

Sorption of water soluble dyes from aqueous solutions on zirconium phosphate

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Amorphous zirconium phosphate (ZP) an inorganic ion exchange material of the class of tetravalent metal acid (tma) salt 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 has been assessed. The sorption behaviour of dyes methylene blue (MB), crystal violet (CV), methyl violet (MV) and janus green B (JGB) towards ZP has been studied at 313, 323 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 dyes towards ZP is found to be $MB > CV \approx MV > JGB$.

Keywords: Zr (IV) phosphate, Inorganic ion exchanger, Tetravalent metal acid salt, Waste treatment containing dyes

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The disposal of dyes in wastewater has attracted wide attention as wastewaters containing dyes are poisonous, carcinogenic and teratogenic to human beings. Dyestuffs are synthetic organic compounds with complex molecular structures and high molecular weight; these properties augment treatment difficulties of dye wastewater¹⁻³. Various techniques have been employed to remove dyes from wastewaters, that include the membrane filtration⁴, coagulation/flocculation^{5,6}, adsorption^{4,5,7}, ion exchange^{8,9}, oxidation using chlorine and ozone^{10,11}, chemical reduction¹² and biological treatment^{13,14}. Amongst various techniques, adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances and has often been used as a method to remove dissolved contaminated organic compounds¹⁵. A large number of suitable sorbents such as activated carbon^{16,17}, polymeric resins¹⁸, various low cost adsorbents¹⁹⁻²³ (non-modified or modified cellulose biomass, chitin, soil material, activated alumina, bacterial biomass) etc. have been studied.

Dyes in general contain one or more of the following functional groups in their structure (-OH, -COOH, -SO₃H, NO₂, N=N etc.). It is believed that in adsorption the interaction of the above functional groups 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 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 dyes²⁴⁻²⁷.

Tetravalent metal acid (tma) salts have emerged as promising advanced materials, as they possess robust properties—good ion exchange characteristics, thermal stability and chemical resistivity. Tma salts have the general formula, $M(IV)(HXO_4)_2 \cdot nH_2O$, where $M(IV) = Zr, Ti, Ce, Th, Sn$ etc and $X = P, Mo, W, As, Sb$ etc. The protons contained in the structural hydroxyl groups of these materials can be exchanged for several cations and thus they behave as cation exchangers. Though the cation exchange characteristics of tma salts are well established, not much work has been done on the adsorption characteristics of these materials.

In the present endeavour amorphous zirconium phosphate (ZP) of the class of tma salt 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. Due to the presence of structural hydroxyl groups in ZP, it is expected that the dye could either be bound to the matrix material (ZP) 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 ZP as a sorbent for wastewater treatment containing dyes. The sorption behaviour of dyes namely methylene blue (MB), crystal violet (CV), methyl violet (MV) and janus green B (JGB) (Fig. 1) towards ZP has been studied at 313, 323 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.

Experimental Procedure

All chemicals and reagents used were of analytical grade.

Synthesis of zirconium phosphate (ZP)

ZP was prepared by mixing aqueous solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (0.1 M, 250 mL) and sodium dihydrogen phosphate (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 and sieving and converted to the acid form by taking about 5 g of the material and treating it with 50 mL of 1 M HNO_3 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^+ ion exchange capacity (IEC) of the material was determined by the column method²⁸. This material was used for all studies.

Calcination studies

The effect of heating on IEC was studied by heating 1 g of ZP for 2 h at temperatures between 100 to 500°C with 100°C intervals in a muffle furnace and determining the Na^+ ion exchange capacity by the column method²⁸ at room temperature.

Chemical resistivity

The chemical resistivity of the material in various media – acids (H_2SO_4 , HNO_3 , HCl), bases (NaOH and KOH) and organic solvents (ethanol, benzene and acetone) was studied by taking 500 mg of sample in

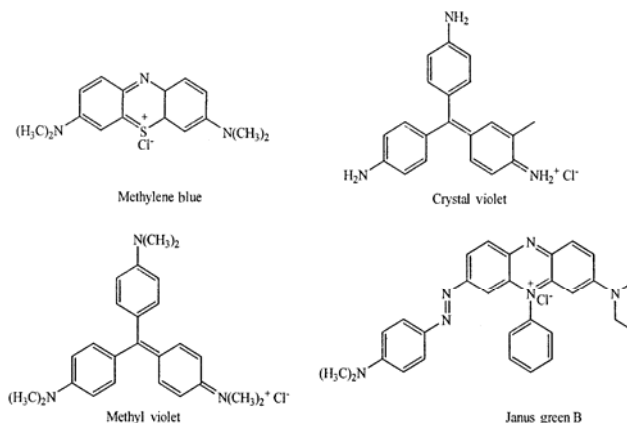


Fig. 1 – Structure of dyes

50 mL of the particular medium and allowing it to stand for 24 h. The change in nature, weight and color was observed.

Instrumentation

ZP 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 $10^\circ\text{C}/\text{min}$. DSC of the sample was performed on Metler TA 4000 system at a heating rate of $20^\circ\text{C}/\text{min}$. FTIR spectra was obtained using KBr wafer on BOMEM MB series with Epson Hi 80 printer/plotter. X-ray diffractogram was obtained on an X-ray diffractometer BRUCKER AXS D8 using $\text{Cu-K}\alpha$ radiation with a nickel filter. A temperature controlled shaker bath having a temperature variation of $\pm 0.5^\circ\text{C}$ was used for the equilibrium studies. % Dye sorption / desorption was determined using visible spectrophotometer.

Sorption studies

Effect of pH

Sorption of various dyes MB, CV, MV and JGB on ZP was carried out in the pH range of 1-9. To 100 mg of ZP, 10 mL of 100 ppm of each dye solution was added and pH adjusted in acidic range using dilute HNO_3 and in alkaline range using dilute NaOH and mixture shaken for 30 min at 30°C in stoppered conical flask. The supernatant liquid was removed immediately and dye concentration was determined spectrophotometrically using calibration curve of the individual dye.

Sorption kinetics and thermodynamics

ZP particles [30-60mesh (ASTM)] was used to evaluate various kinetic and thermodynamic

parameters. 10 mL of 100 ppm dye solution, was shaken with 100 mg of ZP in stoppered conical flasks at the desired temperatures (313, 323 and 333 K) at different time intervals with increments of 5 (5, 10, 15, -----50 min). The pH of the solution was adjusted to the value at which maximum sorption of respective dye takes place. Results obtained from this study are utilized to evaluate kinetic parameters [$U(t)$, k' , k_1 , k_2 and k_c] and thermodynamic parameters [ΔG^0 , ΔH^0 and ΔS^0].

Adsorption isotherm studies

100 mg of ZP [30-60 mesh (ASTM)] was shaken with 10 mL of individual dye solution, varying concentration with increment of 10 ppm (10, 20 ----- 50 ppm) was equilibrated in stoppered conical flasks at desired temperatures (313, 323 and 333K) till attainment of equilibrium (50 min for MB, 40 min for CV, 30 min for MV and 35 min for JGB). The 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.

Break through capacity

A 5 mL aliquot of feed solution containing (100 ppm in case of CV, MV and JGB and 500 ppm in case of MB) was allowed to pass through the column, maintaining a flow rate of 0.1 mL min⁻¹. The process was continued till the amount of dyes was same in feed and effluent. Break through capacity was calculated using the ratio C_e/C_0 , where C_e is the concentration of the dye in the effluent and C_0 is the concentration of dye in the feed²⁹.

Elution behaviour of adsorbed dyes

A 5 mL (100 ppm) aliquot of each dye solution 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 with reagents like HCl, HNO₃, H₂SO₄ and KCl of 0.01 M concentration. The amount of dye recovered was calculated as $(C_e/C_0) \times 100$, where C_e = concentration of dye in eluted solution and C_0 is initial concentration of dye. The amount of dye adsorbed or eluted was determined spectrophotometrically in all cases.

Case study

In order to explore the utility of ZP in wastewater treatment containing dyes, a synthetic effluent

containing MB, having similar composition of textile wastewater was prepared. 50 mL of synthetic effluent was shaken with 500 mg of ZP 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 COD measured each time to measure the extent of dye removal.

Results and Discussion

Characterization

ZP was obtained as white granules. Elemental analysis by ICP-AES shows zirconium to phosphorous ratio to be 1:2. FTIR spectrum of ZP (Fig. 2) shows broad band in the region ~3422 cm⁻¹ attributed to symmetric and asymmetric -OH stretching, while band at ~1635 cm⁻¹ is attributed to H-O-H bending. A band in the region ~1031 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)³⁰. 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 IEC values that has been evaluated. The Na⁺ ion exchange capacity, determined by column method²⁸ is found to be 2.77 meq g⁻¹. The effect of calcination on IEC was studied in the temperature range of 100 to 500°C at an interval of 100°C and found to be 2.82, 2.55, 2.39, 1.69 and 1.46 meq g⁻¹ respectively. The initial increase in the IEC value at 100°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. Further, decrease in IEC beyond 300°C

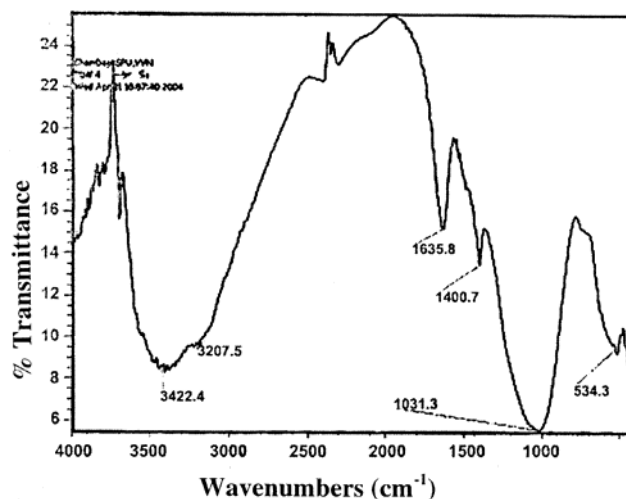


Fig. 2 – FTIR spectra of ZP

is attributed to the condensation of structural hydroxyl groups. TGA of ZP (Fig. 3) shows a sharp change within the temperature range 71-375°C corresponding to the loss of moisture/hydrated water after which weight loss is observed in the range of 379-479°C. This may be due to the condensation of structural hydroxyl groups. DSC of ZP (Fig. 4) exhibits 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 has been formulated as $\text{Zr}(\text{HPO}_4)_2 \cdot 2.5\text{H}_2\text{O}$ using Alberti & Torracca formula³¹. No characteristic peaks in X-ray diffractogram of ZP (Fig. 5) indicates that the material is amorphous in nature. ZP is stable in acid medium, maximum tolerable limits being (36 N H_2SO_4 , 16 N HNO_3 , 10 N HCl) and also stable in organic solvent media ethanol, benzene and acetone. It is, however, not so stable in basic media, maximum tolerable limit being (5 N NaOH and 5 N KOH).

Sorption studies

Figure 6 indicates maximum sorption for MB and CV at pH 6 and for MV and JGB at pH 4. It is observed that, sorption increases with increase in contact time and temperature, indicating endothermic nature of sorption³². Percentage uptake has been calculated using formula, $[(C_i - C_f) / C_i] \times 100$; where C_i = initial concentration of dye in mg/L and C_f = final concentration of dye in mg/L.

Generally both Langmuir and Freundlich isotherms are used for explaining the adsorption of dyes on materials. 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 and C_e is the equilibrium concentration of the adsorbate in the solution. Freundlich constant K represents the quantity of dye sorbed in mg g^{-1} and $1/n$ is a measure for the sorption intensity³³. If the adsorption process follows Freundlich pattern, plot of $\text{Log}(X/m)$ versus $\text{Log } C_e$ is a straight line. Further, from the above plot, $1/n$ and K are calculated from the slope and intercept, respectively. Langmuir adsorption isotherm is represented by, $C_e / (X/m) = 1 / (bV_m) + C_e / V_m$ (2) where C_e , X and m have the same meaning as described in Freundlich isotherm; b is a constant that represents intensity of the sorption and V_m a constant that represents maximum adsorption capacity

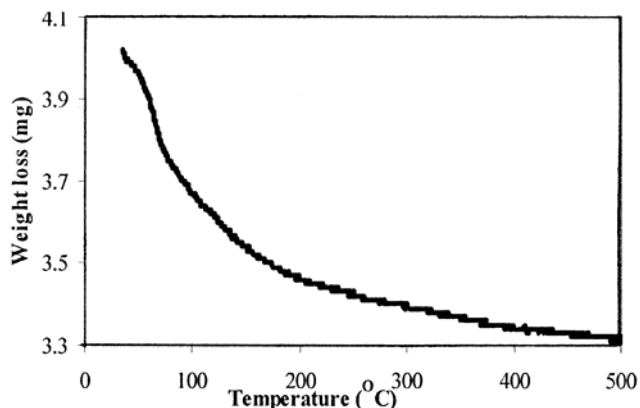


Fig. 3 – TGA plot of ZP

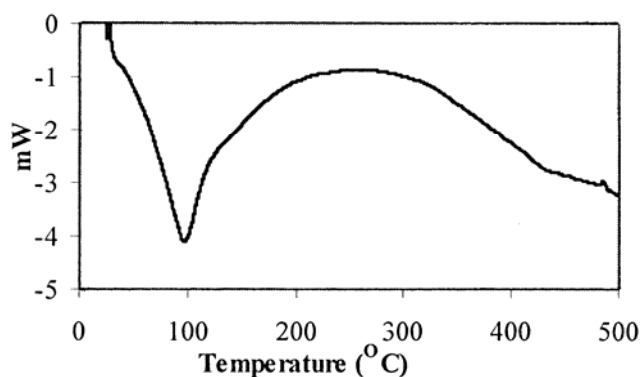


Fig. 4 – DSC curve of ZP

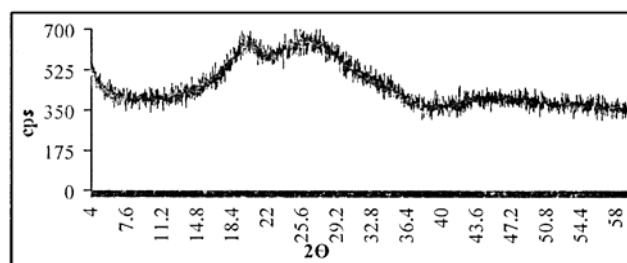


Fig. 5 – X-ray profile of ZP

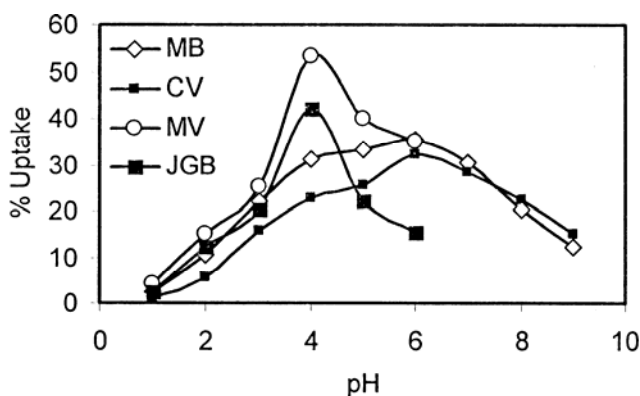


Fig. 6 – Effect of pH on sorption of dyes

corresponding to a monolayer covering the surface of the adsorbent. If the adsorption process follows the Langmuir pattern, plot of $C_e/(X/m)$ versus C_e is a straight line. Further from the above plot b and V_m are calculated from the slope and intercept³³.

Based on R^2 (correlation coefficient) (Table 1) and Figs 7-9, it is observed that the adsorption process follows the Langmuir pattern for CV and MV while MB follows the Freundlich pattern. JGB does not follow any pattern, therefore the plots have not been presented. Deviations in R^2 values in case of MV and JGB may be due to the phenyl rings causing steric effects and hence difficulty in sorption. Further, 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 sorption³⁴. In case of CV and MV that follow the Langmuir pattern, with increase in temperature, V_m values increase (CV- 357.1, 384.6 and 400.0; MV- 415.2, 555.2 and 585.6 at temperatures 313, 323 and 333 K respectively). This in keeping with the endothermic nature of the sorption³², as explained earlier. As indicated earlier, $1/n$ is a measure of sorption intensity. It has been shown earlier that in cases where $1/n > 1$, indicates cooperative sorption³³ (MB - 2.21, 0.64 and 1.85 at 313, 323 and 333 K respectively). This is also reflected in the R^2 values of MB (both Langmuir and Freundlich, Table 1) where values in both cases are close to unity. Plot of C_e versus X for all dyes (Figs 10-13), indicate that sorption increases with equilibrium concentration and later becomes constant.

Sorption of dyes from the liquid phase onto the solid phase can be considered as a reversible reaction with two phases. Therefore, a simple first order

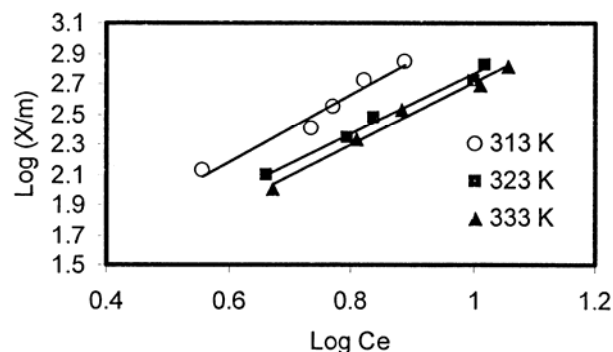


Fig. 7 – Freundlich adsorption isotherm for MB

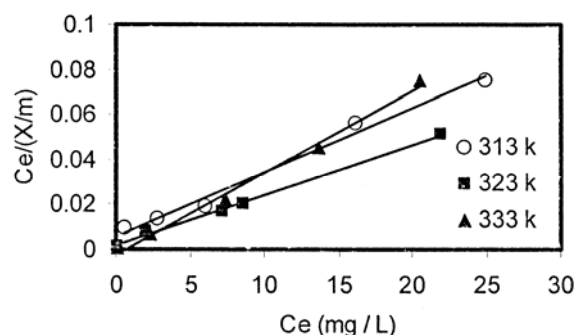


Fig. 8 – Langmuir adsorption isotherm for CV

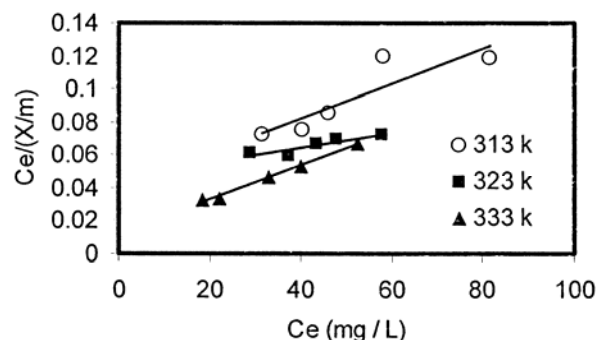


Fig. 9 – Langmuir adsorption isotherm for MV

Table 1—Regression value, kinetic and thermodynamic parameters for the sorption of MB, CV, MV and JGB on ZP

Dye	Temperature	k_c	ΔG° kJ/mole	ΔH° kJ/mole	ΔS° kJ/mole	R^2	
						Langmuir	Fruendlich
MB	313 K	10.77	-6.185	10.23	0.052	0.88	0.93
	323 K	12.16	-6.709	29.99	0.113	0.92	0.96
	333 K	17.01	-7.845	-	-	0.94	0.99
CV	313 K	630.3	-16.78	34.13	0.162	0.99	0.85
	323 K	946.0	-18.40	62.03	0.249	0.98	0.88
	333 K	1893.0	-20.89	-	-	0.96	0.84
MV	313 K	4.037	-3.631	67.81	0.228	0.60	0.13
	323 K	9.046	-5.941	26.88	0.101	0.92	0.88
	333 K	12.21	-6.929	-	-	0.97	0.04
JGB	313 K	1.641	-1.288	53.23	0.174	0.15	0.41
	323 K	3.091	-3.030	1.322	0.013	0.34	0.66
	333 K	3.137	-3.165	-	-	0.29	0.55

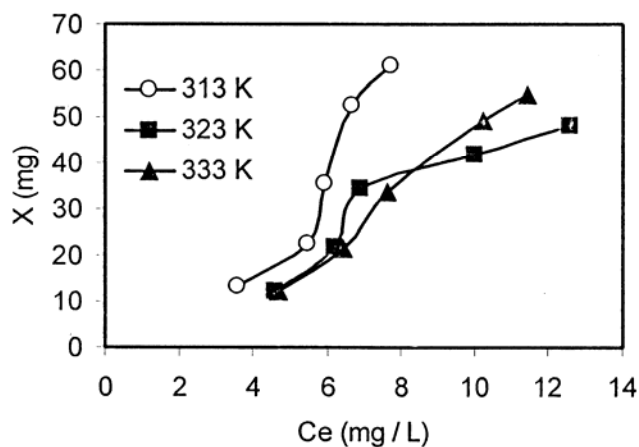


Fig. 10 – Equilibrium curve for MB

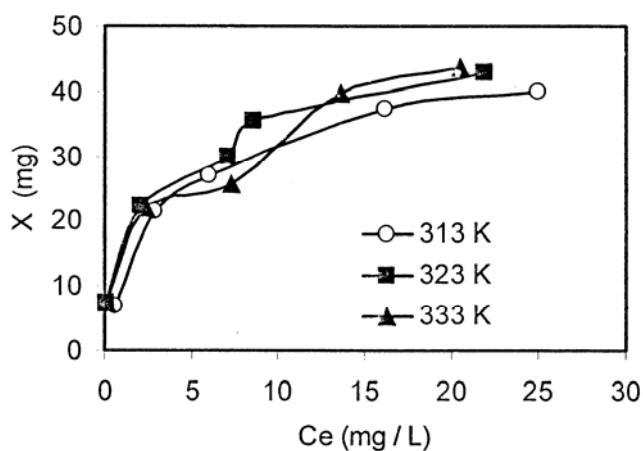


Fig. 11 – Equilibrium curve for CV

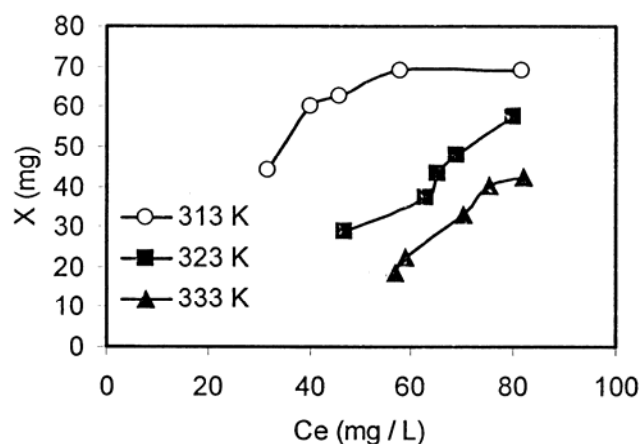


Fig. 12 – Equilibrium curve for MV

kinetic model is used to establish the rate of reaction³⁵. Kinetic plots [$\ln \{1-U(t)\}$ versus time] for the sorption behaviour of the dyes towards ZP have been presented in Figs 14-17. All plots are linear indicating that the sorption process follows first order reversible

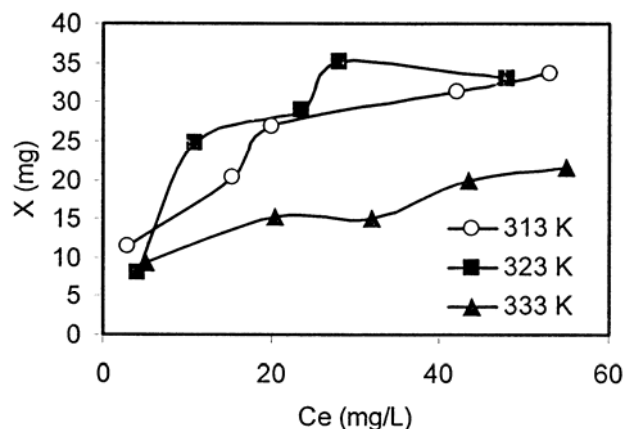


Fig. 13 – Equilibrium curve for JGB

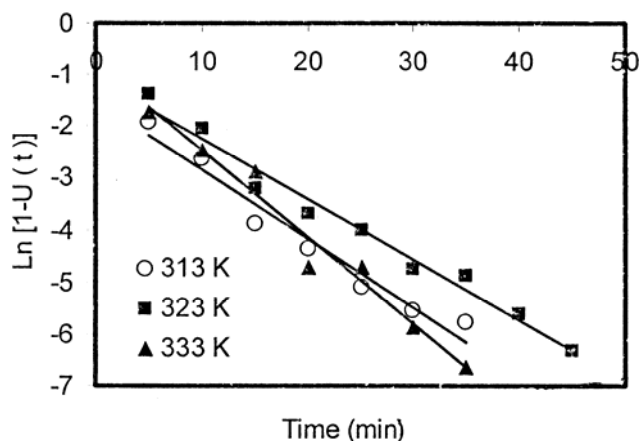


Fig. 14 – Kinetic plot of MB

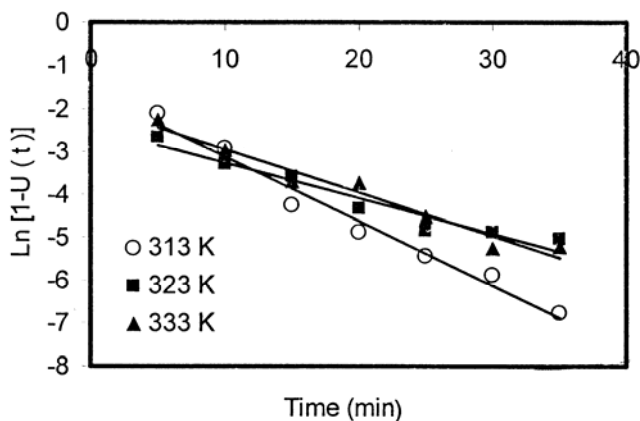


Fig. 15 – Kinetic plot of CV

kinetics. The first order kinetic equation is, $\ln [1-U(t)] = -k't$ (3) where k' is the overall rate constant and $U(t)$ is fractional attainment of equilibrium. Further, $k' = k_1 (1+1/k_c) = k_1 + k_2$ (4) where k_c is the equilibrium constant and k_1 and k_2 are the first order forward and reverse rate constants, respectively.

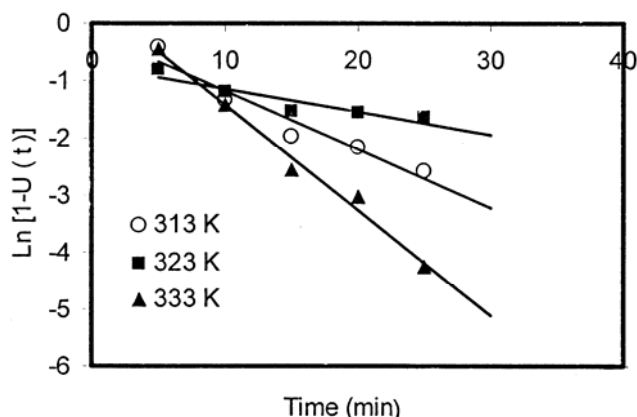


Fig. 16 – Kinetic plot of MV

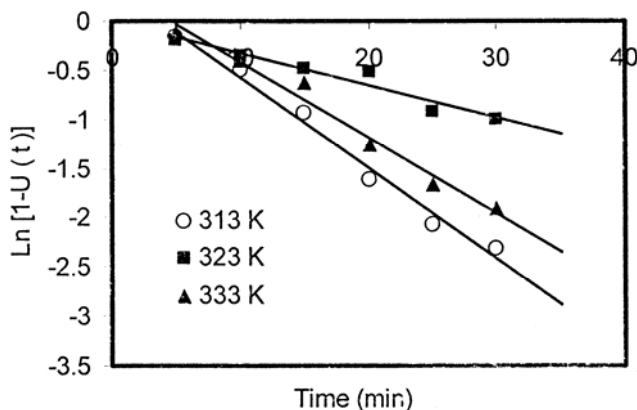


Fig. 17 – Kinetic plot of JGB

$U(t) = C_0 - C_t / C_0 - C_e$ (5) where C_0 , C_t and C_e (all in mole/L) are concentrations of dyes in solution, initially, at time t and at equilibrium respectively.

In order to explain the effect of temperature on the sorption³⁵, thermodynamic parameters, standard free energy ΔG° , standard enthalpy ΔH° , and standard entropy ΔS° were determined³⁵ using the 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 the temperature T , T_1 and T_2 , respectively. Numerical values of the equilibrium constants were calculated from $k = C_{Be} / C_{Ae}$ (9) where C_{Be} and C_{Ae} are the equilibrium concentrations of dyes on the sorbent and in solution, respectively³⁵.

The values of k_c , ΔG° , ΔH° and ΔS° have been presented in Table 1. It is observed that k_c , equilibrium constant, increases with increase in temperature for all dyes. When sorbent is in contact with dye solution, mainly two reactions may take place, either ion exchange or sorption (on the surface or inside the pores of the sorbent material). As

physical forces are responsible for the sorption, the value of k_c may decrease with increasing temperature. Ion exchange being a chemical reaction, some energy is required for crossing the barrier (energy of activation). In the present study, an increase in k_c values with increase in temperature, indicates that the mechanism may be ion exchange. It is observed that ΔG° values are negative for the dyes MB, CV, MV and JGB. Negative ΔG° values indicate feasibility and spontaneous nature of the sorption process and attainment of a more stable energy level after sorption of dyes. Further, decrease in ΔG° values with increase in temperature indicates increase in feasibility and spontaneity of the sorption process with rise in temperature³⁴. Adsorption is generally an exothermic process. In the present study, sorption increases with increase in temperature which has been attributed to endothermic nature of sorption³². In the present study ΔH° values observed are also positive which is attributed to endothermic nature of the sorption process^{32,36}. Positive values of entropy indicate an increased randomness after the adsorption of the dyes on the sorbent, indicating that the mechanism of sorption is an entropy controlled process^{32,36}.

All dyes exhibit good sorption which could be attributed to both cation exchange nature of sorbent and cationic nature of dyes. The observed order of break through capacity (BTC), for sorption of dyes on ZP is MB > CV $\approx$ MV > JGB (Fig. 18). However, sorption is expected to be MV > MB > JGB > CV as per basicity order of dyes. 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, BTC is less which may be attributed to phenyl rings causing steric effects. Probably, even small changes in the dye structure may significantly influence the adsorption capacity. Sorbent ZP possesses structural hydroxyl groups. Therefore, bonding of dyes onto the sorbent could be either hydrogen bonds or weak Van der waal's forces.

The elution of dyes sorbed on ZP (Table 2) ranges between 97 – 100 %, indicating acids, electrolytes and alcohols to be good eluting agents. In the present study, maximum sorption capacity of MB towards ZP is 334.783 mg g⁻¹. Similar studies³⁷ carried out on activated carbon made from gauva seeds towards sorption of MB is 0.667 mg g⁻¹. Though activated carbon obtained from gauva seeds is a low cost material, ZP is more effective towards removal of

Table 2—% Elution of dyes using various eluants

Eluting agent	MB		CV		MV		JGB	
	E_v	%E	E_v	%E	E_v	%E	E_v	%E
0.01 M HNO_3	100	98.30	80	99.92	80	98.30	120	99.82
0.01 M HCl	110	98.10	90	99.70	80	98.10	100	99.85
0.01 M H_2SO_4	110	99.10	110	99.80	80	99.10	110	99.89
0.01 M KCl	120	100.0	120	99.35	90	100.0	140	99.65
Methanol	150	98.0	150	97.25	150	98.0	80	99.85

E_v = mL of eluting agent %E = Percentage elution

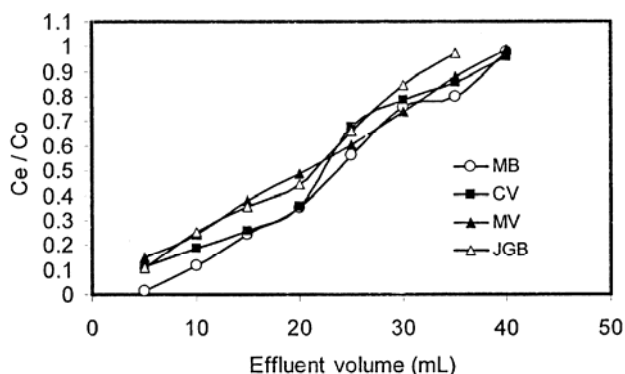


Fig. 18 – Breakthrough curve for ZP

dyes probably due to its cation exchange characteristics. A case study using a synthetic effluent containing MB shows that % COD reduction at different time intervals is found to be 15 min (72.02), 30 min (83.05), 45 min (86.09), 60 min (89.32) and 75 min (90.31) indicating good efficiency of ZP towards removal of MB from textile wastewater.

Conclusion

Sorbent material ZP, 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 the dyes studied reveal good sorption behaviour. Breakthrough capacity indicates good affinity of dyes towards ZP, found to be in the order $\text{MB} > \text{CV} \approx \text{MV} > \text{JGB}$. Elution of dyes using various eluants is greater than 97% in all cases. Good sorption as well as elution of dyes using ZP indicates its promising use in wastewater treatment containing dyes.

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