

Bimetallic Ion Exchange Material Titanium Tin Molybdate as an Efficient and Eco-friendly Adsorbent for the Removal of Methylene Blue from Aqueous Solution

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Abstract: The objective of current study is to explore the potential use of a bimetallic inorganic cation exchanger, titanium tin molybdate (TSM) for the removal of methylene blue from aqueous solution. TSM was synthesized by co-precipitation method, surface morphology was studied by using SEM and other physico-chemical characteristics were done using FTIR, XRD, TGA etc. The exchanger shows high ion exchange capacity of 1.56 meqg^{-1} as well as good chemical and thermal stability. The distribution studies of various metal ions on this material in different solvent systems showed that it was highly selective for Pb(II), Cd(II) and Cu(II). The UV-Vis DRS studies exposed the enhanced adsorption capability of the material towards methylene blue (MB), a hazardous organic pollutant. Batch studies were performed to evaluate various experimental parameters such as contact time, pH, adsorbent dosage, initial concentration of MB and temperature on the adsorption of MB. The isotherm studies showed that the equilibrium data were mathematically fitted to Langmuir equation. The results of kinetic studies showed that the process follows pseudo-second order kinetics. The entire studies revealed that the new exchanger TSM could be employed as an effective and economically viable adsorbent in wastewater treatment for the removal of hazardous organic dye.

Keywords: Bimetallic ion exchanger, distribution studies, methylene blue, equilibrium studies etc.

I. Introduction

Environmental problem caused by toxic organic pollutants from the domestic and industrial output is now the subject of considerable concern from environmental remediation point of view [1]. Many industries such as textile, rubber, leather, paper, cosmetics, plastics, food, and pulp use synthetic organic dyes to colour their products. Dyes are extensively used in the textile industry because of their wide variety of color shades, ease of application and minimal energy consumption. Disposal of these dyes into the environment causes pollution and serious damage, and also they are toxic to some aquatic organisms [2]. Among various cationic dyes, methylene blue has wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools, and coating for paper stock, etc[3-5]. Though methylene blue is not strongly hazardous, it can cause some harmful effects. Removal of dyes from polluted effluent is an essential task for environmental protection. Due to low biodegradability of dyes, a conventional biological treatment process is not very effective in treating a dye wastewater.

The removal of coloured and colourless organic pollutants from industrial wastewater is considered an important application of adsorption processes using a suitable adsorbent [6]. There is growing interest in using low cost and eco-friendly materials for the adsorption of dyes. Adsorption with ion exchanger is one of the best methods for the removal of dyes from wastewater [7]. For a successful scale-up of such a process; we prepared a new bimetallic inorganic cation exchanger titanium tin molybdate, having enhanced adsorption capability towards MB. Kinetic studies are essential since they describe the adsorbate uptake rate, which in turn controls the residence time in the adsorbent-solution interface. Experiments of dye sorption kinetics and equilibrium were performed in batch conditions. Many factors could affect the adsorption rate of the dye solution. In this study, adsorbent dosage, initial dye concentration, pH and agitation time were investigated.

II. Experimental

1. Reagents and chemicals:

Titanium trichloride, stannic chloride and sodium were obtained from Loba Chemie (India). All other chemicals and reagents used were of analytical grade.

2. Instrumentation:

pH measurements were performed using an ELICO LI613 pH meter. Spectrophotometry was done on a UV- Visible Spectrophotometer model JASCO V660 with diffuse reflectance accessory (integrated sphere). IR studies were made using an FTIR spectrometer model Thermo Nicolet Avtar370 and thermogram was run on

Perkin Elmer Diamond TG/DTA Analyzer. X-ray diffractometer BrukerAXS D8 Advance for X-ray diffraction studies and an electric temperature controlled shaker was used for shaking. Chemical composition was determined using EDS. A glass column was used for column operations.

3. Synthesis of the exchanger:

Different samples of TSM were prepared by adding 0.05 M sodium molybdate solution to a mixture of 0.05M titanium trichloride solution and 0.05M stannic chloride solution in different volume ratios with intermittent shaking of the mixture and keeping the pH at 1.0 as given in table 1. The precipitates were filtered, washed with deionized water and dried. The exchangers were then converted in to the H⁺ form by treating with 1M nitric acid for 24 hrs with occasional shaking and intermittent changing of acid. Then the samples were washed with deionized water to remove the excess acid, dried and sieved to obtain particles of 60-100 mesh.

Properties like ion exchange capacity (IEC), chemical resistivity and pH titration studies, distribution studies and effect of temperature on IEC were carried out as reported earlier [8].

4. Application of TSM for the Removal of dyes:

Batch experiments were performed according to Mahanta et al [9]. The initial and final concentrations of methylene blue solutions were determined by measuring absorbance at 664 nm using UVvisible absorption spectroscopy. Methylene blue solutions (10 mL) of different concentrations (20 ppm to 50 ppm) were mixed with 0.2g of material and kept for 2hrs and their absorbance was measured. The effect of pH (2-12), contact time (10-180), and adsorbent dosage (100-500mg), temperature (30-60°C) and initial concentration of MB (10-50ppm) were carried out. The percentage of removal of dyes was calculated using the following formula,

$$\text{Removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

Where, C_i is the initial dye concentration and C_e is the equilibrium dye concentration in mgL⁻¹.

III. Results And Discussion

1. Synthesis and characterization of the exchanger

Samples of titanium tin molybdate of various compositions have been synthesized, but TSM 3 obtained as brown granular solid having maximum ion exchange capacity, 1.56meqg⁻¹ was selected for detailed studies (Table1). The composition of TSM 3 obtained from EDS method was found as Ti:Sn:Mo::1:1.8:2.1.

FTIR spectra (Fig. 1(a)) shows broad band in the region ~3604 cm⁻¹ attributed to symmetric and asymmetric -OH stretching, while band at ~1622 cm⁻¹ is due to H-O-H bending [10]. Bands at ~2368 cm⁻¹, ~950 cm⁻¹ and ~412 cm⁻¹ express the presence of Ti-O, Sn-O and Mo-O groups respectively [11-12]. The X-ray diffractogram (Fig. 1(b)) of the material does not exhibit any sharp peak indicating TSM to be an amorphous material [13]. The thermogram of TSM (Fig. 1(c)) suffers a first weight loss up to 150°C, attributed to the loss of moisture and hydrated water while the second weight loss observed at around 284°C due to condensation of exchangeable hydroxyl groups take place which is the usual behavior of inorganic ion exchangers. Then the sample is almost stable up to 752°C. The Scanning Electron Microscope image (Fig. 1(d)) of TSM explains that the particles were broad in size range, having an irregular shape and no sign of crystalline structure [14].

pH titration studies (Fig. 2(a)) using NaCl/NaOH, KCl/KOH systems show nearly monofunctional behaviour indicating only one ionizing group. The exchange capacity obtained from the curve is in agreement with that obtained by the column method. The sodium ion exchange capacity decreases (Fig. 2(b)) slightly with temperature and the sample retained prominent capacity up to 600°C which can be explained with the obtained thermogram also.

The distribution studies of metal ions in water and various other electrolytes (Table 2) showed that the exchanger has very high affinity towards Pb²⁺ ions in comparison to other metal ions studied. The selectivity was found to be in the order Pb²⁺ > Cu²⁺ > Cd²⁺ > Ca²⁺ > Co²⁺ > Zn²⁺ > Mn²⁺ > Mg²⁺ > Al³⁺ > Ni²⁺ > Bi³⁺ > Hg²⁺. The effect of electrolyte concentrations on distribution coefficients showed that the value decreases with increase in electrolyte concentrations (Table 2).

2. Adsorptive 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 onto the exchanger was studied by using UV-visible spectroscopy under batch conditions. The adsorption experiments were carried out by agitating 200 mg of the adsorbent with 10 mL of 40 ppm solution of methylene blue [15]. The adsorption of MB on exchanger was confirmed by UV-Visible Diffuse Reflectance Spectroscopy (Fig. 3(a)). MB shows an intense absorption peak in the visible region at 660 nm which corresponds to its maximum absorption peak as monomer. Concentrations of methylene blue (MB) in the supernatant solutions were

estimated by measuring absorbance at maximum wavelengths of the dye (λ_{max} = 660 nm). Fig.3(b) illustrates that the original peaks of methylene blue gets disappeared after its treatment with the adsorbent.

2.1 Effect of various experimental parameters on dye removal

Agitation time is an important parameter in concern with dye adsorption. To study the effect of reaction time on the adsorption of MB, 200mg of TSM was shaken with 10 ml of 40ppm MB dye solutions at room temperature, keeping the pH of the medium neutral. Adsorption capability was measured by taking optical density at different time intervals using UV-Vis DRS. The extent of removal of Methylene Blue by TSM was found to increase, reach a maximum value with increase in contact time (Fig. 4(a)). In some cases it almost become constant with increase in contact time, after 120 min. based on these results, 120 min was taken as the equilibrium time in adsorption experiments. Similar results have been reported in literature for removal of dyes [16-17].

The pH of the dye solution is likely to affect the adsorption of the dye; hence the effect of pH on the rate of adsorption of MB dye was investigated in the pH range 2-12. The results are presented in Fig. 4(b). The pH was measured after the addition of the exchanger. The results showed that the adsorption was less at lower pH values, whereas maximum adsorption was seen at higher pH values (pH= 10). It indicated that 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, whereas at higher pH electrostatic, repulsion between positively charged methylene blue and the surface of adsorbent was lowered. Consequently, removal efficiency was increased at higher pH.

Adsorbent dosage is an important factor which must be carefully optimized during waste water treatment. The effect of adsorbent dosage (100- 500mg) was studied on 40ppm concentration of dye solution at room temperature and neutral pH, and the results were accessible in Fig. 4(c). Removal of dye with increasing adsorbent dosage was observed which was due to the availability of more reactive sites for adsorption [18].

Experiments were conducted with different concentrations of MB in the presence of 200 mg of exchanger for 2 hrs, and its effect on sorption of dye was determined, shown in Fig. 4(d). This study revealed that the percentage removal of dye decreases 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 (50ppm) the removal rate was decreased (29.70%) because the dye molecules needed to diffuse to the adsorbent sites by intraparticle diffusion. In addition, steric repulsion between the solute molecules could slow down the adsorption process and thereby decrease the removal rate [19].

Temperature has important effects on the adsorption process. As the temperature increase, rate of diffusion of adsorbate molecules across the external boundary layer and interval pores of the adsorbent particle increase. Changing to temperature will change the equilibrium capacity of the adsorbent for particular adsorbate [20-21]. Fig. 5 shows effects of different temperatures for Methylene Blue adsorption on TSM. The removal of Methylene Blue by adsorption on TSM increases slightly from 49.29 to 90.61% by increasing temperature of the solution from 30 to 60°C, indicating the process to be endothermic.

2.2 Adsorption isotherms

For solid-liquid adsorption system, adsorption isotherm is important model in the description of adsorption behavior. When the adsorption reaction reaches equilibrium state, the adsorption isotherm can indicate the distribution of dye molecules between the solid phase and the liquid phase [22]. It is significant for understanding the adsorption behavior to identify the most appropriate adsorption isotherm model. In this paper, Langmuir and Freundlich isotherms were employed to investigate the adsorption behaviour. Adsorption isotherm was studied at four different temperatures viz 303, 313, 323 and 333K.

2.2.1 Langmuir isotherm

Langmuir isotherm is rested on the assumption that adsorption occurs at specific homogenous sites within the adsorbent. Once an adsorbate molecule occupies a site, no further adsorption can take place. Thus, an equilibrium value can be reached and the saturated monolayer curve can be express in the equation below which has been successful for the explanation of monolayer adsorption. The linear form of Langmuir equation is given as,

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (3)$$

where q_{max} is the maximum or monolayer adsorption capacity of the adsorbent (mgg^{-1}) and K_L is the Langmuir adsorption constant (Lmg^{-1}), which is related to the free energy of adsorption. Plots of C_e/q_e against C_e at different temperatures are shown in Fig. 6(a). The maximum adsorption capacity, q_{max} and Langmuir constant, K_L were calculated from the slopes and intercepts of the plots respectively. Values obtained for the

adsorption of methylene blue onto the adsorbent are presented in Table 3. The correlation coefficient values ($R^2 > 0.9995$) (Table 3) show strong positive correlation indicating that adsorption follows Langmuir isotherm.

2.2.2 Freundlich isotherm

The Freundlich isotherm model is used to describe heterogeneous adsorption process i.e adsorption which takes place on a heterogeneous surface through a multilayer adsorption mechanism. Freundlich isotherm is expressed by the equation,

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

Where, K_F and n are Freundlich constants that are related to the adsorption capacity and adsorption intensity respectively. The values of K_F and n were obtained from the linear plots of $\log q_e$ versus $\log C_e$. The slope, $1/n$, ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity. The plots of the linear form of Freundlich isotherm curves at different temperatures are presented in Fig. 6(b). The Freundlich parameters and correlation coefficients (R^2) evaluated from the plots are listed in Table 1.

2.3 Adsorption Kinetics

For the examination of the controlling mechanisms of adsorption process, such as chemical reaction, diffusion control and mass transfer [23-24], several kinetic models are used to test the experimental data. For the present study, two kinetic models were applied in order to understand the mechanism of adsorption of the dye onto the adsorbent. The models are the pseudo-first order and pseudo-second-order models. The pseudo-first order kinetic model can be represented by Lagergren rate equation [23],

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (5)$$

where q_e and q_t represent the amounts of dye adsorbed (mgg^{-1}) at equilibrium and at any time, t (min), k_1 is the rate constant (min^{-1}). The values of q_e and k_1 were deduced from the intercepts and slopes of the linear plots of $\log (q_e - q_t)$ against t (Fig. 7(a)). For the present study however, Lagergren pseudo-first order kinetics parameters (Table 4) was not proved to be effective in representing the experimental kinetic data for the entire adsorption period and at all dye concentrations. Report of non fitting of pseudo-first order kinetic to adsorption has been published [25]. This result suggests that the kinetics of MB adsorption onto TSM cannot be accounted for using the pseudo-first order model and hence not a chemisorption process.

The pseudo-second order kinetic model can be represented with the following equation [26],

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where k_2 is the rate constant of pseudo-second order adsorption ($\text{gmg}^{-1} \text{min}^{-1}$). Fig. 7(b) shows pseudo-second order plots for the adsorption process for five different concentrations of the dye. K_2 and q_e values were determined from the intercepts and slopes of the linear plots of respectively (Figure 7(b)). Calculated values of the adsorption capacity q_e , (mgg^{-1}) gave a good correlation coefficient ($R^2 > 0.99$) (Table 4). Thus adsorption process could be said to follow pseudo-second order kinetic model for all concentrations of the dye. The applicability of the pseudo-second order model suggests that chemical reaction might be responsible for adsorption of MB onto TSM. The kinetics of adsorption of many dye species onto various materials have been reported to conform to pseudo-second order kinetic model [27-28].

IV. Figures And Tables

Table1: Synthesis and properties of various samples of exchanger using 0.05 M solutions each.

Sample	Volume ratio	pH	Appearance	IEC for Na ⁺ (meq/g)
TSM 1	1:1:1	1		0.95
TSM 2	1:1:2	1	All forms	1.02
TSM 3	1:2:3	1	Brown	1.56
TSM 4	1:2:4	1	granular	1.20
TSM 5	2:1:4	1	solids	1.19

Table 2: Distribution coefficients in various electrolytes

Cations	Distribution coefficients (K_d)						
	DMW		HNO ₃		NH ₄ NO ₃		
			0.01 M	0.1 M	0.001 M	0.01 M	0.1 M
Al ³⁺	72.27	48.02	24.56	8.65	52.43	26.34	9.45
Bi ³⁺	23.46	12.23	2.87	NS	15.98	3.12	NS
Ca ²⁺	99.23	56.35	35.85	13.25	59.41	38.87	15.12
Cd ²⁺	211.0	128.36	72.78	35.79	145.67	85.54	47.54

Co ²⁺	96.66	53.12	23.65	2.43	58.76	29.87	3.66
Cu ²⁺	317	173.16	89.74	26.85	184.26	93.34	31.65
Hg ²⁺	NS	NS	NS	NS	NS	NS	NS
Mg ²⁺	75	45.67	21.45	5.67	51.05	25.23	6.06
Mn ²⁺	87.87	60.67	24.98	6.32	64.34	28.35	8.43
Ni ²⁺	63	48.94	19.79	2.12	53.12	21.76	3.06
Pb ²⁺	980	754.67	487.36	287.65	767.49	494.44	292.43
Zn ²⁺	90	50.45	16.89	NS	57.26	18.53	18.45

Table 3: Parameters for Langmuir and Freundlich isotherms

T (K)	Langmuir isotherm			Freundlich isotherm		
	q _{max} (mg/g)	K _L (L/mol)	R ²	K _f	n	R ²
303	1.1601	131.68	0.9997	0.0154	2.2050	0.7257
313	0.9961	162.36	0.9996	0.0363	2.0963	0.8021
323	1.0590	185.04	0.9999	0.0466	2.0898	0.8029
333	1.1498	186.51	0.9999	0.0698	2.3444	0.8058

Table 4: Kinetic parameters for the adsorption of Methylene blue onto TSM

First order			Second order		
K ₁	q _e (mg/L)	R ²	K ₂	q _e (mg/L)	R ²
0.0046	3.49	0.8279	0.0033	4.53	0.9888

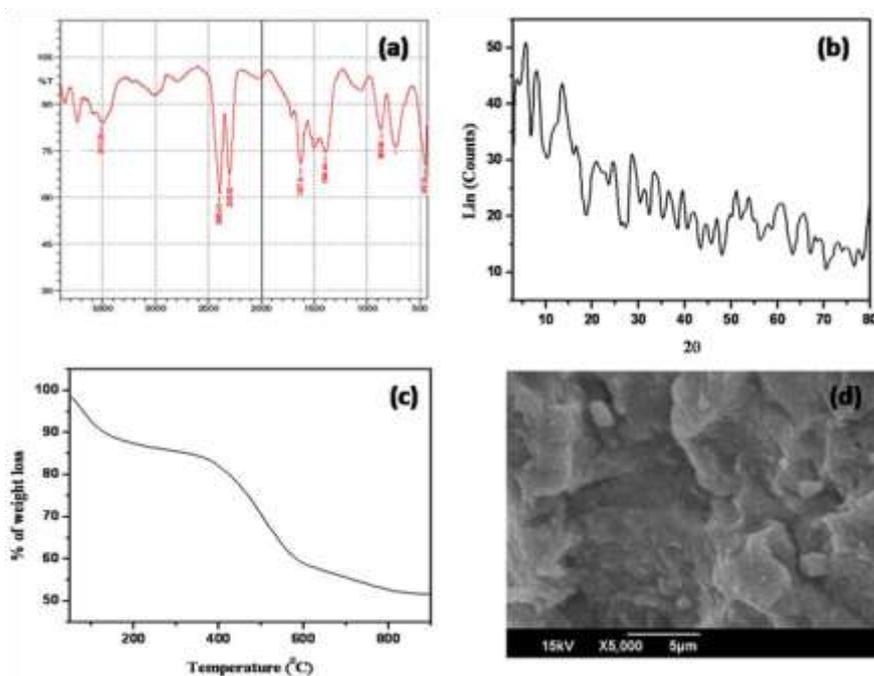


Figure 1: (a) FTIR, (b) XRD, (c) TGA and (d) SEM of TSM

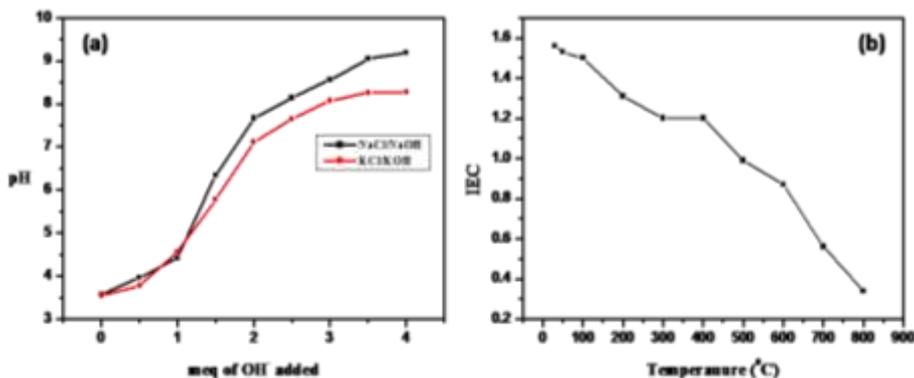


Figure 2: (a) pH titration curves and (b) Effect of temperature on IEC

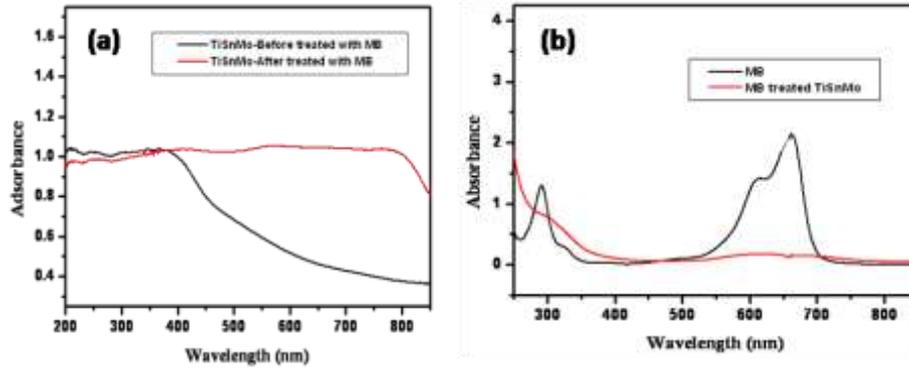


Figure 3: UV-Visible Spectra of (a) TSM before and after treatment with MB and (b) pure MB and MB after treatment with TSM

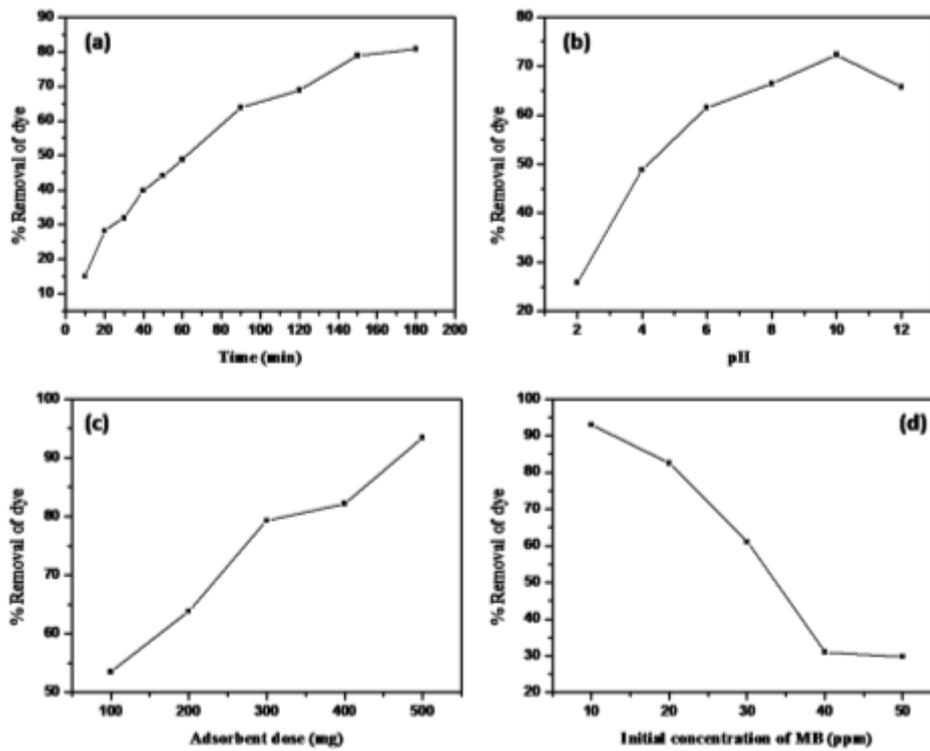


Figure 4: Effect of (a) Reaction time, (b) pH, (c) Adsorbent dose and (d) Initial concentration of MB on the removal of MB

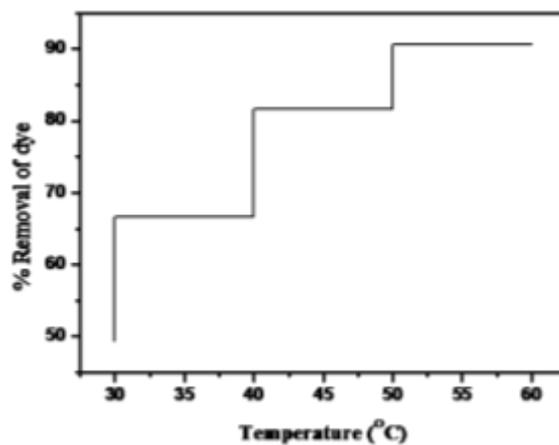


Figure 5: Effect of temperature on the removal of MB

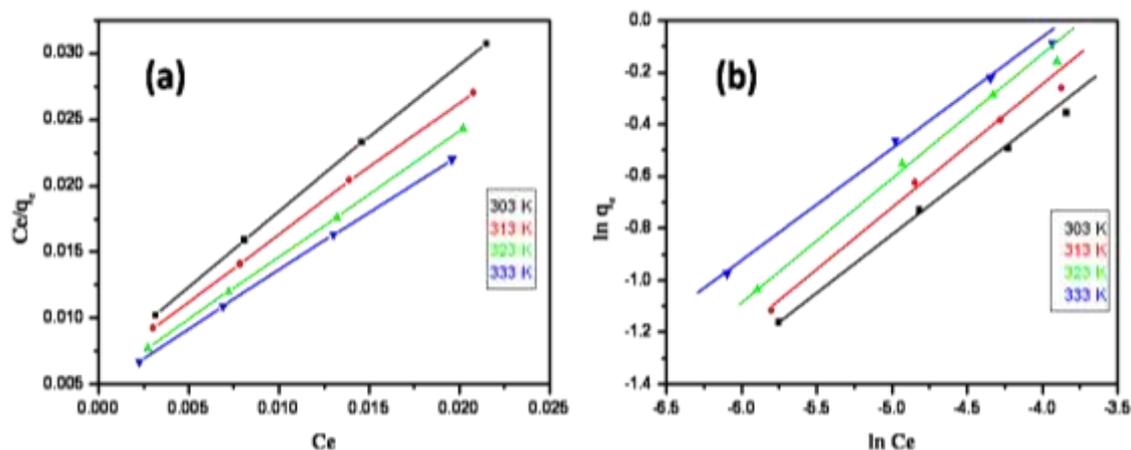


Figure 6: (a) Langmuir isotherm and (b) Freundlich isotherm

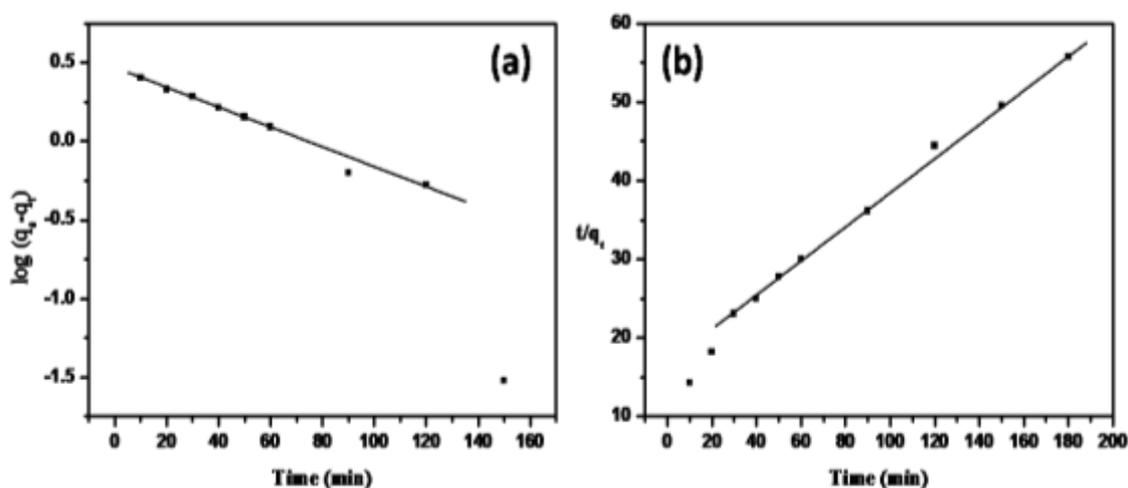


Figure 7: (a) First order kinetics and (b) Second order kinetics

V. Conclusion

Adsorption studies indicate that the exchanger titanium tin molybdate is an effective adsorbent for the removal of methylene blue dye from aqueous solution. The isotherm models such as Langmuir and Freundlich were studied, amongst them Langmuir equation showed the more applicability to the experimental data than Freundlich isotherm. The rate of adsorption was studied using pseudo first order and second order kinetic equations, and it was found that the data fits better with pseudo-second order model. The whole studies revealed that the new exchanger TSM could be employed as an effective and economically viable adsorbent in wastewater treatment for the removal of toxic heavy metal ions and hazardous organic dyes.

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