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Evaluate the Adsorptive Efficacy of Thermally Stable Tin zirconium phosphate Ion Exchange Material for the Removal of Cationic Dye from Aqueous Solution

P.Vinisha Valsaraj, C. Janardanan*

Post Graduate and Research Department of Chemistry, Sree Narayana College, Kannur, Kerala 670007, **INDIA**

Email: vinipunep@gmail.com

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ABSTRACT

Tetravalent metal acid salts based cation exchanger; tin zirconium phosphate was synthesized by co-precipitation method. The ion exchange capacity, chemical stability, effect of temperature on ion exchange capacity and pH titration studies carried out to understand the ion exchange capability. The physico-chemical characterization was studied by elemental analysis, XRD, FT-IR and TGA. The thermal analysis depicted the enhanced thermal stability of this material. The X-ray diffraction study showed that the material formed is semicrystalline in nature. The distribution studies of different metal ions on this material were performed in different solvent systems and it was found to be selective for Pb^{II} *and* Cu^{II} *ions. On the basis of distribution coefficient values, some analytically important binary separations of metal ions viz. like* Co^{II}-Pb^{II}, Ni^{II}-Pb^{II}, Hg^{II}-Pb^{II}, Mg^{II}-Pb^{II}, Bi^{III}-Cu^{II}, Th^{IV}-Cu^{II}, Mg^{II}-Cu^{II}, *and* Hg^{II}-Cu^{II} *were achieved on tin zirconium phosphate columns. The UV-Visible spectrophotometric studies revealed the enhanced adsorption ability of this material towards organic pollutants like dyes. The effect of some important parameters such as pH, initial concentration of dye, adsorbent dosage, and contact time on the uptake of methylene blue solution was also investigated. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption of dye was best described by pseudo first order mechanism. It was found that the material can be used for the wastewater treatment which containing heavy toxic metal ions as well as organic pollutant like dyes.*

Keywords: Ion exchanger, methylene blue, adsorption, distribution coefficient, isotherm.

INTRODUCTION

Many industries such as textile, rubber, leather, paper, cosmetics, plastics, food, and pulp use synthetic organic dyes to colour their products. It has been reported that wastewater containing dyes is poisonous, carcinogenic and teratogenic to human beings [1-3]. Therefore, removal of dyes from the wastewater has been an important environmental concern to minimize the water and soil pollution. Dye stuff is generally a synthetic organic compound with complex molecular structures and large molecular weight. These properties augment treatment difficulties of dye wastewater [4]. Various techniques such as precipitation, membrane filtration, coagulation, electrochemical, ion exchange, chemical oxidation, adsorption etc., are used for the removal of dyes from wastewater.

Adsorption is a procedure of choice for the removal of dyes from wastewater due to its low generation of residues and the possibility of recycling and reuse of the adsorbent [5]. A large number of suitable sorbents such as activated carbon [6], conducting polymer [7], various low cost adsorbents [8-10] (non modified or modified cellulose biomass, chitin, soil material, activated alumina) etc have been studied. Adsorption with ion exchanger is one of the best methods for the removal of dyes from wastewater [11]. But, there are a few publications, where ion exchange materials have been used as sorbents for the removal of dyes [12]. 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 ion exchange the interaction of the above functional groups with the matrix material (ion exchanger) being used, could be anywhere from covalent to columbic, hydrogen bonding or weak Vander Waals forces. The ability of the dyes to be eluted out depends on the strength and type of interaction.

Amongst the important inorganic ion exchangers, tetravalent metal acid (TMA) salts are promising materials as they possess robust properties, good ion exchange characteristics, thermal stability and chemical resistivity. Among TMA salts mixed materials containing two different cations and one anion show improved ion exchange properties and selectivity for particular metal ions compared to their single salt counter parts [13,14]. It was therefore thought of interest to use TMA salts for removal of aqueous solution of dyes. Due to the presence of structural hydroxyl groups, it is expected that the dye could either be bound by hydrogen bonds or weak Vander Waals forces.

In the present endeavour, an advanced inorganic material of the class of tetravalent metal acid salts, tin zirconium phosphate (SnZrP) had been synthesized by co-precipitation technique. The thermal stability of material was characterized using TGA analysis and the effect of temperature on ion exchange capacity of these materials was investigated. The aim of this work is to investigate the possibility of using tin zirconium phosphate for the adsorptive removal of organic pollutants such as methylene blue.

MATERIALS AND METHODS

Reagents: Zirconium oxy chloride (LobaChemie, India), stannic chloride (E.Merck) and sodium dihydrogen phosphate (E.Merck) were used for the synthesis of the exchangers. All other reagents and chemicals used were of analytical grade.

Apparatus and instruments: A glass column was used for column operations. ELICO LI613 pH meter was used for pH measurements. Chemical composition was determined by ICP-AES method using ICP-AE Spectrometer Thermo Electron IRIS Intrepid II. FT-IR Spectrometer model Thermo-Nicolet Avtar 370 for IR studies, X-ray Diffractometer Bruker AXS D8 Advance for X-ray diffraction studies were used. UV-Visible Spectrophotometer model JASCO V660 was used for spectrophotometric measurements. Perkin Elmer Diamond TG/DTA Analysis System for thermal analysis and an electric shaking machine for shaking were also used.

Synthesis of the exchanger: The preparation method for the inorganic precipitate of tin zirconium phosphate was very similar to that of Alberti and Constantino [15], with slight modification [16]. Zirconium oxy chloride solution (0.05 M), stannic chloride solution (0.05 M) and sodium dihydrogen phosphate solution (0.05 M) were prepared. Sodium dihydrogen phosphate solution was added to mixtures of zirconium oxy chloride solution and stannic chloride solution with constant stirring in different volume ratios so that final volume was 500 mL. The resulting gel was kept for 24h at room temperature maintaining the pH at 1 by adjusted with 1.0 M NaOH/1.0 M HNO_3. It was then filtered, washed with deionized water and dried. The exchanger was then converted into the H^+ form by treating with 1.0 M HNO_3 for 24h with occasional shaking and intermittent changing of acid. It was then washed with deionized water to remove the excess acid, dried and sieved to obtain particles of 60- 100 mesh.

Ion exchange capacity (IEC): The ion exchange capacity of the material was determined by column method. 1.0 g of the exchanger in H^+ form was taken in a glass column of 1.1 cm diameter. The H^+ ions were eluted by percolating 100 mL of 1.0 M NaCl solution, maintaining a very slow flow rate (~0.5 ml

min^{-1}). The effluent was collected and titrated against standard sodium hydroxide solution. The ion exchange capacity, IEC in $meqg^{-1}$ was calculated using the formula,

$$IEC = \frac{av}{w}$$

Where, ***a*** is the molarity, ***v*** is the volume of alkali used during titration and, ***w*** is the weight of the exchanger taken [17].

Chemical resistivity: The chemical resistivity of the sample was assessed in mineral acids like HCl, HNO_3 and H_2SO_4, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this, 0.5 g of the sample was soaked in 50 mL of different solvents, kept for 24h and changes in colour, nature and weight of the sample were noted.

Effect of temperature on IEC: The effect of temperature on ion exchange capacity was studied by heating several 1.0 g samples of the exchanger at different temperatures for 2h in an air oven and Na^+ ion exchange capacity in $meqg^{-1}$ was determined by the column method after cooling them to room temperature.

pH titrations: Topp and Pepper method [18] was used for pH titrations using NaOH/NaCl, KOH/KCl, systems. 0.5 g of exchanger was equilibrated with varying amounts of metal chloride and metal hydroxide solutions. At equilibrium (after equilibration), pH of the solutions was measured and plotted against the milliequivalents of OH^- added.

Distribution coefficient (K_d): Distribution studies were carried out for various metal ions in demineralized water by batch process. In this method, 0.1 g of the exchanger (60-100 mesh) was equilibrated with 20 mL of the metal ion solutions for 24h at room temperature. The metal ion concentrations before and after sorption were determined spectrophotometically/ complexometric titration against standard EDTA solution. In the complexometric method, the K_d values were calculated using the formula,

$$K_d = \frac{(I - F)}{F} \times \frac{V}{W}$$

Where, I is the initial volume of EDTA used, F is the final volume of EDTA used, V is the volume of the metal ion solution (mL) and W is the weight of the exchanger [17]. The distribution value of different metal ions on exchanger which heated at different temperature (100 °C, 200 °C, 300 °C, 400 °C and 500 °C) had been also studied.

Binary separation of metal ions: Separations of some metal ions of analytical utility were achieved on the column of tin zirconium phosphate. The column on which the separations were to be carried out was filled uniformly with the exchanger. First of all distilled water was added to pack the granules so that no air bubbles get stuck. Then the mixture of the metal ion solutions was slowly poured. The process was repeated for maximum sorption. The exchanged metal ions were eluted using suitable eluent.

Batch experiments for dye removal: Batch experiments were performed according to Mahanta et al [19]. The initial and final concentrations of methylene blue solutions were determined by measuring absorbance at 664 nm using UV-visible absorption spectroscopy. Methylene blue solutions (10 mL) of different concentrations (20 ppm to 100 ppm) were mixed with 0.2 g of material and kept for 2h and measured its absorbance. The effect of pH, contact time and adsorbent dosage was carried out.

Desorption study: The dye-loaded exchanger which was exposed to 40 ppm of dye was separated from the solution. Later, cation exchanger was dried completely and used for desorption experiments. The dye-loaded materials (0.2 g) were then brought into contact with 1.0 M NaOH, 1.0 M HNO_3, ethanol (95%), and acetone (99%), separately. The mixture was kept for 24h. After desorption, the supernatant was collected, with the remaining procedure being the same as for the sorption experiments.

RESULTS AND DISCUSSION

The exchanger, SnZrP4 obtained as colourless transparent semi crystalline solid having maximum ion exchange capacity 1.15 meqg^{-1} was selected for detailed study (table 1). It was found to be stable in water, acetic acid, 1.0 M NaOH, KOH, HNO_3, HCl and H_2SO_4.

Table 1: Synthesis and properties of various samples of exchanger using 0.05 M solutions each.

Sample	Volume ratios	pH	Appearance	Ion Exchange Capacity for Na^+ (meqg^{-1})
SnZrP1	1: 1: 1	1	Colourless transparent solid	0.46
SnZrP2	1: 1: 2	1		0.94
SnZrP3	1: 2: 2	1		0.85
SnZrP4	1: 1: 3	1		1.15
SnZrP5	2: 1: 3	1		1.13
SnZrP6	1: 2: 3	1		1.09

Sn- $SnCl_4$, Zr-$ZrOCl_2$, P- NaH_2PO_4

Elemental analysis by ICP-AES revealed tin, zirconium, phosphorous ratio of 1: 1: 2.9. FTIR spectra of SnZrP (Figure 1) showed a broad band in the region ~3444 cm^{-1} which was assigned to symmetric and asymmetric –OH stretching, while the band at ~1633 cm^{-1} was attributed to H-O-H bending. A band in the region ~1039 cm^{-1} was attributed to P=O stretching. A band at ~1384 cm^{-1} was an evidence for the presence of δ (POH). This indicated the presence of structural hydroxyl protons in SnZrP, which was more evident from the obtained IEC values. Bands at ~615 cm^{-1} and ~516 cm^{-1} may be due to the presence of Zr-O and Sn-O bonds.

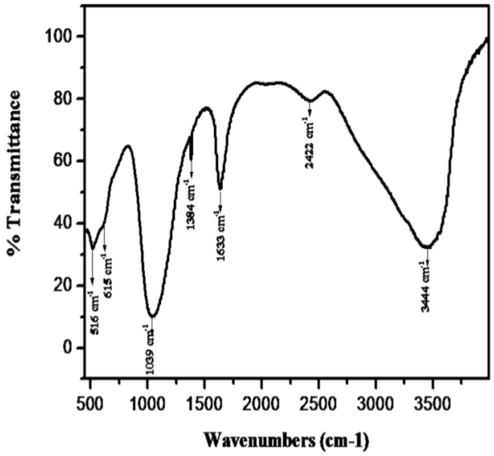

Figure 1:FT-IR of SnZrP

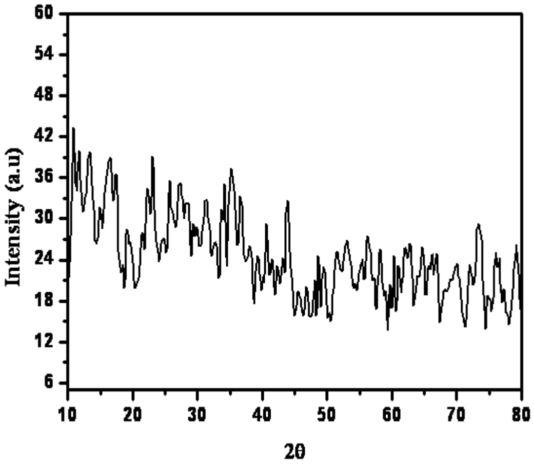

Figure 2: XRD of SnZrP

X-ray diffractogram (Figure 2) exhibited some prominent peaks together with a number of low intensity peaks which suggested semi-crystalline nature of the material.

It was observed that on heating at different temperatures for 2h, the ion-exchange capacity of the dried sample material was not changed as the temperature increased up to 300 °C as shown in Figure 3. Above 300 °C there was slight decrease in ion exchange capacity. However, in respect to ion exchange capacity, this material was found to possess higher thermal stability as the sample maintained 100% of the ion-exchange capacity up to 300 °C.

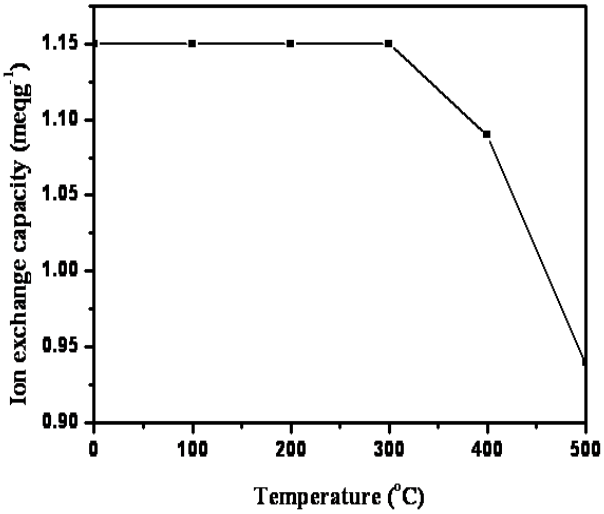

Figure 3. Effect of temperature on IEC

The thermogram of SnZrP cation exchanger (Figure 4) showed that the weight loss (about 20%) of the ion exchanger up to ~147 °C is due to the removal of free external water molecules [20]. Further, a gradual loss of mass (about 8%) up to 500 °C may be due to the condensation of hydroxyl groups. Above 500 °C, the gradual loss in weight (about 3%) up to 800 °C was due to the removal of structural water. There was no sudden decrease in the weight loss which indicated that there was no structural change of this material. The percent weight loss with increasing temperature observed by TGA curve for SnZrP was also supported by the thermal stability experiment Figure 3. pH titration curves apparently showed only one inflexion point (Figure 5).

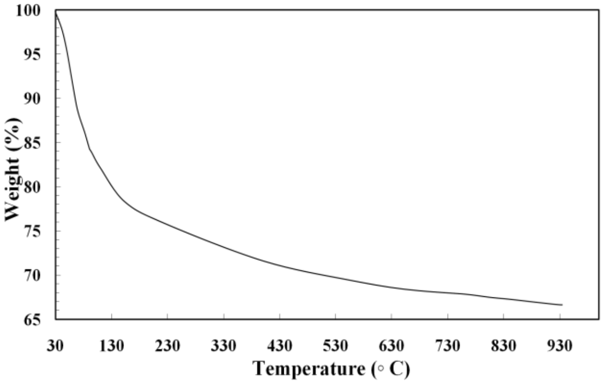

Figure 4: TGA of SnZrP

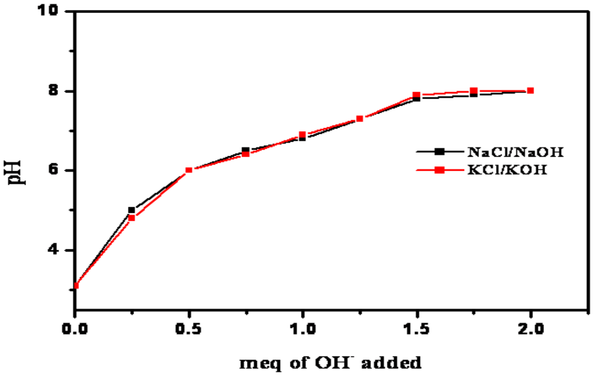

Figure 5: pH titration curve of SnZrP

APPLICATIONS

Distribution Studies: In order to explore the potentiality of the newly synthesized cation exchange material in the separation of metal ions, distribution studies for metal ions were performed in different solvent system (table 2). The distribution studies of metal ions showed that the exchanger had very high affinity towards Pb^{II} and Cu^{II} ions in comparison to other metal ions studied. The selectivity was found to be in the order $Pb^{II} > Cu^{II} > Zn^{II} > Ca^{II} > Mn^{II} > Mg^{II} > Ni^{II} > Co^{II} > Th^{IV} > Hg^{II} > Bi^{III}$. The effect of electrolyte concentrations on distribution coefficients showed that the value decreases with increase in electrolyte concentrations.

The exchanger preheated at 200 °C also showed same distribution values for the metal ions in demineralised water. But the values were decreased when heated above 300 °C. The order of selectivity was also the same even on heating the exchanger at 400 °C. The variation of distribution values of different metal ions on the ion exchanger treated at different temperatures were tabulated in the table 2. These data indicated high distribution capability of the exchanger towards different metal ions and the data was correlated with the ion exchange capacities of the exchanger at different temperatures.

Table 2: K_d values of various metal ions in different electrolyte

Metal ions	Effect of electrolyte concentration							Effect of temperature (DMW)			
	DMW	0.001 M HNO_3	0.01M HNO_3	0.1M HNO_3	0.001M NH_4NO_3	0.01M NH_4NO_3	0.1M NH_4NO_3	100 °C	200 °C	300 °C	400 °C
Pb^{II}	896.5	665.4	423.9	212.1	720.1	439.2	187.9	798.5	669.6	559.7	320.1
Zn^{II}	213.0	100.0	56.7	4.5	210.0	87.9	23.1	199.4	100.3	59.0	21.3
Mn^{II}	159.4	134.1	98.6	42.1	123.1	67.3	21.2	98.2	43.2	12.3	1.1
Ni^{II}	117.6	100.3	52.1	19.1	99.9	34.0	9.9	86.4	23.7	2.3	NA
Hg^{II}	60.0	32.0	20.0	8.0	48.0	18.0	2.1	32.0	3.5	NA	NA
Ca^{II}	180.1	176.0	98.2	34.6	166.0	67.3	12.0	160.1	118.1	53.2	11.9
Co^{II}	108.7	87.8	42.1	11.1	96.2	45.0	10.0	90.1	56.1	23.1	16.0
Cu^{II}	663.9	611.0	567.0	239.3	659.1	589.1	300.0	543.9	412.3	233.3	180.9
Bi^{III}	45.0	32.0	1.9	NA	30.1	12.0	NA	4.1	NA	NA	NA
Mg^{II}	132.4	129.0	67.3	21.0	130.0	87.2	43.0	81.2	44.4	12.1	NA
Th^{IV}	72.1	62.0	20.9	4.6	63.0	15.9	NA	38.7	12.4	NA	NA

NA: No noticeable adsorption, DMW: Demineralised water

The separation capability of the material had been demonstrated by achieving binary separations of some important metal ions viz. Co^{II}-Pb^{II}, Ni^{II}-Pb^{II}, Hg^{II}-Pb^{II}, Mg^{II}-Pb^{II}, Bi^{III}-Cu^{II}, Th^{IV}-Cu^{II}, Mg^{II}-Cu^{II}, and Hg^{II}-Cu^{II}. The separation was based on sequential elution of ions through the column using different eluting agents such as NH_4NO_3 and HNO_3 and recovery was quantitative and reproducible. The sequential elution of ions from the column depends upon the stability of metal-eluting ligand (eluent). The weakly retained metal ions get eluted first, followed by stronger one. The order of elution and eluents used for the binary separation were also shown in table 3.

Removal of dyes: Methylene blue (MB) serves as model compound of the harmful and water soluble organic pollutants, which is widely used in the textile industries and harmful to the environment. The adsorption of MB into the exchanger was studied by using UV– visible spectroscopy. Adsorbant dosage is an important factor which must be carefully optimized during waste water treatment. The effect of adsorbent dosage (0.1 g to 0.5 g) was studied on 40 ppm concentration of dye solution at room temperature and nuetral pH, and the results were presented in Figure 6a. Removal of dye with increasing adsorbent dosage was observed which was due to the availability of reactive sites [21] and above 0.4 g there was not much observable difference in the percentage removal of dye. Thus, further experiments were carried out using 0.2 g of the adsorbant, as it exhibited appreciable removal capacity for the optimization of adsorption parameters.

Table 3. Binary separation of metal ions on SnZrP

Separation achieved	Eluent	Metal ion (mg)		% Efficiency
		Loaded	Eluted	
Co^{II}	0.2 M NH_4NO_3	1.92	1.90	98.96
Pb^{II}	0.4 M HNO_3+0.4 M NH_4NO_3	2.80	2.75	98.21
Ni^{II}	0.2 M NH_4NO_3	3.20	3.10	96.88
Pb^{II}	0.4 M HNO_3+0.4 M NH_4NO_3	2.80	2.75	98.21
Mg^{II}	0.2 M HNO_3	2.80	2.72	97.14
Pb^{II}	0.4 M HNO_3+0.4 M NH_4NO_3	2.41	2.36	97.93

Hg^{II}	0.2 M $NH4NO_3$	2.80	2.77	98.93
Pb^{II}	0.4 M HNO_3 + 0.4 M NH_4NO_3	2.80	2.78	99.29
Bi^{III}	0.1 M HNO_3	3.15	3.11	98.73
Cu^{II}	0.5 M HNO_3 + 0.5 M NH_4NO_3	2.50	2.44	97.60
Th^{IV}	0.1 M NH_4NO_3	9.00	8.74	97.11
Cu^{II}	0.5 M HNO_3 + 0.5 M NH_4NO_3	6.00	6.00	100.00
Mg^{II}	0.2 M HNO_3	10.00	9.98	99.80
Cu^{II}	0.5 M HNO_3 + 0.5 M NH_4NO_3	4.50	4.24	94.22
Hg^{II}	0.2 M NH_4NO_3	3.00	3.00	100.00
Cu^{II}	0.5 M HNO_3 + 0.5 M NH_4NO_3	2.50	2.40	96.00

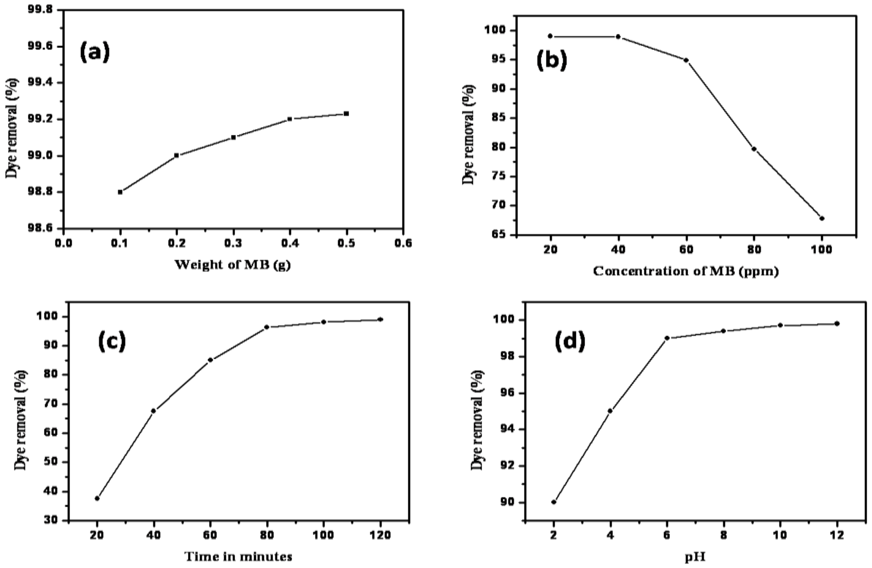

Figure 6. a. Effect of adsorbent dosage, b. Effect of dye concentration, c. Effect of time d. Effect of pH on the removal of MB by SnZrP

Experiment was conducted with different concentration of MB in the presence of 0.2 g of exchanger for 2h and its percentage sorption of dye was shown in Figure 6b. This study revealed that there was significant removal of dye even at higher concentration. The enhanced removal at low concentration could be due to the faster movement of dye into the activated sites of exchanger. However, in higher concentration (100 ppm) the removal rate was decreased (67.8 %) because the dye molecules needed to diffuse to the adsorbent sites by intra particle diffusion. In addition, steric repulsion between the solute molecules could slow down the adsorption process and thereby decreased the removal rate. A similar trend was observed for the adsorption of methyl violet by agricultural waste [22].MB solution (10 mL, 40 ppm) was treated with 0.2 g of exchanger for different periods of time (20-120 min) at room temperature. Results of the adsorption obtained from the analysis of unsorbed MB solution were shown in Figure 6c. The reults indicated low removal of dye in the first 20 min but it increased upto 2h.

Several studies reported the significant role of pH in adsorption reaction. Crini et al [23].reported that the pH of the solution influences the surface charge and functional groups of the adsorbent. In addition, pH influences the degree of ionization of the materials present in the solution and solution chemistry. Hence, 0.2 g of the exchanger was mixed with 40 ppm dye solutions at different pH values (2–12). The pH was measured after the addition of the exchanger. Effect of pH on adsorption of MB on the exchanger showed that the adsorption was less at lower pH values where as at higher pH values the adsorption was high which shown in Figure 6d. It indicated the interaction of MB on exchanger was less at lower pH due to the presence of high concentration of H^+ ions on the surface of exchanger competing with methylene blue for adsorption site in the adsorbent where as at higher pH electrostatic repulsion between positively charge methylene blue and the surface of adsorbent was lowered. Consequently removal efficiency was increased at higher pH. Finally the adsorption process proceeded through the electrostatic attraction between the two counter ions.

Desorption study: After confirming the fact that SnZrP was capable of adsorbing the dye molecules onto its surface, it became necessary to know the process by which the dye molecules remain adhered to the surface of the exchanger. The adherence of dye molecules onto the surface of the exchanger was purely chemical interactions, involving chemical binding of the substances. The increasing effeicency of exchanger towards dye removal was due to both the cation exchange nature of the sorbent and cationic nature of the dye. SnZrP possessed structural hydroxyl groups. Therefore the dyes could bond to the sorbent either by hydrogen bonds or weak van der Waals forces. The chemical bonding can be elicited by subjecting the adhered material to desorption and regeneration process [24, 25]. In this study, desorption experiments were conducted using NaOH (1.0 M), HNO_3 (1.0 M), ethanol, and acetone to ascertain the nature of binding ofdye molecules onto theexchangercomposite surface. Treatment with NaOH (1.0 M), ethanol, acetone and HNO_3 (1.0 M) showed the considerable recovery of the dyes 86%, 89%, 90% and 93% respectively. Under acidic condition, the positively charged sites increased onto the exchnager surface, and it acted as a driving force for the elution of dye by electrostatic repulsion. After five series of sorption- desorption cycle, the loss in the sorption capacity was only 7%. Hence, the cation exchanger could be easily regenerated and reused for the practical purposes.

Adsorption Isotherms: The study of adsorption isotherm has been of important and significant in the waste water treatment by adsorption technique as they provide an approximate estimation of the adsorption capacity of the adsorbent. The adsorption isotherm study was carried out for 40 ppm solution of MB at room temperature and neutral pH using 0.2 g of exchanger. The equilibrium data for the removal of dye on exchanger were used in the Langmuir [26] and Freundlich [27] isotherms.

Freundlich isotherm $\log q_e = \log K_f + (1/n) \log Ce$

Langmuir isotherm $Ce/q_e = (1/Qob) + (Ce / Qo)$

The data obtained from the adsorption experiments were fitted into Langmuir and Freundlich isotherms respectively by plotting Ce/q_e and $\log q_e$ against Ce and log Ce. They are found to be linear, indicating the formation of monolayer of adsorbate on the outer surface of adsorbent and after that no further adsorption takes place (Figure7). Further, the essential characteristics of the Langmuir isotherms can be described by a separation factor (R_L).

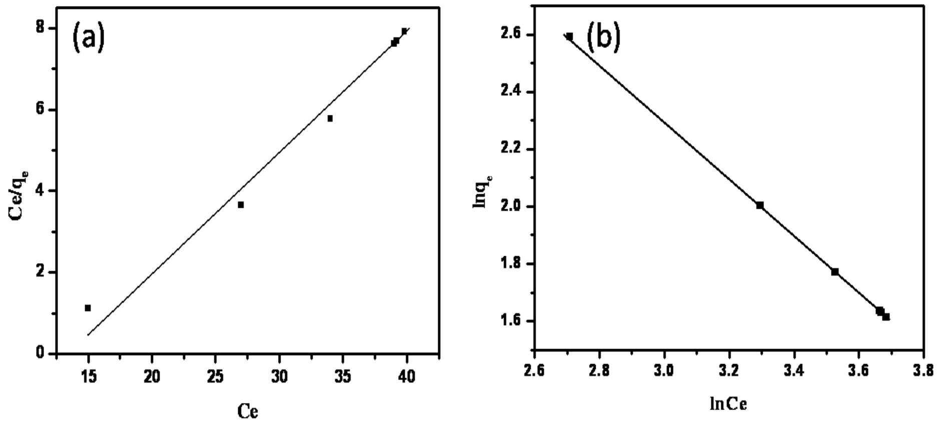

Figure 7. a. Langmuir b. Farundlich adsorption plot

The values of separation factor (R_L) indicates the shape of the isotherm and nature of the adsorption process as given here, R_L values Nature of the adsorption process, $R_L>1$ is Unfavorable, $R_L = 1$ is Linear, $0 < R_L>1$ is Favorable and $R_L = 0$ Irreversible [27].Values of R_L were found to be <1 (0.01 - 0.10) which confirmed that the exchanger is favourable for adsorption of MB under experimental conditions used in this study. The fitting data results suggest that Freundlich model could be applied to the adsorption of MB ($R^2 = 1$) while Langmuir model ($R^2 = 0.985$) is not very suitable for this adsorption. The Freundlich adsorption isotherm is an indication of surface heterogeneity of the adsorbent while the Langmuir isotherm assumes that the adsorption occurs in a monolayer, or the adsorption may only occur at a fixed number of localized sites on a surface on which all adsorption sites are identical and energetically equivalent. The Langmuir model helps to estimate the maximum adsorption capacity (q_m) when these could not be experimentally determined. The q_m values observed for MB was 300.21mg g^{-1}.

Adsorption kinetics: Adsorption kinetics provides valuable information about the reaction pathways and mechanism of the reactions. For the kinetic study 40 ppm concentration of dye solution was treated with 0.2 g of exchanger. Pseudo first-order [28] and pseudo second-order [29] models are employed to elucidated the mechanism embedded in this process.

The pseudo-first-order equation is expressed as follows [30]:

$$dq_t/ dt = k_1 (q_e-q_t)$$

The integrated form of the equation is as follows:

$$\log (q_e-q_t) = \log q_e- k_1t / 2.303$$

Where q_e and q_t are the amounts (mgg^{-1}) of solute bound at the interface at the equilibrium and after time t (min), respectively, k_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}). The pseudo-second-order kinetic model expressed in the most commonly used form, formulated by Ho and McKay [30] is as follows:

$$d_e/ dt = k_2 (q_e-q_t)^2$$

The integrated form of equation is:

$$t / q_t = 1 / k_2q_e^2 + t / q_e$$

Where k_2 is the rate constant of the pseudo-second-order adsorption (gmg^{-1} min), q_t is the adsorbed amount at time t (mg g^{-1}).

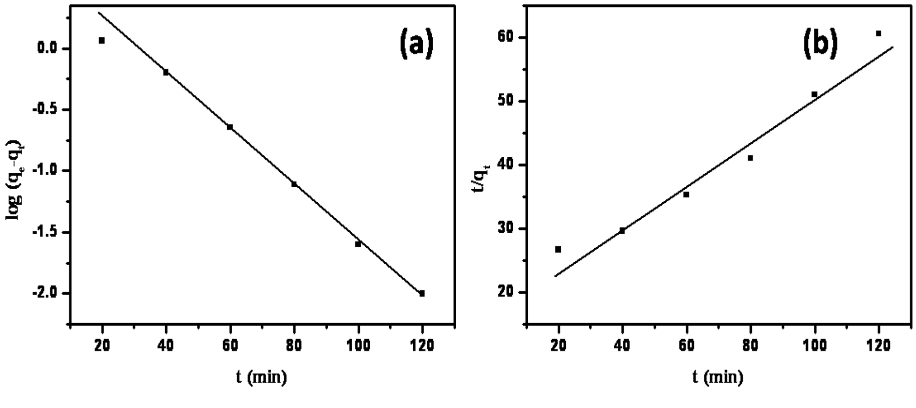

Figure 8. a. Test of the pseudo-first-order adsorption kinetics for MB adsorption on SnZrP
b. Test for the pseudo-second-order adsorption kinetics for MB adsorption on SnZrP

The plots validating the pseudo-first-order model [log (q_e-q_t) versus t] and the pseudo-second-order model [t/q_t versus t]at various initial concentrations of the MB, at 302 K, are given in Figure8a and b, respectively. Parameters of the fitted kinetic models with the correlation coefficients, R^2, are 0.996 and 0.964 for pseudo first order and pseudo second order kinetic models respectively. Examining fittingness of the models in terms of the R^2 value, it shows that the pseudo first order kinetic model describes the system much better than the pseudo second order kinetic model. The negative ΔG_0 values of methylene blue sorption at room temperature, confirmed the feasibility of the process and the spontaneous nature of sorption. The sorption experiment was carried out at different temperatures which show that the adsorption ability of the material was decreased with increased temperature. The temperature effect study revealed the exothermic nature of MB adsorption on SnZrP.

CONCLUSIONS

Thermally stable semi-crystalline tin zirconium phosphate cation exchanger can be operated at elevated temperature up to 300 °C without losing its ion exchange capacity (1.15 meq g^{-1}). It shows selective sorption for Pb^{II} and Cu^{II}. The results presented in this work have shown that the exchanger can be used for the adsorption of dye even at low as well as higher concentration of dye. In addition the adsorbent can be recycled thrice without any loss in its capacity and efficiency by treatment with 1.0 M HNO_3 solution. The material is promising in environmental applications for the removal of heavy metal ions as well as dyes from industrial effluents.

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