factors are temperature,  $pK_h$  ( $K_h$  = hydrolysis constant), and ionic potential. A change in hydration of metal cation plays a dominant role in determining the selectivity of the exchanger. 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 ZrHEDP varies in each case.<sup>25</sup>



Ion exchange of metal ions from the liquid phase on to the solid phase can be considered a reversible reaction with 2 phases; therefore, a simple first order kinetic model is used to establish the rate of reaction.<sup>26</sup> The first order kinetic equation is,  $\text{Ln} [1-U(t)] = -k't$  (3), where  $k'$  is the overall rate constant and  $U(t)$  is fractional attainment of equilibrium. Furthermore,  $k' = k_1 (1+1/k_c) = k_1 + k_2$  (4), where  $k_c$  is the equilibrium constant, and  $k_1$  and  $k_2$  are the first order forward and reverse rate constants, respectively.  $U(t) = C_0 - C_t / C_0 - C_e$  (5), where  $C_0$ ,  $C_t$ , and  $C_e$  (all in mole/L) are concentrations of metal cation in solution, initially, at time  $t$  and at equilibrium, respectively. Kinetic plots are linear, indicating that the sorption process follows first order reversible kinetics.

**Table 3.** Kinetic parameters of the adsorption of Cu(II), Ni(II), Mn(II), and Zn(II) on ZrHEDP.

Metal Ion	Temperature	$k'$ $\text{min}^{-1}$	$k_c$	$k_1$ $\text{min}^{-1}$	$k_2$ $\text{min}^{-1}$
Copper(II)	313 K	0.051	1.618	0.032	0.019
	323 K	0.029	5.859	0.025	0.004
	333 K	0.036	12.026	0.033	0.003
Nickel(II)	313 K	0.054	1.205	0.029	0.025
	323 K	0.065	3.172	0.050	0.015
	333 K	0.068	462	0.067	0.001
Zinc(II)	313 K	0.027	1.087	0.014	0.013
	323 K	0.029	1.673	0.018	0.011
	333 K	0.034	2.667	0.025	0.009
Manganese(II)	313 K	0.063	1.718	0.040	0.023
	323 K	0.068	16.769	0.064	0.004
	333 K	0.068	22.100	0.065	0.003

From the results presented in Table 3, it is seen that  $k_c$  and the equilibrium constant increased as temperature increased for all metal ions, which shows that the phenomenon is ion exchange for metal ions towards ZrHEDP. Increased  $k_c$  with increased temperature is also in keeping with the present observation, i.e. an increase in metal ion sorption as contact time and temperature increase. Such systems are attributed to endothermic processes;  $k_1$  and  $k_2$  are rate constants related to sorption and desorption, respectively. For all metal ions,  $k_1 > k_2$ , which indicates favorable sorption of metal ions at all temperatures.

In order to explain the effect of temperature on sorption, we determined thermodynamic parameters, standard free energy  $\Delta G^\circ$ , standard enthalpy  $\Delta H^\circ$ , and standard entropy  $\Delta S^\circ$  using the following equations:  $\Delta G^\circ = -RT \ln k_c$  (6),  $\Delta H^\circ = R [T_1.T_2 / T_1 - T_2] \ln (k_2/k_1)$  (7), and  $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T$  (8), where  $R$  is the gas constant,  $k_c$ ,  $k_1$ , and  $k_2$  are equilibrium constants at temperatures  $T$ ,  $T_1$ , and  $T_2$ , respectively. Numerical values of the equilibrium constants were calculated from  $k_c = C_{Be} / C_{Ae}$  (9), where  $C_{Be}$  and  $C_{Ae}$  are the equilibrium concentrations of metal cations on the sorbent and in solution, respectively.<sup>30</sup>

Thermodynamic parameters for the sorption of Cu(II), Ni(II), Zn(II), and Mn(II) on ZrHEDP are presented in Table 4. Negative  $\Delta G^\circ$  values, in general, indicate the feasibility and spontaneous nature of the sorption process and attainment of a more stable energy level after ion exchange of metal ions.  $\Delta G^\circ$  depends on several factors, such as temperature, heat consumed and released for removal of  $H^+$ , and intake of the incoming cation, in terms of hydration and dehydration, as well as the size of the hydrated cationic radii. In

the present study, as the ion exchanger used was amorphous in nature, it is expected that all exchange sites may not be energetically equivalent. The incoming cation or the exchanging cation would first occupy the most favorable sites, which require little or no dehydration energy for exchange. As exchange proceeds, the sites become progressively less favorable. This causes greater dehydration at the expense of more energy. The overall  $\Delta G^0$  value is a result of the contribution of the above-mentioned factors. Depending on the predominant factor, the  $\Delta G^0$  values vary in each case. It has been earlier observed that  $\Delta G^0$  up to  $-20 \text{ KJ mol}^{-1}$  is consistent with electrostatic interaction between sorption sites and the metal ion.<sup>28</sup>

**Table 4.** Thermodynamic parameters for the sorption of Cu(II), Ni(II), Mn(II), and Zn(II) towards ZrHEDP.

Metal Ion	Temperature	$k_c$	$\Delta G^0$ kJ/mole	$\Delta H^0$ kJ/mole	$\Delta S^0$ kJ/mole K
Copper(II)	313 K	1.618	-1.252	86.225	0.279
	323 K	5.859	-4.747		0.282
	333 K	12.026	-6.885		0.280
Nickel(II)	313 K	1.205	-0.484	263.407	0.843
	323 K	3.172	-3.099		0.825
	333 K	462	-16.986		0.842
Zinc(II)	313 K	1.087	-0.217	38.964	0.125
	323 K	1.673	-1.382		0.125
	333 K	2.667	-2.715		0.125
Manganese(II)	313 K	1.718	-1.407	108.104	0.350
	323 K	16.769	-7.571		0.358
	333 K	22.100	-8.570		0.350

A positive value of  $\Delta H^0$  indicates an endothermic process. Probably, some energy must be supplied to the cation, as it leaves the hydration sphere to undergo ion exchange with the ion exchange material, ZrHEDP.<sup>31</sup> It has been previously observed that sorption reactions of many cations are endothermic. The equilibrium constants for such sorption processes increase with temperature, indicating a favorable process at high temperature.<sup>23–25</sup> This is also in keeping with the increase in  $k_c$  with increasing temperature observed in the present study.

The entropy reflects the changes in the hydration sphere of the exchanging cation, which occurs during the ion exchange process. A negative entropy change in the ion exchange process is possible, which has been previously observed.<sup>32</sup> A positive  $\Delta S^0$  value indicates the higher randomness of ions nearby the adsorbent surface.<sup>31</sup> A decrease in the  $\Delta S^0$  values of the system indicates greater uptake of the ions. A significant negative contribution of  $\Delta S^0$  results from the replacement of cations with high  $S^0$  in the external aqueous phase by one of lower  $S^0$  in the exchanger phase.<sup>33</sup>

## Conclusion

The novel metal phosphonate, ZrHEDP, possesses good IEC, chemical resistivity, and thermal stability, which are characteristics of a good ion exchange material, highlighting its potential use as an ion exchange material. The kinetics and thermodynamics of exchange, as well as adsorption isotherms for the metal ions studied reveal good sorption for Cu(II) and Zn(II), as compared to Ni(II) and Mn(II) towards ZrHEDP, which further indicates good separation characteristics of the metal ions studied.

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