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Adsorption of methylene blue from industrial effluent using poly (vinyl alcohol)

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Abstract

The application of poly (vinyl alcohol) (PVA) in an unmodified form as an adsorbent for methylene blue (MB) dye removal in waste water at 303–333K was investigated. Effects of operational parameters such as adsorbent dosage, initial dye concentration and pH were determined for optimum conditions for maximum dye removal. Results obtained showed that dye removal efficiency increases as the amount of adsorbent increased. Lowest initial dye concentration and at pH of 4.0 gave maximum adsorption of MB onto PVA. Adsorption parameters were found to fit well into Langmuir, Freundlich and Temkin adsorption isotherm models with correlation coefficient ($R^2 > 0.95$) in the concentration range of MB studied. Adsorption kinetics studies revealed that pseudo-second order provided the best fit to experimental data compared with pseudo-first-order model. Thermodynamic parameters revealed that the adsorption process was non-spontaneous and exothermic with an orderly mixing adherence of the dye molecules on the adsorbent surface.

Keywords: Poly (vinyl alcohol), Methylene blue, Adsorption, Isotherm, Kinetics

1. Introduction

The need to maintain a cleaner environment for the survival of both aquatic and terrestrial lives including human beings is very crucial and is a subject of increasing concern to the environmentalist. Pollution caused by agents such as heavy metals and dyes are amongst the list which rendered the environment unwholesome and posed serious health concern to the populace. Effluents from industries such as dyestuff, textiles, leather, paper, printing, plastic and food [1] contain various dyestuffs. Dye, a highly coloured and synthetic substance contain at least one chromophores (colur bearing group) and auxochromes (colour helpers) [2] which impart intense colours to them and are undesirable and disgusting in wastewater. Water soluble dyes are characterized by their biodegradable ability and conventional treatment techniques such as flocculation, chemical oxidation, and membrane separation are not suitable. Nevertheless, adsorption has proven to be potentially powerful because of its imaginable opportunity to design the chemical composition of the adsorbent surface [3-5].

The dye used in this study is methylene blue. Its structural formula is shown in Fig. 1. Methylene blue is a model cationic dye employed by industries such textile industry for a variety of purposes. It is a heterocyclic aromatic chemical compound with a molecular formula $C_{16}H_{18}N_3SCl$. Methylene blue can cause eye burn which may be responsible for permanent injury to the eyes of human as well as aquatic animals. It can also cause irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. Methylene blue also causes irritation to the skin when in contact with it [6].

Several methods have been developed for the removal of dye from waste water. These include physiochemical, chemical and biological methods such as coagulation and flocculation [7], ozonation [8], electrochemical methods [9], fungal decolonization [10] and adsorption [11-14]. Amongst the techniques mentioned, adsorption is the method of choice because of its ease of operation and design. Adsorption employs adsorbent- a substance which attaches the substrate or solvent molecule to its surface and several materials have been applied as adsorbent for the treatment of waste water. Agricultural waste and activated carbon have proven very efficient as adsorbent for many compounds including various classes of dyes.

In the last few decades however, polymers and polymeric gels which have attracted much interest in the field of biotechnology and medicine [15] have been directed towards separation work and many studies on dye adsorption by polymers have been published. In comparison with classical adsorbents such as activated carbon and clay, synthetic polymeric adsorbent is more attractive because of its favorable physicochemical stability, high selectivity and structural diversity, eco-friendliness and regeneration abilities [16-18]. The application of polymers as adsorbent in the removal of cationic/anionic dyes can be found in literature. For instance Malana et al., [13] reported the removal of industrially important dyes from aqueous media onto polymeric gels by adsorption process. In recent years a wide variety of polymers and polymer composites such as cyclodextrin polymer [19], novel polymer- Jalshakti [20], polystyrene-block-poly(N-isopropylacrylamide) [21], PVA hydrogels and PVA/AC composites [22], polyacrylamide [23], polymer gels [13], Polymer Macronet (MN 200) [16, 24, 25], poly (methacrylic acid)-modified chitosan [25] etc. have been reported as excellent adsorbents for the removal of various dyes and organic contaminants from aqueous solution.

As part of our contribution to the growing interest of using polymeric materials as adsorbent in removal of dye from aqueous solutions, the present work reports on the use of unmodified PVA to remove MB from waste water. The effect of adsorbent amount, pH, and concentration and time on dye removal is also investigated. Langmuir, Freundlich and Temkin isotherm models are applied to examine the nature of adsorption. Adsorption kinetics and thermodynamic studies have also been evaluated.

2. Materials and Methods

2.1 Materials

Poly vinyl alcohol (PVA) DP −1700 to 1800; MW − 74800-79200; Hydrolysis (mole %) − 98-99 was obtained from Burbidges Burgoyne & Co. Mumbai, India. Methylene blue (MB (a cationic dye)) used as an adsorbate was purchased from Smerck fine chemicals, Onitsha, Nigeria. MB has molecular weight of 319.85 g/mol. It was used as received without further purification. Other reagents include concentrated HCl and dilute NaOH solutions. All reagents were of analytical grade. Deionized water was used throughout the experiment. Instruments employed for the work include UV-visible spectrophotometer (Unicam), electric (platform shaker 20-880), mottle P165 weighing balance, pH-meter-16 and centrifuge (model 800D).

2.2 Preparation of adsorbent

Poly (vinyl alcohol) was used as the adsorbent and without further chemical treatment. A measured quantity was immersed in hot water for three hours. The swollen gel was filtered and oven dried at 60^{o}C for 2 hours.

2.3 Determination of point of zero charge

The pHzpc for the adsorbent was determined according to the method of El-sayed [26]. 1.0g of the polymer was placed to 250 mL conical flask; 50 mL of deionized water was added. The initial pH values of the solution were roughly adjusted to 2.0–10 by adding either 0.1 M HCl or 0.1 M NaOH. The mixtures were shaken manually and allowed to equilibrate for 24 h with periodic shaking. The pH values of the supernatant liquids were noted and the relation between the initial and final pH values was deduced and evaluated to obtain the pHzpc 4.3

2.4 Physical characterization of PVA

The properties of the PVA adsorbent including density, pore volume and porosity were determined according to the method of Wana et al. [27]. The apparent surface area was measured from N_2 adsorption at 77K in a Quantrachrome Autosorb I-CLP. Total surface areas were calculated using the BET equation [28]. The values for density, total pore volume, porosity and BET surface area are 1.12-1.16 gcm^{-3}, 0.124 cm^3g^{-1}, 0.119 and 68.2 m^2g^{-1} respectively.

2.5 Batch experiments

Batch equilibrium technique was used to study adsorption of methylene blue onto PVA. Adsorption experiments were carried out in 250 mL flask and the total volume of the reaction solution was kept at 50 mL. The flasks were shaken at 200rpm for an equilibrium time in a platform shaker. Five different concentrations were used to optimize the effect of initial concentration on the adsorption process. The effect of adsorbent dosage on the removal of MB was studied with different adsorbent dosages (0.2−1.0g) with 50 mL dye solution and shaken for equilibrium time. The effect of pH on the removal of MB was investigated over the pH range from 2.0 to 10.0. The initial solution pH was adjusted using 0.1M HCl or 0.1M NaOH. Adsorption equilibrium experiments were performed by stirring 50 mL of MB aqueous solution with initial concentration of (5 −25) mg L^{-1} in each 50 mL flask containing 0.2 g of the adsorbents. The solutions were agitated for different time intervals. Adsorption kinetic experiments were performed by keeping 0.2 g of adsorbent and 50 mL of MB aqueous solution of (5−25) mg L^{-1} in a series of 250 mL flasks, maintained at ambient temperature. Then the flasks were taken out at some intervals. After adsorption, the adsorbent and the supernatants were separated by centrifugation at 4000rpm for 10min. The supernatant were analyzed for residual dye concentration using a UV−Visible Spectrophotometer by monitoring the absorbance changes at λ_{max} 650nm. The amount of dye adsorbed per gram of adsorbent (q_e) and the percentage removal efficiency (*%R*) were calculated using equations (1) and (2), respectively:

$$q_e = \frac{V}{m}(Ce - Co) \tag{1}$$

$$\%\,\mathrm{R} = \frac{Co - Ce}{Co} \times 100 \tag{2}$$

where C_o and C_e are initial and equilibrium MB concentrations, respectively ($mgL{-}^{1}$), V is MB solution volume (L); m is the mass of adsorbent (g). The effects of temperature on the adsorption data were carried out by performing the adsorption experiments at various temperatures (303, 313, 323 and 333K). The equilibrium data were analyzed using the Langmuir, Freundlich and Temkin isotherms and the characteristics parameters for each isotherm have been determined.

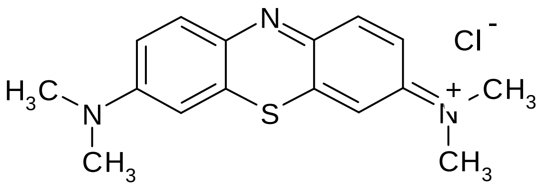

Figure 1: Chemical structure of methylene blue dye

3. Results and discussion

3.1 *Effect of adsorbent dosage*

The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of dye solution. Fig. 2 shows effect of dosage on the adsorption capacity of MB onto PVA. From the figure, it can be deduced that the adsorption capacity increases with decrease in adsorbent dosage. At 0.2mg the adsorption capacity was $2.75mgg^{-1}$ which decreased to $0.95mgg^{-1}$ at 1.0g. This is due to greater availability of the exchangeable sites or surface area at a higher concentration of the adsorbent [29]. However, with increase in the amount of adsorbent percentage removal of the dye was found to increase. Such a trend is mainly attributed to the fact that with increase in the amount of adsorbent the adsorptive surface area increases which provides a greater number of active sites for adsorption [30].

3.2 Effect of pH

The pH of a medium controls the magnitude of electrostatic charges which are imparted by the ionized dye molecules. As a result, the rate of adsorption will vary with the pH of an aqueous medium [31]. Fig. 3 shows the percentage adsorption of MB onto PVA at different pH of the solution at room temperature. It can be seen that maximum adsorption of the dye onto PVA was at the pH of 4.0. The concept of pHzpc could not fully explain the adsorption process. Two mechanism of sorption may be proposed in this case (i) chemical reaction between –OH group of the PVA and the reactive group Cl^{-} in MB, resulting in MB adsorption on the surface and eliminating HCl in solution [32] and (ii) the mechanism of electrostatic interaction between protonated and deprotonated group of the adsorbent with the dye may be at work. At pH ≤ 4, the surface of the polymer is protonated as shown below:

$OH^{-} + H^{+} \rightarrow OH_2^{+}$
$OH_2^{+} + D^{+} \rightarrow OH_2^{+} \ldots D^{+}$ (columbic repulsion)

Interaction with the cations of the dye leads to a decrease adsorption. However, high adsorption was recorded within this pH region. This fact might be through a combination of other forces at play such as vander Waals forces and hydrogen bonding [33].

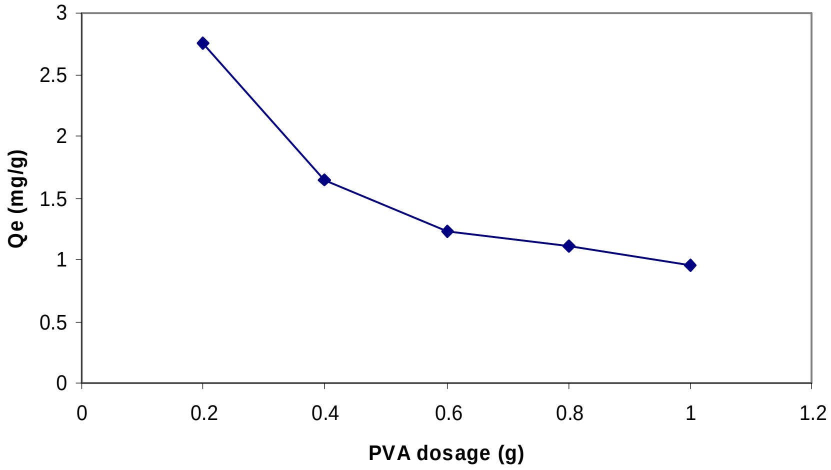

Figure 2: Effect of dosage effect on the adsorption capacity of PVA

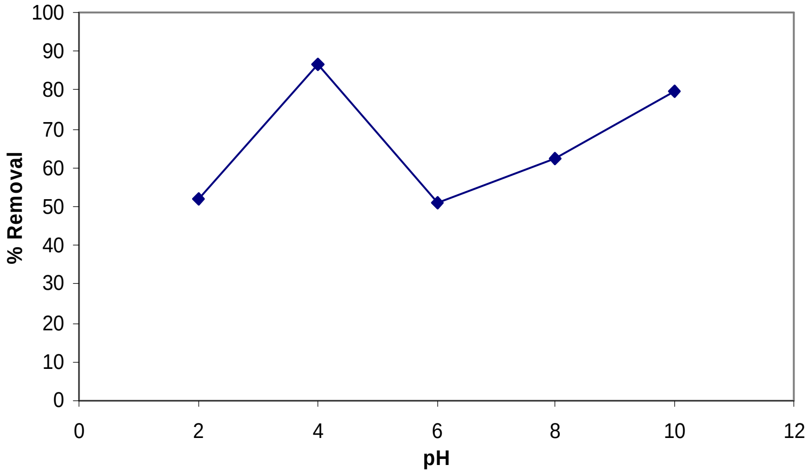

Figure 3: Effect of pH on the adsorption of MB onto PVA

After pH of 6.0, adsorption increased gradually, deprotonation occurs which releases a free oxygen on the surface of the PVA. This creates electrostatic attraction with the cations resulting in increase in adsorption:
$OH^{-} \rightarrow O^{-} + H^{+}$
$O^{-} + D^{+} \rightarrow O^{-} \ldots D^{+}$ (Coloumbic attraction)
This result is in line with reports of other researchers. Maximum adsorption of methylene blue, a cationic dye by banana stalk was noted by Hameed *et al* [34] and adsorption of methyl red by activated carbon prepared from the *Annona squmosa* seed as reported by Santhi *et al* [12] at pH 4.0. From the figure it obvious that high adsorption takes place at low pH. Literature reports indicate that increased pH should result in increase in

adsorption for cationic dyes due to increase in number of negatively charged surface sites on the adsorbent resulting in electrostatic attraction [35].

3.3 Effect of initial concentration

The effect of the initial dye concentration factor depends on the immediate relation between the dye concentration and the available binding sites on an adsorbent surface [36]. Fig.4 shows the effect of initial dye concentration. Generally the percentage of dye removal decreases with an increase in initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface [37]. At low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will disappear [38]. However, the increase in the initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass at a high initial dye concentration [39]. In other words, the residual concentration of dye molecules will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of initial number of dye molecules to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of initial concentration.

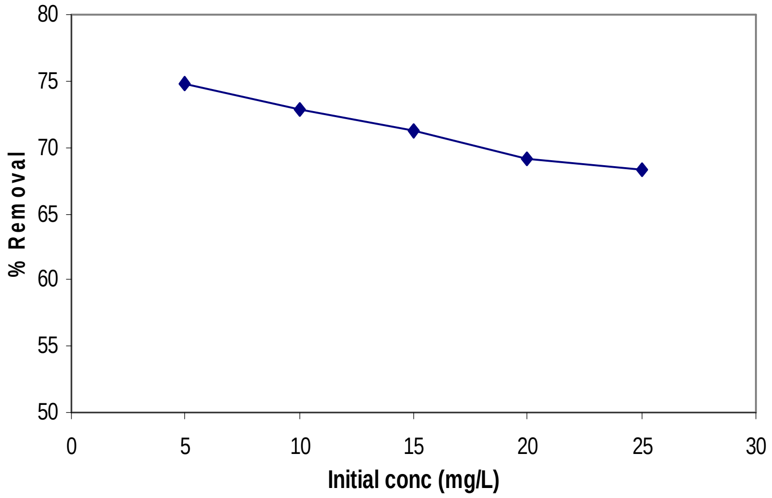

Figure 4: Effect of initial concentration on MB adsorption onto PVA

3.4 Adsorption isotherm

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 [40]. It is significant for understanding the adsorption behavior to identify the most appropriate adsorption isotherm model. In this paper, Langmuir, Freundlich and Temkin isotherm were employed to investigate the adsorption behaviour. Adsorption isotherm was studied at four different temperatures viz 303, 313, 323 and 333K.

3.4.1 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. 5. 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 (PVA) are presented in Table 1.

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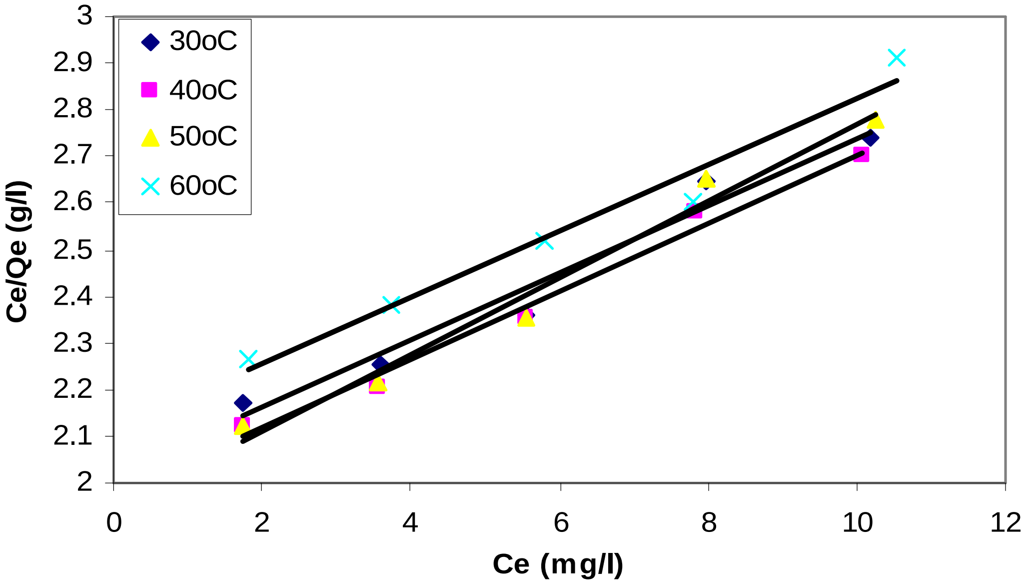

Figure 5: Langmuir isotherm plot for MB adsorption onto PVA

Table 1. Isotherm parameters for the adsorption of Methylene blue on PVA.

Model	Parameters	Temperature (K)			
		303 ± 0.5	313 ± 0.5	323 ± 0.5	333 ± 0.5
Langmuir isotherm	Q_{max} (mg/g^{-1})	13.80	13.70	12.20	12.10
	$b(L/mg^{-1})$	27.8	26.9	23.8	29.7
	R_L	0.0014	0.0015	0.0017	0.0013
	R^2	0.971	0.980	0.987	0.968
Freundlich isotherm	K_F $(mg^{1-1/n}L^{1/n}g^{-1})$	0.50	0.53	0.53	0.51
	$1/n$	0.86	0.85	0.84	0.86
	R^2	0.998	0.997	0.998	0.996
Temkin isotherm	K_T	0.93	0.94	0.93	0.93
	B_1	1.61	1.60	1.58	1.57
	R^2	0.971	0.970	0.972	0.971

The correlation coefficient values ($R^2 > 0.96$) (Table 1) show strong positive correlation indicating that adsorption follows Langmuir isotherm. The maximum adsorption capacity, $q_{max,}$ obtained from the Langmuir plot is 13.8mgg^{-1} at the lowest temperature studied and decreased with increase in temperature which suggests exothermic nature of the adsorption. This value is higher than those reported by other researchers on to polymeric materials. For instance Malana et al. [13], reported adsorption capacity of 1.017, 1.875 and 2.610mgg^{-1} for methylene blue onto three novel polymeric gels. It can be predicted whether an adsorption system is favourable or unfavourable using the essential characteristic of the Langmuir isotherm expressed by means of $R_{L,}$ a dimensionless constant referred to as separation factor or equilibrium parameter defined by:

$$R_L = \frac{1}{1 + K_L C_O} \tag{4},$$

[41], where C_o is the highest initial concentration. The parameter suggests the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$). As can be seen from Table 1, at all the temperatures studied the value of R_L is less 1 which suggest that adsorption is favourable.

3.4.2 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:

$$q_e = K_F C_e^{1/n} \tag{5}$$

This can be linearized to

$$Log\, q_e = Log\, K_F + \frac{1}{n} Log\, C_e \tag{6}$$

where $k_F\,(mg^{1-1/n}L^{1/n}g^{-1})$ is adsorption capacity and n, a dimensionless constant, can be used to explain the extent of adsorption and the adsorption intensity between the solute concentration and adsorbent respectively. The values of k_F and n were calculated from the intercepts and slopes of the 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. It becomes more heterogeneous as its value gets closer to zero and a value of $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption [42, 43]. The plots of the linear form of Freundlich isotherm curves at different temperatures are presented in Fig. 6. The Freundlich parameters and correlation coefficients (R^2) evaluated from the plots are listed in Table 1. Accordingly, the Freundlich constants (K_F and n) and R^2 presented in Table 1, shows that Freundlich model could also be used to explain adsorption process.

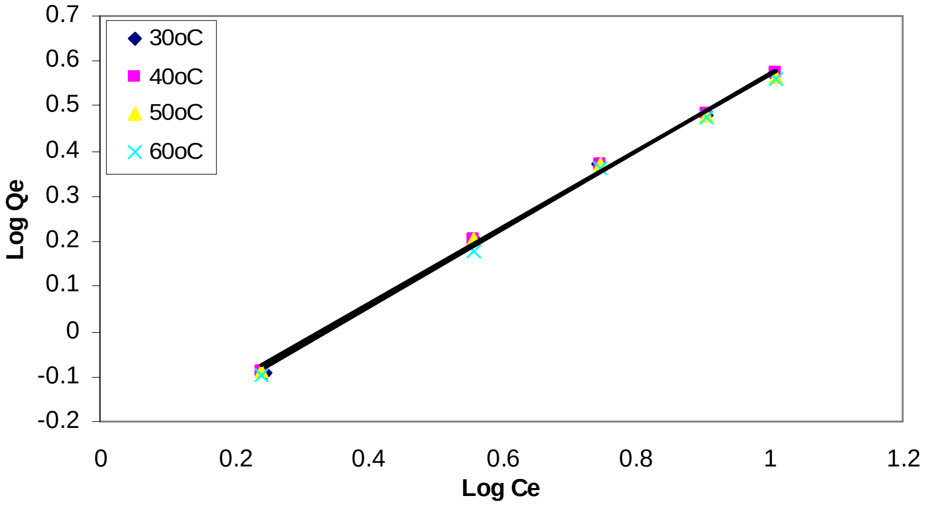

Figure 6: Freundlich isotherm plot for the adsorption of MB onto PVA

3.4.3 Temkin isotherm

Temkin isotherm model considers the effect of indirect adsorbent-adsorbate interactions on adsorption, and suggests that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to these interactions [44]. This model also assumes that adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has commonly been applied in the following form:

$$q_e = B_1 \text{In}\, K_T + B_1 \text{In}\, C_e, \quad (7)$$

where B_1 is the Temkin constant related to the heat of adsorption and K_T is the equilibrium binding constant (Lmg^{-1}). The constant K_T and B_1 can be determined by a plot of q_e versus In C_e shown in Fig. 7. Correlation coefficient, R^2 values and the Temkin isothermic parameters are summarized in Table 1. The Temkin constant, B_1, showed that the heat of adsorption of methylene blue onto PVA showed a slight decrease in value at higher temperatures indicating an exothermic process.

Comparing the isotherm models for the adsorption of MB onto PVA, it could be deduced that all the three isotherm models are applicable as revealed with good regression coefficients ($R^2 > 0.99$) in the concentration range studied (Table 1).

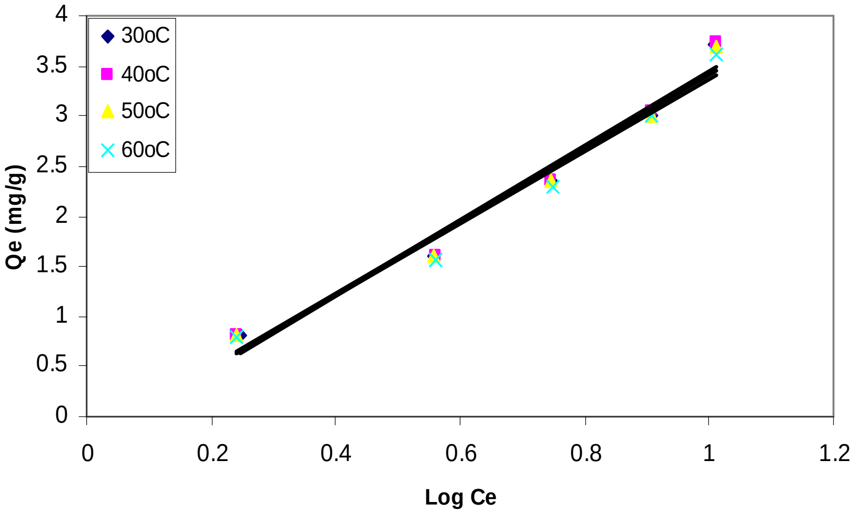

Figure 7: Temkin isotherm plot for the adsorption of MB onto PVA

3.5 Adsorption Kinetics

For the examination of the controlling mechanisms of adsorption process, such as chemical reaction, diffusion control and mass transfer [45, 46], 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 [45]:

$$Log(q_e - q_t) = Log\, q_e - \frac{K_1}{2.303} t \qquad (8)$$

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* $(q_e\text{-}q_t)$ against t (not shown). For the present study however, Lagergren pseudo-first order kinetics parameters (Table 2) was not proved to be effective in representing the experimental kinetic data for the entire adsorption period and at all dye concentrations. Calculated values of the adsorption capacity $q_{e,\,\text{cal}}$ (mgg^{-1}) did not agree with that of the experimental values $q_{e,\ \mathrm{exp}}$ (mgg^{-1}). Report of non fitting of pseudo-first order kinetic to adsorption has been published [47]. This result suggests that the kinetics of MB adsorption onto PVA can not be accounted for using the pseudo-first order model and hence not a chemisorptions' process.

The pseudo-second order kinetic model can be represented with the following equation [10, 48]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t\,, \qquad (9)$$

where k_2 is the rate constant of pseudo-second order adsorption *(gmg*$^{-1}$*min*$^{-1}$*)*. Fig. 8 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 (Fig. 8). Calculated values of the adsorption capacity $q_{e,\mathrm{cal}}$ (mgg^{-1}) gave a better agreement with that of the experimental values $q_{e,\mathrm{exp}}$, (mgg^{-1}) and correlation coefficient ($R^2 > 0.99$) (Table 2). 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 PVA. The kinetics of adsorption of many dye species onto various materials have been reported to conform to pseudo-second order kinetic model [49, 50].

Table 2. Adsorption kinetic parameters for the adsorption of Methylene blue onto PVA at 300 ± 0.5 K.

Conc. of dye (mgg^{-1})	$Q_{e,\ \mathrm{exp}}$ (mgg^{-1})	Pseudo-first order			Second-order order		
		K_1	$Q_{e,\ \mathrm{cal}}$ (mgg^{-1})	R^2	K_2	$Q_{e,\ \mathrm{cal}}$ (mgg^{-1})	R^2
PVA							
5	0.81	0.034	0.20	0.89	0.420	0.83	0.999
10	1.60	0.029	0.42	0.90	0.244	1.70	0.991
15	2.36	0.035	0.89	0.92	0.087	2.44	0.999
20	3.01	0.031	0.78	0.86	0.077	3.11	0.999
25	3.71	0.036	1.02	0.94	0.076	3.83	0.999

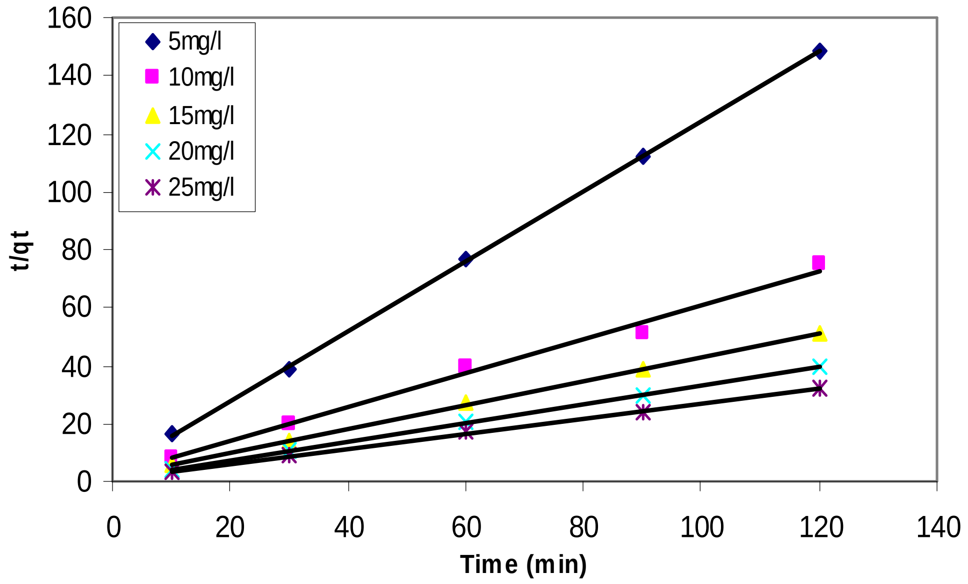

Figure 8: Pseudo-second order kinetic plot for the adsorption of MB onto PVA

3.6 Thermodynamic studies

The thermodynamics of the adsorption process were studied at four different temperatures in a thermostated water bath. The adsorption capacity increased from 0.30 to 1.23mgg^{-1} between 303 and 333K (Fig.9). The results show that the adsorption of PVA decreased with increase in temperature, indicating an exothermic process. This may be due to weakening of the adsorption forces between the active sites of the polymer and the dye species, and also between adjacent dye molecules on the adsorbed phase [50].

Thermodynamic parameters such as the Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) can be used for the characterization of temperature effect. These parameters were calculated using the following equations:

$$\Delta G = -RT In K_L \quad \text{(Gibbs equation)} \tag{10}$$

$$In K_L = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{(Van't Hoff equation)} \tag{11}$$

where $K_L = \frac{q_e}{C_e}$, R is the molar gas constant (8.314 J/mol K) and T is the absolute temperature. K_L is the equilibrium constant obtained for each temperature from the Langmuir model. ΔH and ΔS were obtained from the slopes and intercepts of the linear plots of *In* K_L against *1/T* (Fig. 9).

The values of the thermodynamic parameters are given in Table 3. Increasing temperature may lower the forces of adsorption between the dye molecules and the adsorption sites on the PVA surface causing a decrease in adsorption capacity [36] (Fig. 9). Again, as the temperature is raised it is expected that the intermolecular forces of the adsorbent become weaker resulting in the release of adsorbed dye back to the system. In general the enthalpies of adsorption (ΔH) are negative and ranged between −0.57 to −2.30, which show that the adsorption process was exothermic in nature. However, these values did not indicate a strong chemical interaction between the adsorbent and adsorbate. The change in free energy (ΔG) was positive suggesting that adsorption process was non-spontaneous and led to an increase in the Gibbs free energy. Increase in the values of (ΔG) with increasing temperature also indicated that adsorption was more feasible at lower temperature. Negative values of ΔS shows a decrease in the degree of freedom which means that dye molecules were orderly adsorbed onto the adsorbent surface which increases as the concentration of the dye increased.

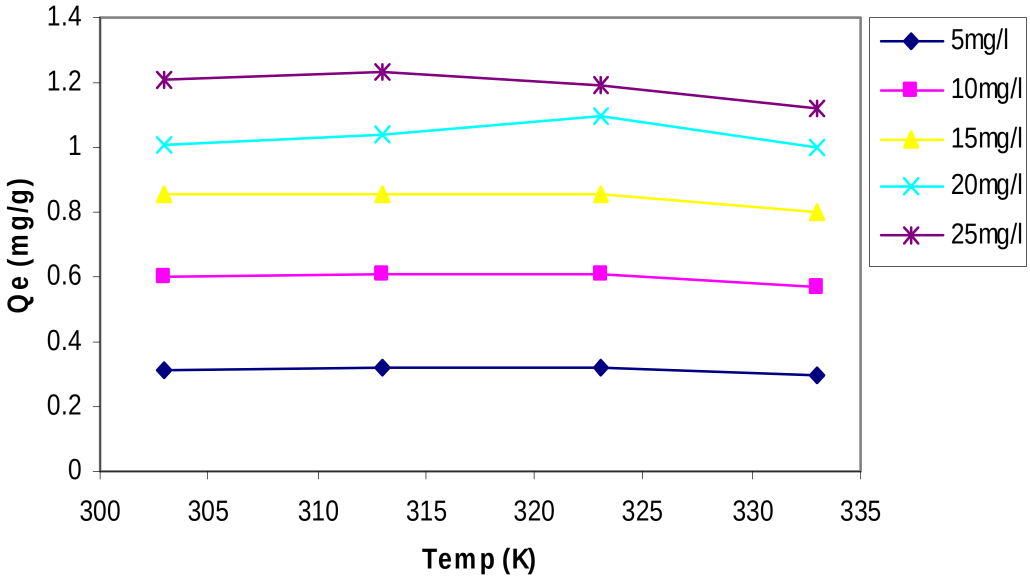

Figure 9: Adsorption capacities of MB adsorption onto PVA at four different temperatures

Table 3. Thermodynamic parameters for the adsorption of Methylene blue onto PVA

PVA						
Conc. of dye(mgl^{-1})	ΔH (kJmol^{-1})	ΔS (Jmol^{-1}K^{-1})	ΔG (kJmol^{-1})			
			303K	313K	323K	333K
5	-0.57	-22.5	6.32	6.41	6.62	7.01
10	-1.15	-24.8	6.44	6.41	6.74	7.21
15	-1.53	-26.5	6.56	6.77	6.74	7.46
20	-0.96	-26.0	6.96	6.71	7.42	7.71
25	-2.30	-30.9	7.08	7.37	7.61	8.03

Conclusions

Adsorption of methylene blue onto PVA at four different temperatures was investigated. Removal of the dye from its aqueous solution by PVA increased as the amount of adsorbent increased. Maximum removal was recorded at acidic pH of 4.0. It was observed that the adsorption of dye was almost constant as the temperature was increased a little above room temperature but showed an observed decreased with further increase in temperature to 333K. Adsorption data was observed to follow Langmuir, Freundlich and Temkin isotherm models at all temperatures studied. Thermodynamic parameters shown by the values of changes in enthalpy, entropy and Gibbs free energy indicated adsorption to be exothermic and adsorption kinetics was well described by pseudo-second order model.

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