

Sorption of Anti-Infective Organic Molecules from Aqueous Solutions onto Zirconium Phosphate

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Amorphous zirconium phosphate (ZP), an inorganic ion exchange material of tetravalent metal acid (tma) salt, is synthesized by the sol-gel method and characterized by elemental analysis (ICP-AES), thermal analysis (TGA, DSC), FT-IR and X-ray diffraction studies. The resistivity of the material to acids, bases and organic solvents is assessed. The sorption behavior of the dyes acriflavin (AF) and brilliant green (BG) toward ZP was studied at 313, 323 and 333 K and the kinetic and thermodynamic parameters evaluated. Adsorption isotherms [Langmuir and Freundlich], breakthrough capacity and elution behavior of these dyes are also studied. The sorption affinity of dyes towards ZP is BG > AF.

Keywords: Zr(IV) phosphate, Inorganic ion exchanger, Tetravalent metal acid salt, Dye sorption, Sorption of anti-infective dyes

INTRODUCTION

Pharmaceuticals and personal care product (PPCP) ingredients constitute a diverse group of chemicals, which comprise all drugs, diagnostic agents, nutraceuticals, fragrances and sun-screen agents, among others, that are detected in wastewater as persistent organic compounds at levels ranging from ng kg^{-1} to g kg^{-1} 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 [1,2].

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 is an economical, simple and easy method used to remove dissolved organic contaminants [3]. A large number of suitable sorbents, such as

activated carbon [4,5], polymeric resins [6] and various low-cost adsorbents [7,8], have been used. Ion exchange is also a highly effective method for eliminating dissolved organic contaminants, as in the adsorption of streptomycin, as well as to remove and recover antibiotics from pharmaceutical wastewater [9]. There are a few publications where ion exchange materials have been used as sorbents for the removal of dyes [10-13].

It has been observed that biological treatment processes are ineffective in the treatment of wastewaters containing antibiotics and other pharmaceuticals, *e.g.* sulfonamides, as they are not readily biodegradable using the activated sludge process [14]. 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 biological oxygen demand (BOD), chemical oxygen demand (COD) and total dissolved solids (TDS) in pharmaceutical wastewater [15].

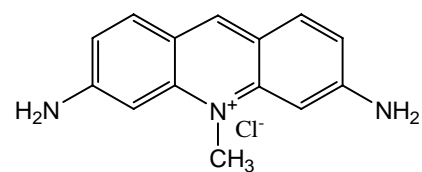
Tetravalent metal acid (tma) salts have emerged as

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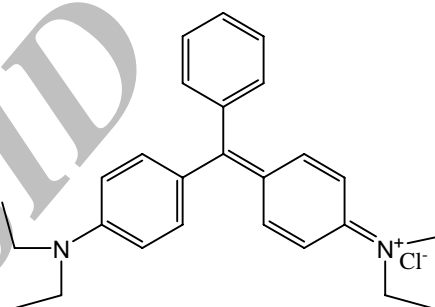
promising advanced materials, as they possess robust properties, including good ion exchange characteristics, thermal stability and chemical resistivity. Tma salts have the general formula, $M(IV)(HXO_4)_2 \cdot nH_2O$, where $M(IV) = Zr, Ti, Ce, Th$ and Sn , among others, and $X = P, Mo, W, As, Sb$ and so forth. The protons contained in the structural hydroxyl groups of these materials can be exchanged for several cations; thus, they behave as cation exchangers. Phosphate tma salts with varying water contents, compositions and crystallinities can be obtained depending on various factors *viz.* the mole ratio of reactants, $M:X$ (M = tetravalent metal and X = polyvalent anion, as above), mode of mixing (metal salt solution to anion salt solution or vice versa), pH, temperature and rate of mixing. Variation in any of these parameters yields materials with different characteristics. The preparation procedure thus affects the structural hydroxyl groups, which is reflected in the variation of ion exchange capacity (IEC), and, hence, its performance as an ion exchanger. Consequently, the study of tma salts is evergreen: newer materials with good IECs are continuously being synthesized/investigated and cation exchange properties explored [16]. Though the cation exchange characteristics of tma salts are well established, not much work has been done on the adsorption characteristics of these materials. Our laboratory has recently reported the sorption of water-soluble dyes using metal phosphonates [17,18].

Dyes in general contain one or more of the following functional groups in their structure: $-OH$, $-COOH$, $-SO_3H$, NO_2 , and $N=N$, among others. The adsorption of the above functional groups with the matrix material/sorbent used in this study could involve covalent, coulombic, hydrogen bonding or weak van der Waals forces. The strength and type of interaction between the dye and sorbent are important factors in determining the elutability of the dye.

In the present endeavor, the tma salt amorphous zirconium phosphate (ZP) is synthesized by the sol-gel method. The material is characterized for elemental analysis, thermal analysis, Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction studies. The chemical resistivity of the material in various media, including acids, bases and organic solvents, is assessed. Due to the presence of structural hydroxyl groups in ZP, it is expected that the dyes could either be bound to the matrix material (ZP) by hydrogen bonds or



Acriflavin



Brilliant green

Fig. 1. Structures of the dyes.

weak van der Waals forces, making sorption and desorption easy and possible. Therefore, we considered that ZP might be a useful sorbent for the treatment of wastewater containing pharmaceutical products.

Acriflavin (AF) and brilliant green (BG) are medicinal dyes that impart color as well as anti-infective properties and are widely used in sun-screen lotions and creams. Since they are water soluble, they are introduced to wastewater as pollutants. In this study, the sorption behavior of the anti-infective molecules AF and BG (Fig. 1) toward ZP are studied at 313, 323 and 333 K and kinetic and thermodynamic parameters evaluated. Adsorption isotherms (Langmuir and Freundlich), the breakthrough capacity and elution behavior of dyes are also studied and discussed.

EXPERIMENTAL

All chemicals and reagents used were of analytical grade.

Synthesis of Zirconium Phosphate [ZP]

ZP was prepared by mixing aqueous solutions of $ZrOCl_2 \cdot 8H_2O$ (0.1 M, 250 ml) and sodium dihydrogen phosphate (0.2 M, 250 ml), dropwise with constant stirring,

maintaining the temperature of the solution at 70 °C. The obtained gelatinous precipitate was digested for one hour at 70 °C, filtered, washed with conductivity water until the chloride ions were removed, and dried at room temperature. The material was then broken down to the desired particle size (30-60 mesh ASTM) by grinding and sieving. To convert this material to the acid form, approximately 5 g was treated with 50 ml of 1 M HNO₃ for 30 min with occasional shaking. The acidic supernatant was decanted and treated with conductivity water to remove adherent acid. This process (acid treatment) was repeated at least five times. After the final wash, the material was dried at room temperature. The Na⁺ ion exchange capacity (IEC) of the final material was determined by the column method [19]. This material (ZP) was used for all studies.

The effect of heating on the IEC was studied by heating ZP (1 g) for 2 h from 100 °C to 500 °C at 100 °C intervals in a muffle furnace, then determining the Na⁺ IEC by the column method at room temperature [19]. The chemical resistivity of the material in various media, including acids (H₂SO₄, HNO₃, 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 color, texture and weight was observed.

Instrumentation

ZP was analyzed for zirconium and phosphorus by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Thermogravimetric analysis (TGA) was carried out on a Shimadzu DT-30 thermal analyzer at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) of the sample was performed on a Mettler TA 4000 system at a heating rate of 20 °C min⁻¹. FTIR spectra were obtained using KBr wafer on a BOMEM MB-series spectrometer with an Epson Hi 80 printer/plotter. X-ray diffractograms were obtained on a BRUCKER AXS D8 X-ray diffractometer using Cu-K_α radiation with a nickel filter. A temperature-controlled shaker bath with a temperature variation of ±0.5 °C was used for the equilibrium studies. Determination of the percent dye sorption/desorption was carried out using a visible spectrophotometer (450 and 625 nm for AF and BG, respectively).

Sorption Studies

Effect of pH. ZP (100 mg) was placed in a stoppered conical flask, to which was added 10 ml of 50 ppm AF or BG. The pH was adjusted and the mixture shaken for 30 min at 30 °C. The supernatant was removed immediately and the dye concentration was determined spectrophotometrically using a calibration curve for that specific dye.

Sorption kinetics and thermodynamics. ZP particles (30-60 mesh ASTM) were used to evaluate various kinetic and thermodynamic parameters. The dye solution (10 ml, 100 ppm) under study, was shaken with 100 mg of ZP in stoppered conical flasks at the desired temperatures (313, 323 and 333 K) and determined at time intervals of 5 min for 50 min. The pH of the solution was adjusted to the value at which maximum sorption of the respective dye takes place. The results obtained from this study were utilized to evaluate the kinetic parameters (U(t), k', k₁, k₂ and k_c) and thermodynamic parameters (ΔG°, ΔH° and ΔS°).

Adsorption isotherm studies. ZP (30-60 mesh ASTM, 100 mg) was shaken with 10 ml of the studied dye solution that varied in concentration, at increments of 10 ppm, up to 50 ppm. The mixtures were equilibrated in stoppered conical flasks at each temperature until they were equilibrated. Each solution was adjusted to the pH at which maximum sorption of the respective dye takes place. The supernatant was removed immediately after the requisite time and the dye concentration evaluated spectrophotometrically.

Breakthrough capacity. Feed solution (5 ml) containing 100 ppm of AF and BG was allowed to pass through the column containing 1 g of ZP, maintaining a flow rate of 0.1 ml min⁻¹. The process was continued until the amount of dye was the same in the feed and the effluent. The breakthrough capacity was calculated using the ratio C_e/C_o, where C_e is the concentration of the dye in the effluent and C_o is the concentration of dye in the feed [20].

Elution Behavior of Adsorbed Dyes

Each of the studied dye solutions (5 ml, 100 ppm) was allowed to pass through a column containing 1 g of ZP, maintaining a flow rate of 0.1 ml min⁻¹. It was then eluted separately with HCl, HNO₃, H₂SO₄ and KCl (0.01 M). The percent of dye recovered was calculated using the formula (C_e/C_o) × 100, where C_e = concentration of dye in eluted

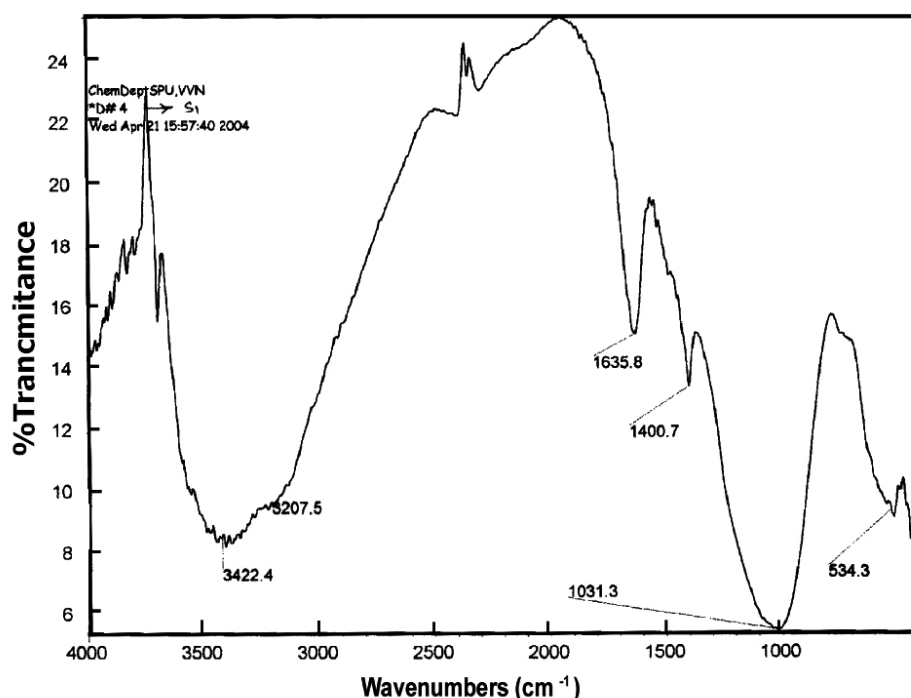


Fig. 2. FTIR spectrum of ZP.

solution and C_0 is initial concentration of dye. The amount of dye adsorbed or eluted was determined spectrophotometrically in all cases.

RESULTS AND DISCUSSION

Characterization

ZP was obtained as white granules. Elemental analysis by ICP-AES shows the zirconium to phosphorous ratio to be 1:2. The FTIR spectrum of ZP (Fig. 2) shows a broad band in the region $\sim 3422\text{ cm}^{-1}$ attributed to symmetric and asymmetric -OH stretching, while a band at $\sim 1635\text{ cm}^{-1}$ is attributed to H-O-H bending. A band in the region $\sim 1031\text{ cm}^{-1}$ is attributed to P=O stretching and a medium intensity band at 1400 cm^{-1} is attributed to the presence of δ (POH) [21]. This indicates the presence of structural hydroxyl groups in ZP, the H of the OH groups being the cation exchange sites. This fact is more evident from the Na^+ IEC value of 2.77 meq g^{-1} , as determined by the column method [19]. The IEC was found to be 2.82, 2.55, 2.39, 1.69 and 1.46 meq g^{-1} , at 100, 200, 300, 400 and 500°C , respectively. The initially high IEC value at 100°C

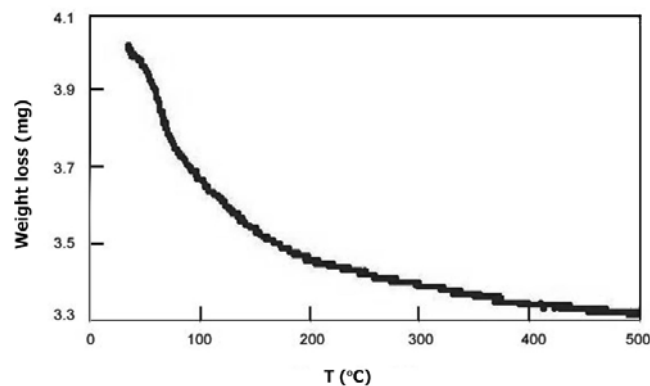


Fig. 3. TGA plot of ZP.

could be attributed to loss of moisture, thereby increasing the active exchanger content for the same weight of material taken for IEC determination. The large decreases in IEC beyond 300°C is attributed to the condensation of structural hydroxyl groups. The TGA of ZP (Fig. 3) shows a 13% weight loss within the temperature range $40\text{--}180^\circ\text{C}$, also attributed to the

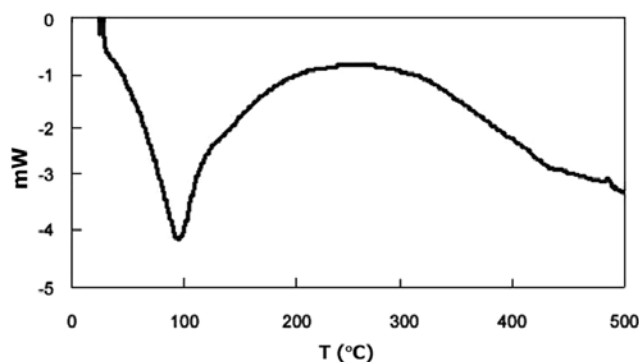


Fig. 4. DSC curve of ZP.

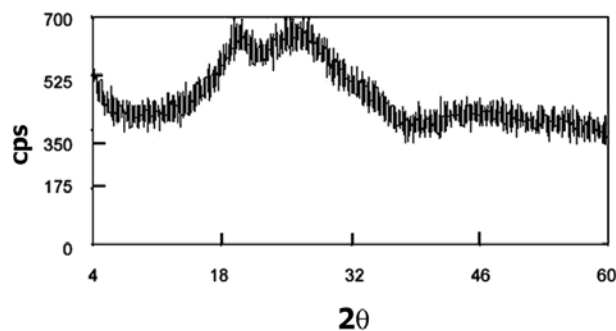


Fig. 5. X-ray profile of ZP.

loss of moisture as well as hydrated water, while a 6% weight loss in the temperature range 200-500 °C is attributed to the condensation of structural hydroxyl groups. The DSC of ZP (Fig. 4) exhibits an endothermic peak at 102 °C, which is attributed to the loss of moisture/hydrated water. Beyond this temperature no peaks are observed indicating no phase change in the material upon thermal treatment.

Based on the elemental analysis (ICP-AES) and thermal analysis (TGA) data, ZP in this study is determined to be $\text{Zr}(\text{HPO}_4)_2 \cdot 2.5\text{H}_2\text{O}$ using the Alberti-Torracca formula [22]. Furthermore, the lack of characteristic peaks in the X-ray diffractogram for ZP (Fig. 5) indicates that the material is amorphous in nature [23].

ZP is stable in acidic media, with maximum tolerable limits as follows: 36 N H_2SO_4 , 16 N HNO_3 , 10 N HCl . ZP is also stable in the organic solvents ethanol, benzene and acetone. It is, however, not as stable in basic media, with maximum tolerable limits of 5 N NaOH and 5 N KOH .

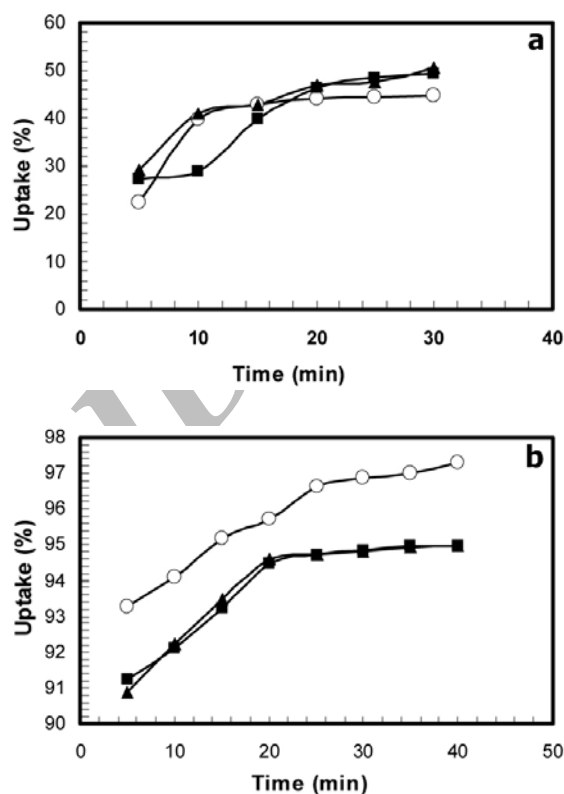


Fig. 6. Uptakes of BG by ZP (a) and AF by ZP (b): (○) 313 K, (■) 323 K and (▲) 333K.

Sorption Studies

The maximum sorption of BG and AF takes place at pH 3 and pH 1, respectively. Beyond these optimal values, changes in the dye color are observed that are attributed to aggregation of the dye molecules [24].

The percent uptake of the dyes by ZP is presented in Fig. 6. Note that sorption increases gradually with an increase in contact time until it reaches a maximum value, after which randomness is observed. Increase in percent uptake of the dyes could be attributed to two different sorption processes, namely, a fast ion exchange followed by chemisorption [25]. Uptake (%) of dyes are calculated using the formula $[(I - F) \times 100]/I$, where I and F are the initial and final concentrations of dye, respectively, in mg l^{-1} .

Generally, both Langmuir and Freundlich isotherms are used to explain the adsorption on materials. Standard equations [26] have been used to find values of various constants of both the isotherms. Based on the R^2 values

presented in Table 1, AF follows the Langmuir pattern, whereas BG follows the Freundlich pattern, as presented in Figs. 7 and 8, respectively. The variation in R^2 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 dye sorption [27].

The sorption of dyes from the liquid phase onto the solid phase can be considered to be a reversible reaction with two phases. Therefore, a simple first-order kinetics model, as presented in Figs. 9a and 9b, is used to establish the rate of reaction. From the data regarding the effect of contact time and reaction temperature on sorption, kinetic parameters have been calculated. The first-order kinetics equation is $\ln [1 - U(t)] = -k't$, where k' is the overall rate constant and $U(t)$ is the fractional attainment of equilibrium. In addition, $k' = k_1 (1 + 1/k_c) = k_1 + k_2$, where k_c is the equilibrium constant and k_1 and k_2 are the first-order forward and reverse rate constants, respectively. For the

equation $U(t) = C_0 - C_t/C_0 - C_e$, C_0 , C_t and C_e (all in M) are the concentration of dye in solution initially, at time t , and at equilibrium, respectively. Numerical values of the equilibrium constants were calculated using the equation $k_c = C_{Be}/C_{Ae}$, where C_{Be} and C_{Ae} are the equilibrium concentrations of the dye on the sorbent and in solution, respectively [26].

In order to explain the effect of temperature on sorption, the thermodynamic parameters of standard free energy ΔG° , standard enthalpy ΔH° , and standard entropy ΔS° were determined using standard equations [26].

In Table 1, note that ΔG° values are negative for BG. This indicates favorable sorption onto ZP as well as feasibility, the spontaneous nature of the sorption process and the attainment of a more stable energy level after sorption of the dye. Positive ΔG° values for AF indicates a lower preference for ZP. However, ΔG° depends on several factors, such as temperature and heat consumed/released upon the uptake of the cationic

Table 1. Langmuir, Freundlich and Thermodynamic Parameters for Sorption of AF and BG

Dye	Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	R^2	
					Langmuir pattern	Freundlich h pattern
AF	313	0.55		0.029	0.9863	0.8740
	323	0.05	9.91	0.031	0.9953	0.7341
	333	-0.06		0.029	0.9990	0.1503
BG	313	-9.31		-0.056	0.0195	0.9879
	323	-7.90	-26.92	-0.059	0.3594	0.9498
	333	-8.13		-0.056	0.6014	0.9835

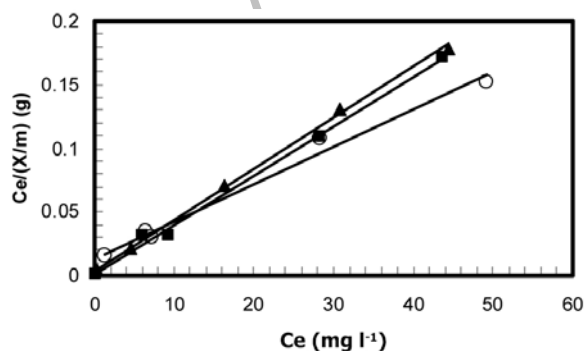


Fig. 7. Langmuir adsorption isotherm of AF uptake by ZP: (○) 313 K, (■) 323 K and (▲) 333K.

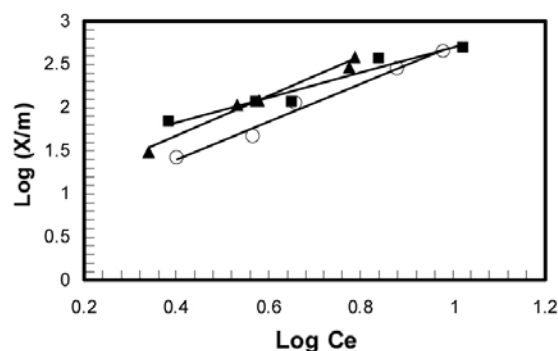


Fig. 8. Freundlich adsorption isotherm of BG towards ZP: (○) 313 K, (■) 323 K and (▲) 333K.

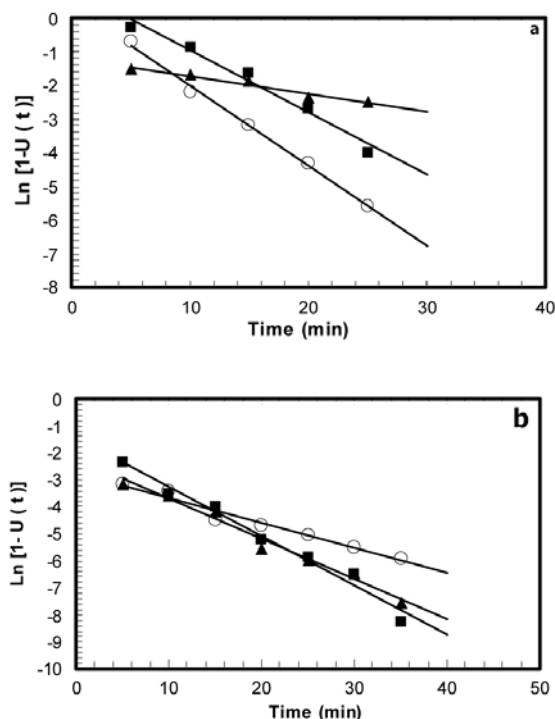


Fig. 9. Kinetic plots for AF uptake by ZP(a) and for BG uptake by ZP (b): (○) 313 K, (■) 323 K and (▲) 333K.

dye. In the present study, the ion exchanger used is amorphous in nature; thus, it is expected that all sorption sites may not be energetically equivalent. The incoming cationic dye would first occupy the most favorable sites, which require little or no energy for sorption. As sorption proceeds, the sites become progressively less favorable. The overall ΔG° value is a result from the contribution of the above-mentioned factors. Depending on the predominant factor, ΔG° values vary in each case [28]. Negative ΔH° values indicate that the sorption of dyes is exothermic in nature. Positive ΔH° values indicate an endothermic process. In this case, probably some energy must be supplied for the dye sorption to occur [29]. The positive entropy for AF indicates an increased disorder of the system, probably due to the loss of water surrounding the dye while adsorbing onto ZP. The decrease in ΔS° values indicates a higher uptake of the dyes, which is a result of the high S° in the external aqueous phase and a lower S° in sorbent phase [30].

The breakthrough capacity of a sorbent depends on the

Table 2. Breakthrough Capacity of ZP^a for AF^b and BG^c

AF (50 ppm)		BG (50 ppm)	
Volume (ml)	C_e/C_o^d	Volume (ml)	C_e/C_o
5	0.135	5	0.125
10	0.395	10	0.182
15	0.989	15	0.568
		20	0.859
		25	0.992

^aZP = zirconium phosphate. ^bAF = acriflavin. ^cBG = brilliant green. ^d C_e/C_o = [dye at effluent]/[dye in the feed].

Table 3. Elution of Dyes Using Various Eluents

Eluting agent	AF		BG	
	E_v	%E	E_v	%E
0.1 M HNO ₃	70	98.7	70	96.9
0.1 M HCl	70	98.5	80	99.1
0.1 M H ₂ SO ₄	80	99.2	90	98.5
0.1 M KCl	80	98.9	120	95.6
Methanol	60	99.9	120	96.9

E_v = ml of eluting agent, %E = Percentage elution.

flow rate of the feed solution through the column, bed depth, selectivity coefficient, particle size and temperature. Several factors contribute to the sorption of dyes on the sorbent material. These include the steric effect, which is in turn dependent on the structure of the dye, the exchange/sorption characteristics, which depend on the charges present on the dye, as well as the physical and chemical forces with which the dye is held onto the sorbent material. Even small changes in the dye structure may significantly influence the adsorption capacity.

In Table 2, notice that the breakthrough capacity follows the order BG > AF, indicating that good sorption is probably due to the cationic nature of dyes, as well as the cation exchange characteristics of ZP.

From Table 3, it is observed that the elution of the AF and BG sorbed onto ZP using acid and electrolytes ranges between 97-100%. In case of AF, the elution of > 99% indicates weak

adsorption, which makes sorption and desorption easy and possible.

CONCLUSIONS

As a sorbent material, ZP 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 behavior. The breakthrough capacity of ZP indicates good affinity toward these dyes, in the order BG > AF. Elution of dyes using various eluants is greater than 95% in all cases. Good sorption as well as elution of the dyes from ZP indicates its promising use in the treatment of wastewater containing dyes.

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