

Technical paper

# The Use of Metal Phosphonates in the Removal of Anti Infective Organic Molecules by Adsorption Process

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## Abstract

A novel hybrid ion exchange material of the class of metal (IV) phosphonate, zirconium – hydroxy ethylidene diphosphonate [ZrHEDP] has been synthesized by sol-gel method. The material has been characterized for elemental analysis (ICP-AES), thermal analysis (TGA, DSC), FT-IR and X-ray diffraction studies. Chemical resistivity of the material in various media – acids, bases and organic solvents has been assessed. The Na<sup>+</sup> ion-exchange capacity (IEC) of the material has been determined and effect of heating on IEC studied. The sorption behaviour of medicinal dyes Acriflavin (AF) and Brilliant Green (BG) towards ZrHEDP has been studied at 313 K, 323 K and 333 K and kinetic and thermodynamic parameters evaluated. Adsorption isotherms [Langmuir and Freundlich], breakthrough capacity and elution behaviour of dyes have also been studied. Sorption affinity of medicinal dyes towards ZrHEDP is found to be BG > AF

**Keywords:** Zr (IV) phosphonate, Inorgano/organic ion exchanger, hybrid ion exchanger, metal phosphonate, zirconium – hydroxy ethylidene diphosphonate

## 1. Introduction

Wastewater contains a number of persistent organic compounds derived from active ingredients in pharmaceuticals and personal care products, which are used in large quantities throughout the world. Both groups are collectively referred to as “Pharmaceuticals and Personal Care Product ingredients” (PPCPs).<sup>1</sup> PPCPs constitute a diverse group of chemicals which comprise all drugs, diagnostic agents, nutraceuticals, fragrances, sun-screen agents etc. A wide range of PPCPs has been detected in a variety of environmental samples at levels ranging from ng kg<sup>-1</sup> to g kg<sup>-1</sup> and little is known about the effects and the involved risk, of long term exposure to low concentrations of these pollutants that have received very little attention as potential environmental pollutants.<sup>2</sup>

It has been observed that biological treatment processes are ineffective in treatment of wastewaters containing antibiotics and other pharmaceuticals. e.g. sulfonamides were not readily biodegradable using activated sludge process.<sup>3</sup> However, combined chemical/biological treatment processes appear to be more effective. Garcia et al

used aerobic digestion integrated with activated carbon filtration and reverse osmosis to reduce BOD, COD and TDS in pharmaceutical wastewater.<sup>4</sup> Adsorption and ion exchange are sorption processes in which certain adsorptives are selectively transferred from fluid phase to the surface of insoluble, rigid particles, suspended in a vessel or packed in a column. Adsorption has often been used as a method to remove dissolved contaminated organic compounds<sup>5</sup>, due to simplicity of design, initial cost, ease of operation and insensitivity to toxic substances. A large number of suitable sorbents such as activated carbon<sup>6,7</sup> polymeric resins,<sup>8</sup> various low cost adsorbents<sup>9,10</sup> have been used. Ion exchange is also a highly effective method for eliminating dissolved contaminants such as to adsorb streptomycin, (which could subsequently be eluted with a dilute acid solution) as well as to remove and recover antibiotics from pharmaceutical waste water.<sup>11</sup>

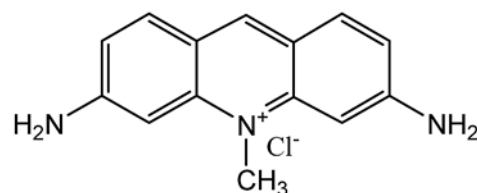
There is currently high interest in engineering mixed materials (organic/inorganic) where features of the organic and inorganic components complement each other leading to the formation of new solid-state structures and materials with new composite properties.<sup>12</sup> Tetra-

valent metal acid (tma) salts are synthetic ion exchangers possessing the general formula  $M(IV) (HXO_4)_2 nH_2O$ , where  $M(IV) = Zr, Ti, Th, Ce, Sn$  etc and  $X = P, Mo, W, As, Sb$  etc. The presence of structural hydroxyl groups (the H of the OH groups being the cation exchange sites) in these materials are responsible for the ion exchange behavior. Zr (IV) phosphate, a tma salt has been widely used as a cation exchanger and has shown a number of advantages as an ideal host lattice. In the tetrahedral moiety of phosphoric acid,  $PO(OH)_3$ , 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 novel metal phosphonates. Depending on the complexity of the phosphonate used, the material gives rise to two or three dimensional hybrid polymeric structures. Though several metal phosphonates have been synthesized and characterized, the focus has been on structure elucidation.<sup>13–15</sup> These materials are interesting because of their potential utility as sorbents<sup>16</sup>, as ion exchangers<sup>17</sup> and in materials chemistry.<sup>18</sup>

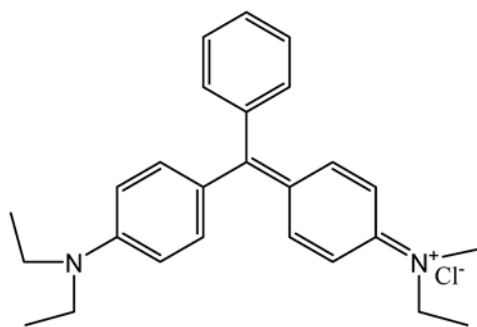
Dyes in general contain one or more of the following functional groups in their structure ( $-OH, -COOH, -SO_3H, NO_2, N=N$  etc.). It is believed that in adsorption the interaction of the above functional groups with the matrix material/sorbent being used, could be anywhere from covalent to coulombic, hydrogen bonding or the weak Van der Waals forces. The ability of the dye to be eluted out depends on the strength and type of interaction between the dye and sorbent. There are a few publications, where ion exchange materials have been used as sorbents for removal of dyes.<sup>19–22</sup>

In the present endeavour a novel metal phosphonate abbreviated as (ZrHEDP) a hybrid ion exchange material of the class of tetravalent metal acid (tma) salt has been synthesized by sol-gel method, using tetravalent zirconium (as  $ZrOCl_2 \cdot 8H_2O$ ) and hydroxy ethylidene diphosphonic acid (HEDP). The material has been characterized for elemental analysis – (ICP-AES), thermal analysis (TGA, DSC), FT-IR and X-ray diffraction studies. Chemical resistivity of the material in various media – acids, bases and organic solvents has been assessed. Though the potential use of metal phosphonate as a sorbent has been suggested, a literature survey reveals that no systematic studies have been carried out on the sorption characteristics of these materials. Metal phosphonate (ZrHEDP) possesses structural hydroxyl groups, the H of the hydroxyl groups being responsible for the cation exchange behaviour. Due to the presence of structural hydroxyl groups it is expected that the dye could either be bound to the matrix material (ZrHEDP) by hydrogen bonds or the weak Van der Waals forces making sorption and desorption easy and possible. It was therefore thought of interest to use metal phosphonate as a sorbent for wastewater treatment containing pharmaceutical product. Acriflavin (AF) and Brilliant Green (BG) are medicinal

dyes that impart colour as well as anti infective property and widely used in sun – screen lotions and creams. Thus since they are water soluble they can be introduced to waste water as pollutants. The sorption behaviour of anti-infective molecules AF and BG [Figure 1] towards ZrHEDP has been studied at 313 K, 323 K and 333 K and kinetic and thermodynamic parameters evaluated. Adsorption isotherms [Langmuir and Freundlich], breakthrough capacity and elution behaviour of dyes have also been studied and discussed.



Acriflavin



Brilliant green

Figure 1. Structure of dyes.

## 2. Experimental

All chemicals and reagents used were of analytical grade.

### 2. 1. Synthesis of ZrHEDP

ZrHEDP was prepared by mixing aqueous solution of  $ZrOCl_2 \cdot 8H_2O$  [0.1 M, 250 mL] and HEDP [0.2 M, 250 mL], dropwise and with constant stirring, maintaining the temperature of the solution at 70 °C. The gelatinous precipitates obtained was digested for one hour at 70 °C, filtered, washed with conductivity water till removal of chloride ions, followed by drying at room temperature. The material was then broken down to the desired particle size [30–60 mesh (ASTM)] by grinding, sieving and then,

converted to the acid form by taking about 5 g of the material and treating it with 50 ml of 1 M HNO<sub>3</sub> for 30 min with occasional shaking. The supernatant acid solution was removed by decantation and treated with conductivity water for removal of adhering acid. This process (acid treatment) was repeated at least five times. After final washing, the material was dried at room temperature. The Na<sup>+</sup> ion exchange capacity (IEC) of the material was determined by the column method<sup>23</sup>. This material was used for all studies.

## 2. 2. Calcination Studies

The effect of heating on IEC was studied by heating 1 g portion of the material ZrHEDP for 2 h at temperatures between 100 °C to 500 °C with 100 °C intervals in a muffle furnace and determining the Na<sup>+</sup> IEC by the column method<sup>23</sup> at room temperature.

## 2. 3. Chemical Resistivity

The chemical resistivity of the material in various media – acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, 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 hours. The change in color, texture and weight was observed.

## 2. 4. Instrumentation

ZrHEDP has been analyzed for zirconium and phosphorus by ICP-AES. Thermal analysis (TGA) was carried out on a Shimadzu thermal analyzer DT-30 at a heating rate of 10 °C min<sup>-1</sup>. DSC of the sample was performed on Metler TA 4000 system at a heating rate of 20 °C min<sup>-1</sup>. FT-IR spectra was obtained using KBr wafer on BOMEM MB series. X-ray diffractogram was obtained on an X-ray diffractometer BRUCKER AXS D8 using Cu-K<sub>α</sub> radiation with a nickel filter. A temperature controlled shaker bath having a temperature variation of ±0.5 °C was used for the equilibrium studies. % Dye sorption/desorption was determined using a visible spectrophotometer, absorbance of AF and BG being measured at the max values 450 and 625 nm respectively.

## 2. 5. Sorption Studies

### 2. 5. 1. Effect of pH

100 mg of ZrHEDP was taken in stoppered conical flasks, to which was added 10 ml of 50 ppm AF or BG, varying pH and mixture shaken for 30 minutes at 30°C. The supernatant liquid was removed immediately and dye concentration was determined spectrophotometrically using calibration curve of the individual dye.

### 2. 5. 2. Sorption Kinetics and Thermodynamics

ZrHEDP particles of [30–60mesh (ASTM)] was used to evaluate various kinetic and thermodynamic parameters. 10 ml of 100 ppm dye solution under study, was shaken with 100 mg of ZrHEDP in stoppered conical flasks at the desired temperatures [313 K, 323 K and 333 K] at different time intervals with increments of 5 min (5, 10, 15, – 50 min). pH of the solution was adjusted to the value at which maximum sorption of respective dye takes place. Results obtained from this study is utilized to evaluate kinetic parameters [U(t), k', k<sub>1</sub>, k<sub>2</sub> and k<sub>c</sub>] and thermodynamic parameters] dG<sup>0</sup>, ΔH<sup>0</sup> and ΔS<sup>0</sup>] explained in section 3.2.

### 2. 5. 3. Adsorption Isotherm Studies

100 mg of ZrHEDP [30–60 mesh (ASTM)] was shaken with 10 ml of individual dye solution under study varying concentration with increment of 10 ppm [10, 20 – 50 ppm] was equilibrated in stoppered conical flasks at desired temperatures [313 K, 323 K and 333 K] till attainment of equilibrium. pH of the solution was adjusted to the value at which maximum sorption of respective dye takes place. The supernatant liquid was removed immediately after requisite time and the dye concentration evaluated spectrophotometrically.

### 2. 5. 4. Break Through Capacity

5 mL of feed solution containing 100 ppm of AF and BG was allowed to pass through the column containing 1g of ZrHEDP, maintaining a flow rate of 0.1 mL min<sup>-1</sup>. The process was continued till the amount of dyes was same in feed and effluent. Break through capacity was calculated using the ratio C<sub>e</sub>/C<sub>0</sub>, where C<sub>e</sub> is the concentration of the dye in the effluent and C<sub>0</sub> is the concentration of dye in the feed.<sup>24</sup>

### 2. 5. 5. Elution Behavior of Adsorbed Dyes

5 mL (100 ppm) of each dye solution under study was allowed to pass through a column containing 1g of ZrHEDP, maintaining a flow rate of 0.1 mL min<sup>-1</sup>. It was then eluted with reagents like HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and KCl of 0.01M concentration. The amount of dye recovered was calculated as (C<sub>e</sub>/C<sub>0</sub>) × 100, where C<sub>e</sub> = concentration of dye in eluted solution and C<sub>0</sub> is initial concentration of dye. The amount of dye adsorbed or eluted was determined spectrophotometrically in all cases.

## 3. Results and Discussion

### 3. 1. Characterization of ZrHEDP

ZrHEDP was obtained as transparent granules. Elemental analysis by ICP-AES shows zirconium to

phosphorus ratio to be 1 : 2. The carbon and hydrogen content were found to be % C = 7.01, % H = 3.21 in ZrHEDP. FTIR spectra of Zr-HEDP (Figure 2) exhibit broad band in the  $3400\text{ cm}^{-1}$ , attributed to symmetric and asymmetric  $\text{-OH}$  stretches. A sharp medium band at  $1638\text{ cm}^{-1}$  is attributed to  $\text{H-O-H}$  bending. This indicates the presence of structural hydroxyl protons in ZrHEDP, the H of  $\text{-OH}$  being the cation exchange sites. A broad band at  $1056\text{ cm}^{-1}$ , is attributed to the  $\text{P=O}$  stretching. A combination of bands at  $1430$  and  $1328\text{ cm}^{-1}$  is attributed to symmetric and asymmetric  $\text{C-CH}_3$  bending.<sup>25</sup>

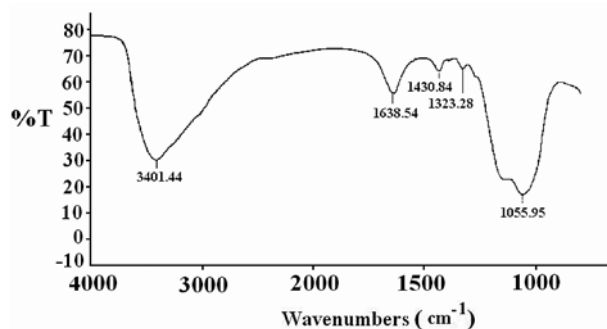


Figure 2. FT-IR spectra of ZrHEDP.

The  $\text{Na}^+$  ion exchange capacity (IEC), determined by column method is found to be  $3.18\text{ meq g}^{-1}$ .<sup>24</sup> The IEC of the samples calcined at the temperature between  $100$  to  $500\text{ }^\circ\text{C}$  with  $100\text{ }^\circ\text{C}$  intervals, was found to be  $3.20$ ,  $3.00$ ,  $3.22$ ,  $1.96$  and  $1.55\text{ meq g}^{-1}$  respectively. The initial increase in the IEC value at  $100\text{ }^\circ\text{C}$  could be attributed to loss of moisture adhered to it, thereby increasing the active exchanger content for same weight of material taken for IEC determination. However, at  $300\text{ }^\circ\text{C}$  an increase in IEC value is observed which is attributed to the decomposition of organic moiety, leading to the formation of active carbon, as evidenced by the change in colour of the heated samples to black. Further, decrease in IEC beyond  $300\text{ }^\circ\text{C}$  is attributed to the complete decomposition of organic moiety / active carbon in the form of  $\text{CO}_2$ .

TGA of Zr-HEDP (Figure 3) shows a sharp change within the temperature range  $52\text{--}224\text{ }^\circ\text{C}$  corresponding to

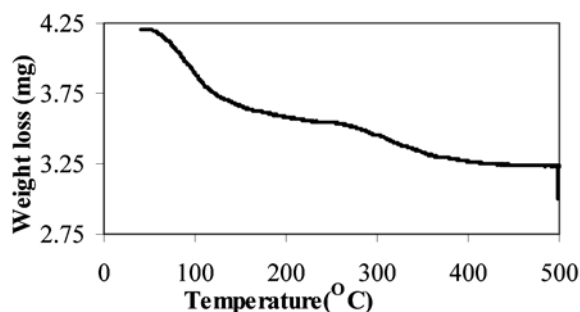


Figure 3. TGA plot of ZrHEDP.

the loss of moisture/hydrated water after which weight loss is observed in the range of  $255\text{--}479\text{ }^\circ\text{C}$ , which may be due to the condensation of structural hydroxyl groups as well as decomposition and dissociation of the organic moieties.

DSC of ZrHEDP (Figure 4) exhibits endothermic peak at  $120\text{ }^\circ\text{C}$ , which is attributed to loss of moisture/hydrated water. However, an exothermic process starts at  $300\text{ }^\circ\text{C}$ , which is attributed to both decomposition of the organic moiety present in the framework as well as condensation of structural hydroxyl groups. The decomposition of the organic moiety predominates the condensation of structural hydroxyl groups which is observed as an exotherm.

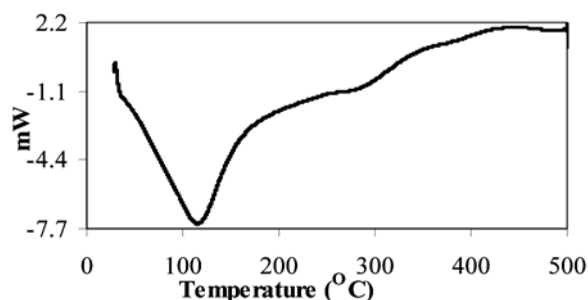


Figure 4. DSC curve of ZrHEDP.

Based on the zirconium and phosphorous content determined by ICP-AES, % carbon and % hydrogen as well as thermal analysis (TGA) data, ZrHEDP has been formulated as  $\text{Zr}(\text{C}_2\text{H}_8\text{P}_2\text{O}_7) \cdot 2\text{H}_2\text{O}$  using Alberti & Torracca formula.<sup>26</sup> No characteristic peak in X-ray diffractogram of ZrHEDP (Figure 5) indicates that the material is amorphous in nature.

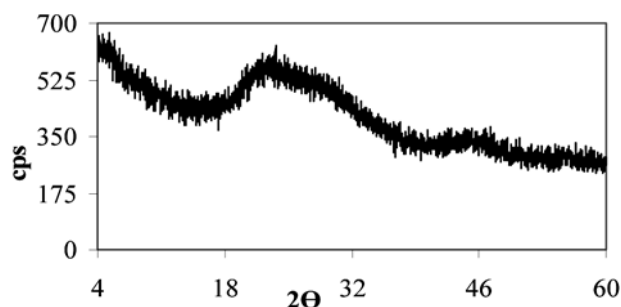


Figure 5. X-ray profile of ZrHEDP.

ZrHEDP is stable in acid medium, maximum tolerable limits being ( $36\text{ N H}_2\text{SO}_4$ ,  $16\text{ N HNO}_3$ ,  $11.3\text{ N HCl}$ ) and also stable in organic solvent media (ethanol, benzene and acetone). It is however not so stable in base medium, maximum tolerable limits being ( $3\text{ N NaOH}$  and  $0.1\text{ N KOH}$ ).

### 3. 2. Sorption Studies

Maximum sorption of BG takes place at pH 3, while for AF at pH 1. Beyond pH 3 for BG and pH 1 for AF, change in colour of dye is observed which is attributed to aggregation of dye molecules.<sup>27</sup>

Figure 6–7 exhibit % uptake of dyes towards ZrHEDP with respect to time. It is observed that sorption increases gradually with increase in contact time and temperature.<sup>28</sup>

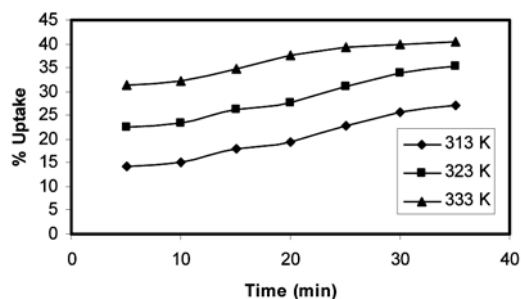


Figure 6. Percentage uptake of AF towards ZrHEDP.

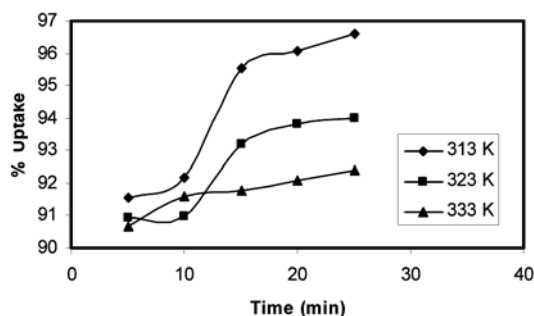


Figure 7. Percentage uptake of BG towards ZrHEDP.

Generally both Langmuir and Freundlich isotherms are used for explaining the adsorption on materials. Standard equations<sup>28</sup> have been used to find values of various constants of both the isotherms. Based on  $R^2$  values presented in Table 1 AF follows Langmuir pattern whereas BG follows Freundlich pattern which are also presented in Figure 8 and 9 respectively. Variation in  $R^2$  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 dye sorption.<sup>29</sup>

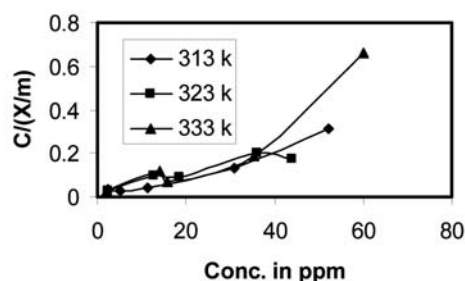


Figure 8. Langmuir adsorption isotherm of AF towards ZrHEDP.

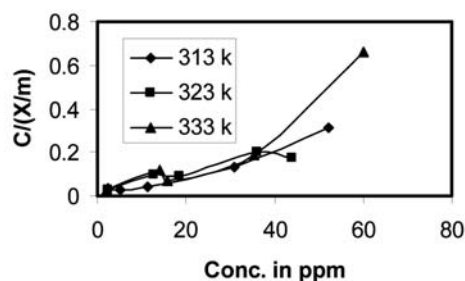


Figure 9. Freundlich adsorption isotherm of BG towards ZrHEDP.

Sorption of dyes from the liquid phase on to the solid phase can be considered as a reversible reaction with two phases. Therefore, a simple first order kinetic model is used to establish the rate of reaction. From the data obtained for the effect of contact time and reaction temperature on sorption, kinetic parameters can be calculated. The first order kinetic equation is,  $\ln [1-U(t)] = -k't$  where  $k'$  is the overall rate constant and  $U(t)$  is fractional attainment of equilibrium. Further,  $k' = k_1(1 + 1/k_c) = k_1 + k_2$ , where  $k_c$  is the equilibrium constant and  $k_1$  and  $k_2$  are the first order forward and reverse rate constants, respectively.  $U(t) = C_0 - C_t / C_0 - C_e$  where,  $C_0$ ,  $C_t$  and  $C_e$  (all in mole/L) are concentration of dye in solution initially, at time  $t$ , and at equilibrium respectively. Numerical values of the equilibrium constants were calculated from  $k_c = C_{Be} / C_{Ae}$  where  $C_{Be}$  and  $C_{Ae}$  are the equilibrium concentrations of dye on the sorbent and in solution, respectively.<sup>28</sup>

In order to explain the effect of temperature on the sorption, thermodynamic parameters, standard free energy  $\Delta G^\circ$ , standard enthalpy  $\Delta H^\circ$ , and standard entropy  $\Delta S^\circ$  were determined using standard equations.<sup>28</sup>

Table 1. Langmuir, Freundlich and Thermodynamic parameters of the adsorption of AF and BG on ZrHEDP.

Dye	Temperature	$\Delta G^\circ$ kJ/mole	$\Delta H^\circ$ kJ/mole	$\Delta S^\circ$ kJ/mole	$R^2$	
					Langmuir Pattern	Freundlich Pattern
AF	313 K	2.443	25.918	0.075	0.9637	0.3053
	323 K	1.693		0.075	0.9772	0.8977
	333 K	0.943		0.075	0.9791	0.1502
BG	313 K	-8.722	-37.470	-0.091	0.8897	0.9257
	323 K	-8.199		-0.091	0.8543	0.8839
	333 K	-6.910		-0.092	0.6706	0.9995

From Table 1, It is observed that  $\Delta G^\circ$  values are negative in case of BG. This indicates favourable sorption towards ZrHEDP and feasibility as well as spontaneous nature of the sorption process and attainment of a more stable energy level after sorption of the dye. Positive  $\Delta G^\circ$  values in case of AF indicates lower preference towards ZrHEDP. However,  $\Delta G^\circ$  depends on several factors such as temperature, heat consumed and released for removal of  $H^+$  and intake of the incoming cationic dye. In the present study, the ion exchanger used being amorphous in nature, it is expected that all exchange sites may not be energetically equivalent. The incoming cationic dye would first occupy the most favourable sites, which require little or no dehydration energy for exchange. As exchange proceeds, the sites become progressively less favourable. This causes greater dehydration at expense of more energy. The overall  $\Delta G^\circ$  value is a result from the contribution of the above mentioned factors. Depending on the predominant factor the  $\Delta G^\circ$  values vary in each case. Negative  $\Delta H^\circ$  values indicate sorption of dyes to be exothermic in nature. Positive  $\Delta H^\circ$  values indicate an endothermic process. Probably some energy must be supplied for the dye sorption to occur.<sup>30</sup> The positive entropy in case of AF indicates an increased disorder of the system probably, due to the loss of water surrounding the dye while getting adsorbed onto ZrHEDP. Decrease in  $\Delta S^\circ$  values indicates higher uptake of the dyes, which is a result of high  $S^\circ$  in the external aqueous phase and a lower  $S^\circ$  in sorbent phase.<sup>31</sup>

The break through capacity of a sorbent depends on, the flow rate of feed solution through the column, bed depth, selectivity coefficient, particle size and temperature. Several factors contribute to sorption of dyes on the sorbent material. These include steric effect which is dependent on structure of dyes, exchange / sorption characteristics dependant on charges present on the dye as well as sorbent and chemical forces with which the dye is held onto sorbent material ranging from covalent to coulombic, hydrogen bonding or the weak van der waals forces. Even small changes in the dye structure may significantly influence the adsorption capacity.

**Table 2.** Breakthrough capacity of AF and BG.

AF		BG	
Co = 50 ppm		Co = 50 ppm	
Volume (ml)	Ce/Co	Volume (ml)	Ce/Co
5	0.150	5	0.142
10	0.488	10	0.252
15	0.998	15	0.458
		20	0.656
		25	0.982

From table 2, it is observed that break through capacity follows the order BG > AF. It is observed that %

AF and BG sorbed onto ZrHEDP is  $\approx 85\%$ , which shows good sorption probably due to cationic nature of dyes as well as cation exchange characteristics of ZrHEDP.

**Table 3.** Elution of dyes using various eluants.

Eluting Agent	AF		BG	
	$E_v$	% E	$E_v$	% E
0.1M HNO <sub>3</sub>	70	99.2	70	97.8
0.1M HCl	80	99.2	80	98.9
0.1M H <sub>2</sub> SO <sub>4</sub>	60	98.2	90	97.9
0.1M KCl	80	99.1	120	98.6
Methanol	60	99.5	120	97.9

$E_v$  = mL of eluting agent; % E = Percentage elution

From table 3, it is observed that elution of AF and BG sorbed onto ZrHEDP using acid and electrolytes ranges between 97–100%. In case of AF % elution >99% indicates weak adsorption which makes sorption and desorption easy and possible.

## 4. Conclusion

Sorbent material ZrHEDP, possesses good chemical resistivity, thermal stability and is insensitive to dye sorption. The kinetics and thermodynamics of sorption as well as adsorption isotherms for the dyes studied reveal good sorption behaviour. Breakthrough capacity indicates good affinity of dyes towards ZrHEDP, found to be in the order BG > AF. Elution of dyes using various eluants is greater than 97% in all cases. Good sorption as well as elution of dyes using ZrHEDP indicates its promising use in waste water treatment containing dyes.

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## Povzetek

Z uporabo sol-gel metode smo sintetizirali cirkonijev hidroksietilen difosfonat (ZrHEDP), ki lahko služi kot material za ionske izmenjevalce. Material smo raziskovali z elementno analizo (ICP-AES), termično analizo (TGA, DSC), FT-IR spektroskopijo in X-ray difrakcijo. Ocenili smo odpornost materiala v različnih medijih (kislo, bazično, organska topila). Določili smo kapaciteto izmenjave Na<sup>+</sup> ionov in vpliv temperature na izmenjavo. Raziskovali smo tudi sorpcijo medicinskih barvil akrilavin in briljantno zeleno pri 313 K, 323 K in 333 K smo ter določili kinetične in termodinamske parametre adsorpcije.