

## Sorption of Water Soluble Dyes using Zirconium - Hydroxy Ethylidene Diphosphonate from Aqueous Solutions

Amit Jayswal and Uma Chudasama\*

Applied Chemistry Department, Faculty of Technology and Engineering,  
The M.S.University of Baroda, Vadodara – 390 001, Gujarat, India.

\*Email : uvces@gmail.com

**Abstract :** A novel hybrid ion exchange material, Zirconium - hydroxy ethylidene diphosphonate [ZrHEDP] has been synthesized by sol-gel method. The material has been characterized by 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 sorption behaviour of dyes Methylene Blue (MB), Crystal Violet (CV), Methyl Violet (MV) and Janus Green B (JGB) towards ZrHEDP has been studied at 313 K, 323 K and 333 K and kinetic and thermodynamic parameters were evaluated. Adsorption isotherms [Langmuir and Freundlich], breakthrough capacity and elution behaviour of dyes have also been studied. Sorption affinity of dyes towards ZrHEDP is found to be MB > CV  $\approx$  MV > JGB.

**Keywords :** Zr (IV) phosphonate, Inorgano / organic ion exchanger, Hybrid ion exchanger, Metal phosphonate, Zirconium - hydroxy ethylidene diphosphonate

Received : 14.09.06; accepted : 23.05.07

### Introduction

Wastewaters from dyeing and finishing operations associated with the textile industry are highly contaminated in both colour and organic content. Colour removal from textile effluents has been the target of great attention in the last few years, not only because of its potential toxicity, but also due to visibility problems[1]. Various physicochemical and biological techniques have been employed to remove dyes from wastewaters. They include membrane filtration[2], coagulation / flocculation[3,4], adsorption[2,3,5], ion exchange[6,7], advanced oxidation (chlorination, ozonation)[8,9], chemical reduction[10] and biological treatment (bacterial and fungal biosorption, biodegradation in aerobic or anaerobic conditions)[11,12]. The technical and economic feasibility of each technique is determined by several factors such as dye type, wastewater composition, operation costs and generated waste products. Also, the use of one individual technique is not sufficient to achieve complete decolorization. Therefore dye removal strategies consist of a combination of different techniques. Amongst various techniques, adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances. Adsorption has often been used as a method to remove dissolved contaminated organic compounds[13]. A large number of suitable sorbents such as activated carbon[14, 15] polymeric resins[16] or various low cost adsorbents (non-modified or modified cellulose biomass, chitin, soil material, activated alumina, bacterial biomass, etc.) have been studied [17-21]. Identification of a potential dye sorbent must be in good agreement with its dye-binding capacity, its regeneration properties, its

requirements and limitations with respect to environmental condition[22].

There is currently a 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[23]. Zr (IV) phosphate 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)<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 novel metal phosphonates[24-26]. 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[24-26]. These materials are interesting because of their potential utilization as sorbents and supports[27] in the area of catalysis[28], ion exchangers[29], in proton conduction[30], intercalation chemistry[31], photochemistry[32] and materials chemistry[33].

Several phosphonic acids such as hydroxy ethylidene diphosphonic acid (HEDP), amino tris(methylenephosphonic acid) (ATMP) and diethylenetriamine penta(methylenephosphonic acid) (DETPMP) have been widely used as sequestering agents, dispersants, scale and corrosion inhibitors and therapeutic agents[34].

In the present endeavour, a novel metal phosphonate (ZrHEDP) has been synthesized by

sol-gel method, using tetravalent zirconium (as  $ZrOCl_2 \cdot 8H_2O$ ) and HEDP. The material has been characterized by 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.

Dyes in general contain one or more of the following functional groups in their structure (-OH, -COOH, -SO<sub>3</sub>H, NO<sub>2</sub>, N=N etc.). It is believed that in adsorption, the interaction of functional groups of the dyes with the matrix material 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 removed depends on the strength and type of interaction. 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. The use of ZrHEDP as a sorbent for wastewater treatment containing dyes is therefore of interest. The sorption behaviour of dyes, Methylene Blue (MB), Crystal Violet (CV), Methyl Violet (MV) and Janus Green B (JGB) [Figure 1] towards ZrHEDP has been studied at 313 K, 323 K and 333 K and kinetic and thermodynamic parameters were evaluated. Adsorption isotherms [Langmuir and Freundlich], breakthrough capacity and elution behaviour of dyes have also been studied and discussed.

## Experimental

All chemicals and reagents used were of analytical grade.

### 1. Synthesis of Zirconium Hydroxy Ethylidene Diphosphonate [ZrHEDP]

ZrHEDP has been prepared by mixing aqueous solutions of  $ZrOCl_2 \cdot 8H_2O$  [0.1 M, 250 ml] and sodium salt of HEDP [0.2 M, 250 ml], dropwise and with constant stirring at ~70 °C. The gelatinous precipitates obtained was digested for one hour at ~70 °C, filtered, washed with double distilled water for 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 and sieving. The material was converted to the acid form by taking 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 sample was then separated from acid by decantation and treated with double distilled water for removal of adhering acid. This process was repeated at least five times. After final washing, the material was dried at room temperature. This material was used for all studies. The Na<sup>+</sup> i.e.c. of the material was determined by the column method[35].

### 2. Calcination studies

The effect of heating on i.e.c. was studied by heating 1 g portion of the material 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> i.e.c. by the column method[35] at room temperature.

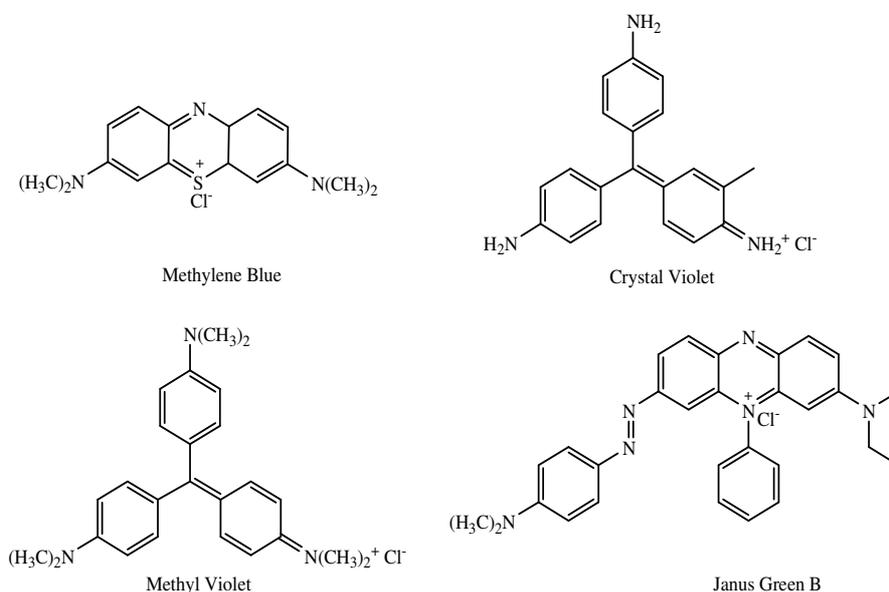


Figure 1 : Structures of dyes

### 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 h. The change in weight and color of the samples were observed.

### 4. Instrumentation

ZrHEDP has been analyzed for Zirconium and Phosphorus by ICP-AES. Carbon and Hydrogen have been determined using Coleman CHN analyzer (model 33). Thermal analysis (TGA) was carried out on a Shimadzu thermal analyzer (model DT-30) at a heating rate of 10°C / min. DSC was performed on Mettler (model TA 4000) system at a heating rate of 20°C / min. FTIR spectra was obtained using KBr wafer on BOMEM MB series with Epon Hi 80 printer / plotter. X-ray diffractogram was obtained on an X-ray diffractometer (model BRUCKER AXS D8) using Cu-K $\alpha$  radiation with a nickel filter. A temperature controlled shaker bath having a temperature variation of  $\pm 0.5$  °C was used for the equilibrium studies. A visible spectrophotometer was used for measuring absorbance.

### 5. Sorption studies

#### 5.1. Effect of pH

Sorption of various dyes MB, CV, MV and JGB on ZrHEDP was carried out in the pH range 1-9. To 100 mg of ZrHEDP, 10 ml of 100 ppm dye solution was added and pH adjusted in acidic range using dilute HNO<sub>3</sub> and in alkaline range using dilute NaOH and the mixture shaken for 30 minutes. Dye concentration was determined spectrophotometrically using a calibration curve for each dye.

#### 5.2. Sorption Kinetics and Thermodynamics

ZrHEDP particles of definite mesh size [30-60 mesh (ASTM)] was used to evaluate various kinetic and thermodynamic parameters. 10 ml of 100 ppm dye solution, 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 (5, 10, 15, -----50 min). pH of the solution was adjusted to the value at which maximum sorption of respective dye takes place.

#### 5.3. Adsorption isotherm studies

For adsorption isotherm studies, 10 ml dye solutions of different concentration with increments of 10 ppm [10, 20 ----- 50 ppm] were equilibrated for specific period of time (equilibrium point) with 100 mg of ZrHEDP in stoppered conical flasks at desired temperatures [313 K, 323 K and 333 K]. At

equilibrium point, the supernatant liquid was removed immediately and the dye concentration evaluated by measuring the absorbance.

#### 5.4. Breakthrough capacity

The breakthrough capacity depends on, flow rate of feed solution through the column, bed depth, selectivity coefficient, particle size and temperature. Breakthrough capacity was studied by passing 5 ml of feed solution (100 ppm in case of CV, MV and JGB, and 500 ppm in case of MB) through the resin, maintaining a flow rate of 0.1 ml/min. The process was continued until the amount of dyes was the same in feed and effluent. Breakthrough capacity was calculated using the ratio Ce/Co, where Ce is the concentration of the dye in the effluent and Co is the concentration of dye in the feed[36].

#### 5.5. Elution Behavior of adsorbed dyes

The resin loaded with 10 ml of 100 ppm of each dye MB, CV, MV and JGB, was eluted with acids like HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> each of 0.01 M concentration, 0.01M KCl and methanol. The amount of dye recovered was calculated as (Ce/Co) x 100 where Ce is the concentration of the dye in the eluted solution and Co is the initial concentration = 100 ppm. The amount of dye adsorbed or eluted was determined spectrophotometrically.

#### 5.6. Case study

In order to explore the utilization of ZrHEDP in treatment of dye-containing waste water, a synthetic effluent containing MB, having similar composition as textile waste water was prepared. 50 ml of synthetic effluent was shaken with 500 mg of ZrHEDP in stoppered conical flasks at constant temperature (30°C) at different time intervals with increments of 15 (15, 30 -----75 min). The supernatant liquid was removed immediately and the Chemical oxygen demand (COD) measured each time to determine the extent of dye removal.

## Results and Discussion

### 1. Characterization

ZrHEDP was obtained as transparent granules. Elemental analysis by ICP-AES shows zirconium to phosphorus ratio of 1:2. The carbon and hydrogen contents were found to be % C = 7.01, % H = 3.21 in ZrHEDP. FTIR spectra of Zr-HEDP shows broad band in the 3400 cm<sup>-1</sup> region, 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 the presence of structural hydroxyl protons in ZrHEDP responsible for cation exchange, which is further evident from the Na<sup>+</sup> i.e.c. value that has been 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  $\text{cm}^{-1}$  are attributed to symmetric and asymmetric C-CH<sub>3</sub> bending[37]. The Na<sup>+</sup> i.e.c., determined by column method[35] is found to be 3.18 meq g<sup>-1</sup>. The effect of calcination on i.e.c. was studied in the temperature range 100 to 500 °C at an interval of 100 °C and found to be 3.20, 3.00, 3.22, 1.96 and 1.55 meq / g respectively. The initial slight increase in the i.e.c. value at 100 °C could be attributed to loss of moisture adhered to it, thereby increasing the active exchanger content for the same weight of material taken for i.e.c. determination. However, at 300 °C an increase in i.e.c. 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 i.e.c. beyond 300 °C is attributed to the complete decomposition of organic moiety / active carbon in the form of CO<sub>2</sub>.

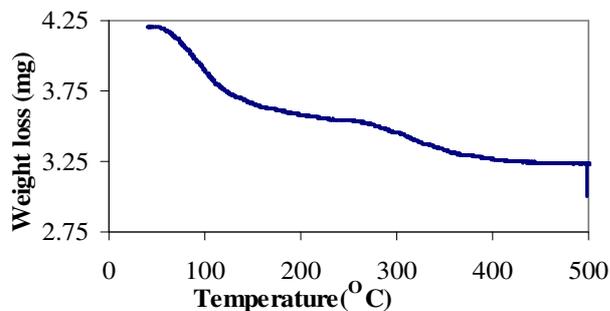


Figure 2 : TGA curve of ZrHEDP

TGA of Zr-HEDP (Figure 2) exhibits a sharp change within the temperature range 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 be due to the condensation of structural hydroxyl groups as well as decomposition and dissociation of the organic moieties.

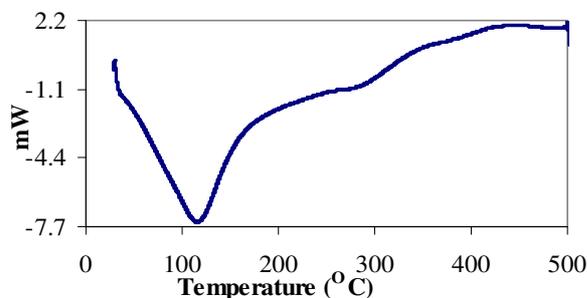


Figure 3 : DSC of ZrHEDP

DSC of ZrHEDP (Figure 3) exhibits endothermic peak at 120 °C, which is attributed to loss of moisture/hydrated water. However, an exothermic process starts at 300 °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.

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[38]. Absence of characteristic peak in X-ray diffractogram of ZrHEDP indicates that the material is amorphous in nature.

ZrHEDP is stable in acid medium, maximum tolerable limits being (18 M H<sub>2</sub>SO<sub>4</sub>, 16 M HNO<sub>3</sub>, 11.3 M 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 M NaOH and 0.1 M KOH).

## 2. Sorption studies

### 2.1. Effect of pH on sorption

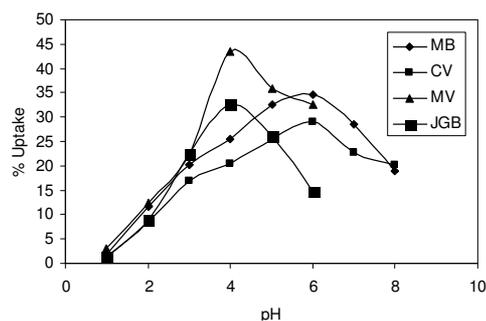


Figure 4 : Effect of pH on sorption

As observed from figure 4, maximum sorption of MB and CV takes place at pH 6 while for MV and JGB at pH 4. At pH values of less than ~3, very little sorption has been observed for all dyes. This lack of sorption at low pH could be attributed to the hydrogen ions competing with the cationic dyes for sorption sites.

### 2.2. Effect of contact time and reaction temperature on the sorption

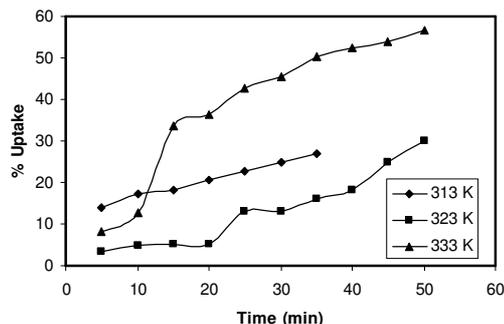


Figure 5 : Percentage Uptake of MB towards ZrHEDP at pH 6

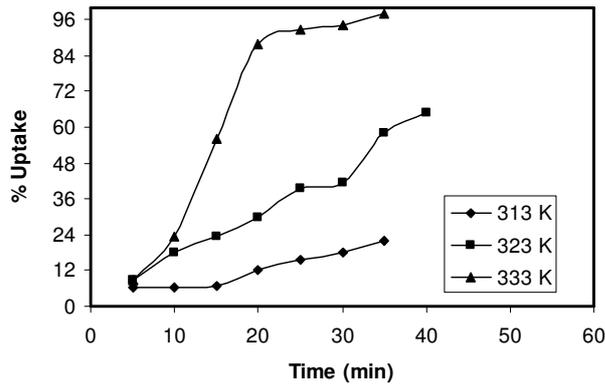


Figure 6 : Percentage Uptake of CV towards ZrHEDP at pH 6

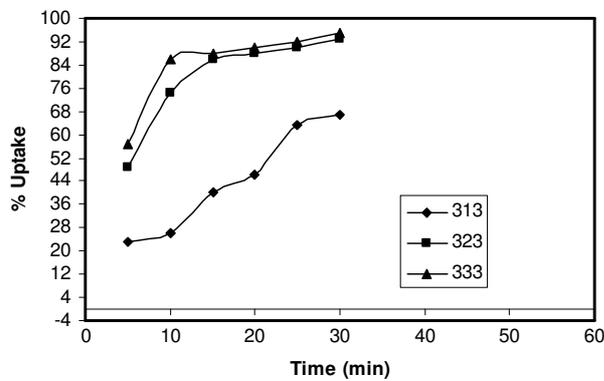


Figure 7 : Percentage Uptake of MV towards ZrHEDP at pH 4

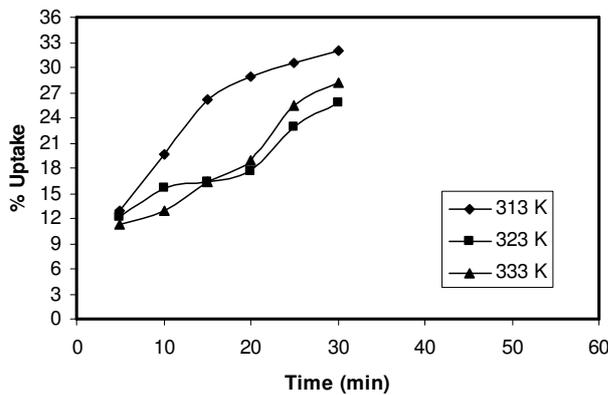


Figure 8 : Percentage Uptake of JGB towards ZrHEDP at pH 4

The effect of contact time and reaction temperature towards sorption of dyes onto ZrHEDP has been presented in Figures 5-8. It is observed that sorption increases gradually with increase in contact time and reaches a maximum. Increase in % uptake could be attributed to two different sorption processes, namely, a fast ion exchange followed by chemisorption[39]. For CV and MV it is observed that uptake of dyes increases with increase in temperature. Probably sorption is facilitated by cationic nature of dyes as well as

cation exchange characteristic of ZrHEDP. In case of JGB uptake decreases with increase in temperature which indicates physisorption. Percentage uptake has been calculated using formula,  $[(Co - Ce) / Co] \times 100$ ; where  $Co$  = initial concentration of dye in mg / L and  $Ce$  = final concentration of dye in mg / L

2.3. Adsorption Isotherms

Generally both Langmuir and Freundlich isotherms are used for explaining the adsorption of dyes on materials. In the present study none of the processes conformed to Freundlich isotherm.

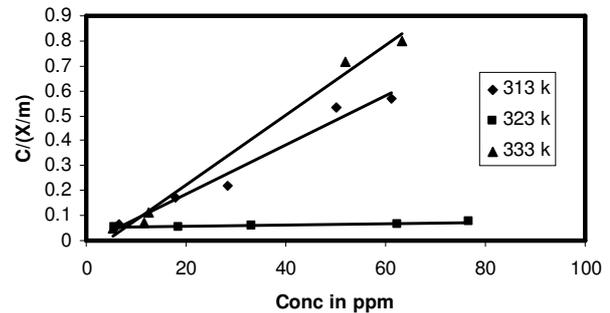


Figure 9 (a) : Langmuir adsorption isotherm of MB towards ZrHEDP

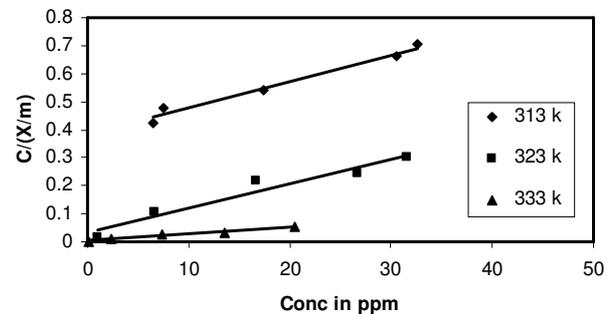


Figure 9 (b) : Langmuir adsorption isotherm of CV towards ZrHEDP

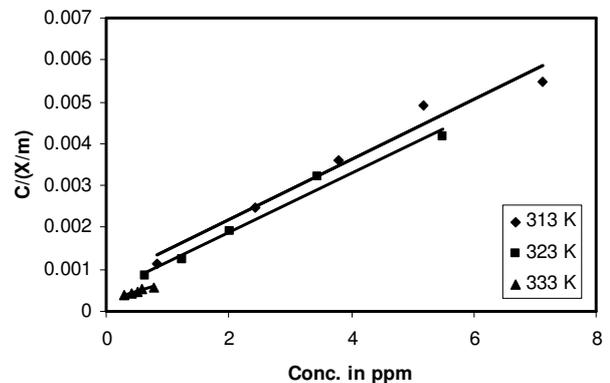


Figure 9 (c) : Langmuir adsorption isotherm of MV towards ZrHEDP

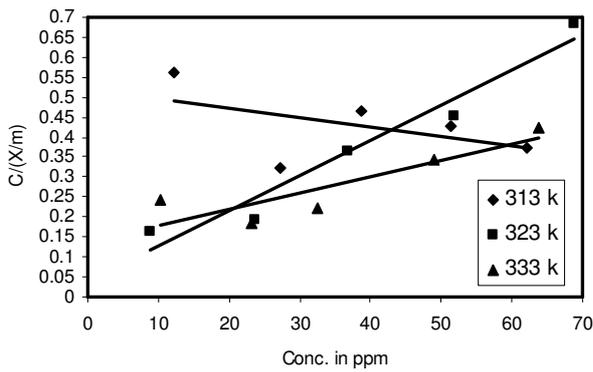


Figure 9 (d) : Langmuir adsorption isotherm of JGB towards ZrHEDP

Langmuir adsorption isotherm is represented by,

$$C_e / (X/m) = 1 / (bV_m) + C_e / V_m \text{----- (1)}$$

where X is the amount of adsorbate, m is the amount of adsorbent, C<sub>e</sub> is the equilibrium concentration of the adsorbate in the solution, b is a constant that represents adsorption bond energy and V<sub>m</sub> 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 plot of C<sub>e</sub> / (X/m) versus C<sub>e</sub> is a straight line [Figure 9 (a)- 9 (d)]. Further from the above plot b and V<sub>m</sub> are calculated from the slope and intercept.

Based on R<sup>2</sup> values (Table 1) it is observed that adsorption process follows the Langmuir pattern for MB, CV and MV whereas in case of JGB, it neither follows Freundlich nor Langmuir pattern. Variation in R<sup>2</sup> (Langmuir) 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[40].

2.4. Kinetic studies

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[41].

The first order kinetic equation is,

$$\ln [1-U(t)] = -k't \text{----- (2)}$$

where k' is the overall rate constant and U ( t ) is fractional attainment of equilibrium. Further,

$$k' = k_1 (1+1/k_c) = k_1 + k_2 \text{----- (3)}$$

where k<sub>c</sub> is the equilibrium constant and k<sub>1</sub> and k<sub>2</sub> are the first order forward and reverse rate constants, respectively.

$$U(t) = (C_0 - C_t) / (C_0 - C_e) \text{----- (4)}$$

C<sub>0</sub> , C<sub>t</sub> and C<sub>e</sub> (all in mole/L) are concentrations of dyes in solution initially, at time t and at equilibrium respectively. Kinetic plots for sorption behaviour of the dyes under study, MB, CV, MV and JGB towards ZrHEDP have been presented in figures 10 (a), (b), (c) and (d) respectively.

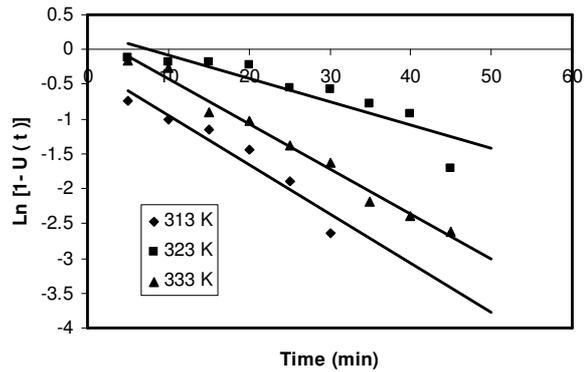


Figure 10 (a) : Kinetic plot for MB towards ZrHEDP

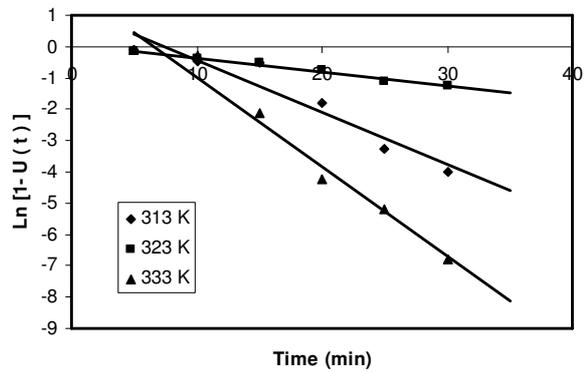


Figure 10 (b) : Kinetic plot for CV towards ZrHEDP

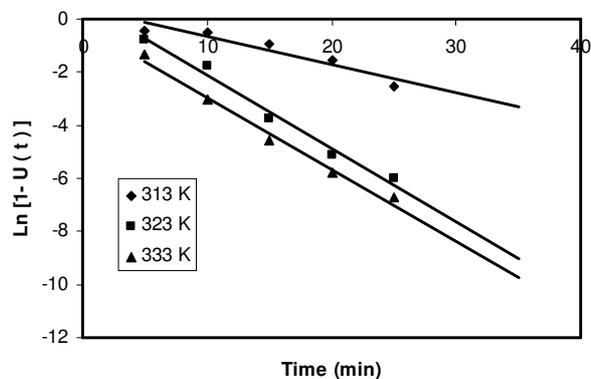
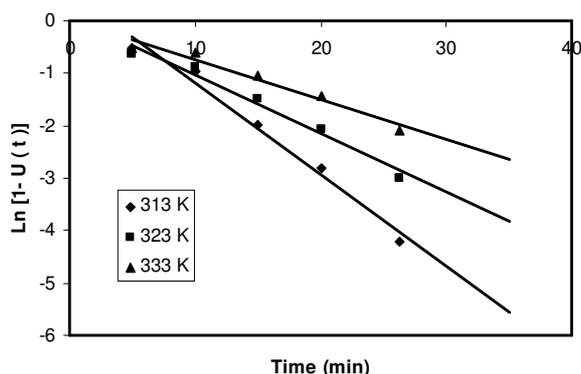


Figure 10 (c) : Kinetic plot for MV towards ZrHEDP



**Figure 10 (d)** : Kinetic plot for JGB towards ZrHEDP

For all dyes,  $k_c$ , equilibrium constant (Table 1) increases as temperature increases indicating the phenomenon to be chemisorption towards ZrHEDP. In case of JGB randomness is observed probably due to steric hindrance as indicated earlier in text.

#### 2.5. Thermodynamic Parameters

In order to explain the effect of temperature on sorption, thermodynamic parameters, standard free energy  $\Delta G_o$ , standard enthalpy  $\Delta H_o$  and standard entropy  $\Delta S_o$  were determined using the following equations:

$$\Delta G_o = -RT \ln k_c \text{ -----( 5 )}$$

$$\Delta H_o = R [T_1.T_2/T_1-T_2 ] \ln (k_2/k_1) \text{ ---( 6 )}$$

$$\Delta S_o = (\Delta H_o - \Delta G_o)/T \text{ -----( 7 )}$$

where  $R$  is the gas constant,  $k_c$ ,  $k_1$  and  $k_2$  are equilibrium constants at the temperature  $T$ ,  $T_1$  and  $T_2$ , respectively. Numerical values of the equilibrium constants were calculated from

$$k = C_{Be} / C_{Ae} \text{ -----( 8 )}$$

where  $C_{Be}$  and  $C_{Ae}$  are the equilibrium concentrations of dyes on the sorbent and in solution, respectively[41].

Thermodynamic parameters for the sorption of MB, CV, MV and JGB on ZrHEDP are presented in Table 1. It is observed that  $\Delta G_o$  values in most cases are negative, except in case of JGB indicating that the systems reach a more stable energy level after sorption. Positive value of  $\Delta H_o$  indicates an endothermic process. Probably some energy must be supplied for the dye sorption to occur[42]. A decrease in  $\Delta S_o$  values, indicates higher uptake of the dyes, which is a result of high  $S_o$  in the external aqueous phase and a lower  $S_o$  in sorbent phase[43].

Breakthrough capacity for the sorption of the dyes, MB, CV, MV and JGB on ZrHEDP are presented in Table 2. It is observed that breakthrough capacity follows the order MB > CV  $\approx$  MV > JGB which could be attributed to the cationic nature of dyes. It seems that even small changes in the dye structure may significantly influence the adsorption capacity. The very high value observed in case of MB could be due to positive charge at the hetero atom. Though there is a positive charge in case of CV, MV and JGB breakthrough capacity is less which may be attributed to phenyl rings causing steric effects.

% Elution of dyes sorbed onto ZrHEDP (Table 3) ranges between 97 – 99 % indicating acids, electrolyte and alcohol to be good eluting agents. Due to structural hydroxyl groups present in ZrHEDP the dyes are probably bound by hydrogen bonds / weak Van der Waals forces making sorption and desorption easy and possible. In the present study maximum sorption capacity of MB towards ZrHEDP is 74.01 mg g<sup>-1</sup>. Similar studies carried out on activated carbon made from Gauva Seeds towards sorption of MB is 0.667 mg g<sup>-1</sup> [44]. Though activated carbon obtained from Gauva Seeds is a low cost material, ZrHEDP is more effective towards removal of dyes, probably due to its cation exchange property. A case study using a synthetic effluent containing MB shows that % COD reduction at different time intervals was 65.82 (15 min), 72.32 (30 min), 84.65 (45 min), 86.62 (60 min) and 87.72 (75 min) indicating good efficiency of ZrHEDP towards removal of MB from textile waste water.

#### Conclusion

The novel metal phosphonate, ZrHEDP, possesses good chemical resistivity and thermal stability, which are characteristics of a good sorbent. The kinetics and thermodynamics of sorption as well as adsorption isotherms for dyes studied, reveal good sorption behaviour. Breakthrough capacity indicates good affinity of dyes towards ZrHEDP, found to be in the order MB > CV  $\approx$  MV > JGB. 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.

#### References:

1. Voudrias, E., Fytianos, K. and Bozani, E. (2002) *Global Nest : the Int. J.*, **4(1)**, 75-83.
2. Peper Cooper Ed, "Color in dyehouse effluent" Society of Dyers and Colourist, Courtlands Textiles, Nottingham (1995).
3. Vandevivere, P. C., Bianchi, R. and Verstaete, W. (1998) *J Chem Technol Biotechnol*, **72**, 289.
4. Smith, K. T. and Brent, H. S. (1993) *Am Dyest Rep*, **82**, 18.

**Table 1 :** Regression values, Kinetic and Thermodynamic data for the sorption of MB, CV, MV and JGB on ZrHEDP

Dye	Temperature	k' min <sup>-1</sup>	kc	$\Delta G_0$ kJ/mole	$\Delta H_0$ kJ/mole	$\Delta S_0$ kJ/Kmole	R <sup>2</sup>	
							Langmuir	Fruendlich
MB	313 K	0.038	0.367	2.606	13.04	0.033	0.9728	0.1824
	323 K	0.021	0.429	2.273	100.1	0.302	0.9059	0.2470
	333 K	0.044	1.313	-0.754	-	-	0.9768	0.1439
CV	313 K	0.015	0.200	4.184	1.6 x 10 <sup>2</sup>	0.506	0.9193	0.7843
	323 K	0.042	1.388	-0.881	210.7	0.655	0.7895	0.6542
	333 K	0.226	14.652	-7.432	-	-	0.9646	0.7181
MV	313 K	0.118	2.025	-1.835	123.2	0.399	0.9285	0.5641
	323 K	0.241	8.766	-5.829	3.772	0.029	0.9636	0.3083
	333 K	0.269	9.144	-6.126	-	-	0.9542	0.6931
JGB	313 K	0.170	0.467	1.981	-24.58	-0.084	0.2585	0.947
	323 K	0.130	0.349	2.829	-1.971	-0.015	0.9545	0.5777
	333 K	0.095	0.341	2.987	-	-	0.7650	0.7932

**Table 2 :** Breakthrough capacity of MB, CV, MV and JGB

Methylene Blue		Crystal Violet		Methyl Violet		Janus Green B	
Co = 500 ppm		Co = 100 ppm		Co = 100 ppm		Co = 100 ppm	
Through put (ml)	Ce/Co						
5	0.250	5	0.122	5	0.152	5	0.458
10	0.598	10	0.152	10	0.284	10	0.689
15	0.988	15	0.298	15	0.325	15	0.889
		20	0.346	20	0.456	20	0.984
		25	0.650	25	0.789		
		30	0.989	30	0.969		

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

Eluting Agent	MB		CV		MV		JGB	
	Ev	%E	Ev	%E	Ev	%E	Ev	%E
0.01M HNO <sub>3</sub>	90	99.30	70	98.92	100	99.92	70	99.25
0.01M HCl	110	99.10	80	99.90	120	99.70	70	99.45
0.01M H <sub>2</sub> SO <sub>4</sub>	110	98.10	110	98.80	120	99.80	70	99.50
0.01M KCl	150	99.0	110	98.35	130	99.35	80	99.15
Methanol	150	97.0	150	98.25	150	97.25	70	99.86

Ev = ml of eluting agent

%E = Percentage elution

- Albanis, T. A., Hela, D. G., Sakellarides, T. M. and Danis, T. G. (2000) *Global Nest : the Int. J.*, **2**, 237.
- Annadurai, G., Juang, R. S. and Lee, D. J. (2002) *Journal of Hazardous Materials*, **92**, 263.
- Suteu, D., Bilba, D. and Zaharia, C. (2002) *Hung J Chem.*, **30**, 7.
- Arslan – Alaton Ik, Kornmuller, A. and Jekel, M. R. (2002) *Color Technol.*, **118**, 185.
- Masan Mahbabal Md and Hawkyard, C. J. (2003) *Color Technol*, **118**, 104.
- Namboodri, C.G. and Perkins, W. K. (1994) *Am Dyest Rep.*, **83**, 17.
- Wafra, M., Abd EI-Rahim and Moawad, H. (2003) *J Basic Microbiology*, **43(5)**, 367.

12. Padmawathy, S., Sandhya, S. and Swaminathan, K. (2003) *Chem Biochem Eng Q*, **17(2)**, 147.
13. Safarik, I., Safarikova, M. and Buricova, V. (1995) *Collect Czech Chem Commu.*, **60**, 1448.
14. Hwang, M. C. and Chen, K. M. (1993) *J Appl Polym Sci*, **49**, 975.
15. Rachuvanshi, S. P., Singh, R. and Kaushik, C. P. (2004) *Applied Ecology and Environmental Research*, **2(2)**, 35.
16. Hwang, M. C. & Chen K M, (1993) *J Appl Polym Sci*, **50**, 735.
17. Kannan, N. and Sundaram, M. (2001) *Dyes and Pigments*, **51**, 25.
18. Filipkowska, O., Klimink, E., Grabowski, S., and Siedlecka, E. (2002) *Polish Journal Of Environ Studies*, **11**, 315.
19. Longhinotti, E., Pozza, F., Furlan, L., Klug, M., Laranjeira, C. M. and Favere, V. F. (1998) *J Braz Chem Soc*, **9**, 435.
20. Gorduza, V. M., Suteu, D. and Vizitiu, M. (1999) *Journal of Balkan Ecology*, **2**, 100.
21. Gorduza, V. M., Suteu, D. and Vizitiu, M. (2000) *Ovidius University Annals of chemistry (Constantza – Romania)*, **12 (1)**, 120.
22. Suteu, D. and Bilba, D. (2005) *Acta Chim Slov*, **52**, 73.
23. Clearfield, A. (1998) “*Progress in Inorganic Chemistry*” John Wiley and Sons., New York, Vol. 47, **371**.
24. Alberti, G., Costantino, U., Alluli, S. and Tomassini, N. (1978) *Inorg. Chem.*, **40**, 1113.
25. Clearfield, A., Stein, E. and Subramanian, M. A. (1996) *Solid State Ionics.*, **77**, 229.
26. Clearfield, A., Zhang, B., Poojary, D. M. and Peng, G. Z. (1996) *Chem. Mater.*, **8**, 1333.
27. Deniaud, D., Schollom, B., Mansuy, D., Rouxel, J., Battioni, P. and Bujoli, B. (1995) *Chem. Mater.*, **7**, 995.
28. Clearfield, A., Cheng, S. and Peng, G. Z. (1984) *Ind. Eng. Chem. Prod. Res. Dev.*, **232**.
29. Clearfield, A., Wang, J. D. and Peng, G. Z., (1993) *Mater. Chem. Phys.*, **35**, 208.
30. Clearfield, A., Stein, E. and Subramanian, M. A., (1996) *Solid State Ionics*, **83**, 113.
31. Alberti, G. and Costantino, U. (1996) “*Comprehensive Supramolecular Chemistry*”, (Eds), Lehn, J. M., Pergamon – Elsevier Science Ltd., London, **1**.
32. Vermeulen, L. A. and Thompson, M. E., (1992) *Nature*, **358**.
33. Clearfield, A. (1996) *Curr. Opin. Solid State Mater.Sci.*, **1**, 268.
34. Nowack, B. (2003) *Water Research*, **31 (11)**, 2533.
35. Samuelson, O. (1953) “*Ion exchangers in Analytical Chemistry*” John Wiley & sons, Inc., New York, **45** and 117.
36. Benefield, L. D., Judkins, J. F. and Weand, B. L. (1982) “*Process Chemistry for Water and Wastewater Treatment*” Prentice-Hall Inc, Englewood cliffs N.J.
37. Silverstein, R. M., Bassler, G. C. and Morill, T. C. (1991) “*Spectrometric identification of organic compounds*” John Wiley ad Sons, New York, 5th edition, **3**.
38. Alberti, G. and Torracca, E. (1968) *J.Inorg.Nucl.Chem.*, **30**, 3075.
39. Low, K. S. (1993) *Bioresource Technology*, **44**, 109.
40. Horsfall, M. Jnr, Spiff, A. I. (2005) *Electronic J. Biotechnology*, Vol. 8, No.2, **162**.
41. Bereket, G. and Ozel, M.Z. (1997) *Journal of colloid and interface science*, **187**, 338.
42. Tagami, L. Onella Aparecida Andreo dos Santos (2001) *Acta Scientiarum, Maringa*, Vol 23, No. 6, **1351**.
43. Qureshi, M. and Rawat, J.P. (1981) *J. Indian Chem. Soc.*, Vol LVIII, **855**.
44. Rahman, I. A. and Saad, B. (2003) *Malaysian Journal of Chemistry*, **5(1)**, 008.