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ISOTHERM AND KINETICS STUDIES FOR THE ADSORPTION OF METHYLENE BLUE AND METHYL RED DYES FROM AQUEOUS SOLUTIONS USING CHITOSAN

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ABSTRACT

These days, water pollution is very common, due to industrial progress thus the abundance of pollutants such as fertilizers, dyes, heavy metal, petroleum oils and many other pollutants. Chitosan is a very promising material to be used as an adsorbent due to the presence of hydroxyl and amino groups in its molecules which contribute to the adsorption of chitosan to various pollutants including dyes, phenols, ions, metals, pesticides and herbicides. In this research Chitosan is used to adsorb two different types of dyes which are Methylene Blue which is an anionic dye and Methyl Red which is a cationic dye. Effects of factors; initial solution pH, adsorbent dose, contact time and initial dye concentration were studied for both dyes. To obtain the best contact time at which the maximum removal efficiency reached its maximum value, the experiments were performed at different times and under the following fixed conditions; adsorbent dose = 2 g/L, initial dye concentration = 0.5 mg/L and pH = 4. The removal percentage of Methylene Blue and Methyl Red increased from 86.8 to 90.84 % and from 85.5 to 94.8 %, respectively with increasing in the contact time from 5 to 90 minutes. To obtain the best pH at which the Methylene Blue removal efficiency reached its maximum value, the experiments were performed at different levels of pH and under the following fixed conditions; optimum time 90 min, adsorbent dose 2 g/L and initial dye concentration of 0.5 mg/L. The removal efficiency of Methylene Blue and Methyl Red increased from 86.16 to 94.89 % and from 89.88 % to 91.6 %, respectively with increasing in the pH from 2 to 4. With further increase in the pH from 6 to 12, the removal efficiency for Methylene Blue and Methyl Red decreased from 93.61 to 88.08 % and from 4.7 to 74.1 %. To obtain the best initial concentrations for both of dyes at which the removal efficiency reached its maximum value, the experiments were performed at different levels of initial dye concentrations and under the following conditions; optimum time 90 min, optimum pH = 4 and adsorbent dose 2 g/L. The removal efficiency of Methylene Blue increased from 89.35 to 93.25 % with increasing in the initial dye concentration in range from 0.1 to 0.3 mg/L and with further increase in the initial dye concentration from 0.3 to 0.5 mg/L resulted in decreasing in the removal efficiency from 93.25 to 92.76 %. The removal efficiency of Methyl Red increased from 91.39 to 84.93 % with increasing in the initial Methyl Red concentration from 0.1 to 0.5 mg/L. To obtain the best adsorbent dose at which the removal efficiency reached its maximum value, the experiments were performed at different levels of adsorbent dose and under the following conditions; optimum time 90 min, pH = 4 and initial dye concentration of 0.3 mg/L. The removal efficiency of Methylene Blue and Methyl Red increased from 79.77 to 93.61 % and from 69.86 to 91.6%, respectively with increasing in the adsorbent dose from 0.25 to 2 g/L. The Methylene Blue and Methyl Red adsorption were well described by pseudo second order kinetic model (R^2 value for both = 0.999) as it fitted with the experimental results of both dyes. The rate limiting step was determined using intra-particle diffusion model and Byod plot. For two parameters isotherm model; Freundlich and Halsey isotherms for Methylene Blue and Methyl Red R^2 = 0.964 and 0.995, respectively were fitted with the experimental results. For three parameters isotherm; Koble-Corrigan isotherm where the less value of Sum of Squared Error (SSE) = 0.0001 is fitted with the experimental results of Methylene Blue more than Langmuir –Freundlich and Redlich-Peterson isotherms. While for Methyl Red; the best fitted Three-Parameter model with the experimental results was Koble-Corrigan isotherm with SSE = 0.006 lower that Langmuir-Freundlich and Redlich-Peterson isotherm models.

Keywords: methylene blue, methyl red, adsorption, isotherm, kinetics.

1. INTRODUCTION

Dyes industry is started to expand with the beginning of the last century, where natural dyes are replaced by synthetic dyes [1]. As textile industry depends heavily on dyes [1]. Dyes consist of many categories such as azo and carbonyl dyes as anionic dyes, arylcarbonium and methine dyes as cationic dyes [2]. Those dyes used by mixing with water in huge basins, then, the materials to be dyed are submerged in this basin, where an amount of dyes remain in the water which will be wastewater later [2]. The formed wastewater is containing organic waste, heavy metal, hydrocarbons and other harmful compounds to human health and environment [3]. The need for materials to remove water pollutants becomes necessary. Hence the multiplicity of methods, including physical method like Filtration by membranes, Coagulation and flocculation method and adsorption technique [4]. Chemical method like Fenton's reagent and ozone (O_3) [5] and other depend on bio-treatment methods [6]. On other hand, Chitosan is a natural biopolymer is produced from chitin which obtained from sea food waste [7]. It found that it has high ability to adsorb dyes [7]. At time the world is searching for safe and cheap way to get rid of water pollutants such as dyes and to increase the environmental remediation.

2. BATCH ADSORPTION EXPERIMENTS

Batch experiments were performed to determine the efficiency of Chitosan in Methylene Blue and Methyl Red removing using four effecting factors including initial solution pH from 2 to 12 which were adjusted by using 0.1 M NaOH and 0.1 M HCl solutions, initial dyes' concentrations range from 0.1 mg/L to 0.5 mg/L, adsorbent dose ranges from 0.25 g/L to 2 g/L and contact time ranges from 5 min to 90 min. Experiments were performed in glass conical flasks and they were shaken vigorously at 180 rpm. Upon shaking, samples were separated by using vacuum filtration. The concentrations for both dyes in the filtered solutions were measured by using a UV/VIS spectrophotometer.

3. RESULTS AND DISCUSSIONS

3.1 Effect of Changing the Contact Time

Equilibrium time was determined by calculating the concentration after adsorption process by using standard curve where the concentration of Methylene Blue after adsorption was almost constant. The removal percentage of Methylene Blue and Methyl Red increased from 86.8 to 90.84 % and from 85.5 to 94.8%, respectively. Tables 1 and 2 represented the effect of changing the contact time on the removal efficiencies of Methylene Blue and Methyl Red.

Table-1. Determination of the Equilibrium time for removal of Methylene Blue using Chitosan.

	Time (min)	Absorbance (nm)	Concentration After Adsorption (mg/L)	% Removal
	5	0.062	0.066	86.8
	10	0.053	0.056	88.71
	20	0.049	0.052	89.57
	30	0.046	0.048	90.21
	60	0.045	0.047	90.42
Best Time	90	0.043	0.045	90.84

Table-2. Determination of the Equilibrium time for removal of Methyl Red using Chitosan.

	Time (min.)	Absorbance (nm)	Concentration After Adsorption (mg/L)	% Removal
	5	0.067	0.072	85.58
	10	0.058	0.062	87.51
	20	0.039	0.042	91.6
	30	0.03	0.032	93.54
	60	0.028	0.03	93.97
Best Time	90	0.024	0.026	94.83

3.2 Effect of Changing pH

pH experiments were performed at different levels of pH and under the following fixed conditions; optimum time 90 min, adsorbent dose 2 g/L and initial dye concentration of 0.5 mg/L. The best pH was achieved at the lowest concentration of Methylene Blue after adsorption process. The removal efficiency of Methylene Blue and Methyl Red increased from 86.16 to 94.89 % and from 89.88 to 91.6%, respectively with increasing in the pH from 2 to 4. While in a pH range from 6 to 12, the removal efficiency of Methylene Blue and Methyl Red decreased from 93.61 to 88.08 % and from 84.7 to 74.1 % due to increasing in the OH- groups in the solution leading to decreasing in the removal efficiency of the anionic dye. Tables 3 and 4 represented the effect of changing the initial solution pH on the removal efficiencies of Methylene Blue and Methyl Red.

Table-3. Data of adsorption process pH vs concentration of Methylene Blue.

	pH	Absorbance (nm)	Concentration After Adsorption (mg/L)	% Removal
	2	0.065	0.069	86.16
Best pH	4	0.024	0.025	94.89
	6	0.03	0.032	93.61
	8	0.041	0.043	91.27
	10	0.051	0.054	89.14
	12	0.056	0.059	88.08

Table-4. Data of adsorption process pH vs concentration of Methyl Red.

	pH	Absorbance (nm)	Concentration After Adsorption (mg/L)	% Removal
	2	0.047	0.05	89.88
Best pH	4	0.039	0.042	91.6
	6	0.071	0.076	84.72
	8	0.084	0.090	81.92
	10	0.093	0.10	79.98
	12	0.12	0.13	74.17

3.3 Effect of Changing Initial Concentrations of Methylene Blue and Methyl Red

Optimum initial dye concentration experiments are performed at different levels of initial dye concentrations and under the following conditions; optimum time 90 min, optimum pH = 4 and adsorbent dose 2 g/L. The best initial concentration of Methylene Blue (0.3 mg/L) was determined by calculating the concentration after adsorption process where the lowest concentration of Methylene Blue after adsorption process was achieved. The removal efficiency increased from 89.35 to 93.25 % with increasing in the initial dye concentration in range from 0.1 to 0.3 mg/L. This may be happened because, in earlier adsorption stages the reaction between the dye and the adsorbent is in a high rate so, the efficiency of dye removal increases. While with further increase in the initial dye concentration from 0.3 to 0.5 mg/L results in decreasing in the removal efficiency from 93.25 to 92.76 % as when the initial dye concentration increased from 0.3 to 0.5 mg/L. While for Methyl Red the removal efficiency increased from 91.39 to 84.93 % with increasing in the initial concentration from 0.1 to 0.5 mg/L. This is due to the increase in dye particles when the concentration increases leading to the saturation of the active sites of the adsorbent which decreases its efficiency to remove more dye particles. Tables 5 and 6 represented the effect of changing of initial concentrations of Methylene Blue and Methyl Red on their removal efficiencies.

Table-5. Different concentrations of Methylene Blue before adsorbing vs after adsorption.

	Initial Concentration (mg/L)	Absorbance (nm)	Concentration After Adsorption (mg/L)	% Removal
	0.1	0.01	0.01	89.35
	0.2	0.015	0.016	92.01
Best Initial Concentration	0.3	0.019	0.020	93.26
	0.4	0.028	0.029	92.55
	0.5	0.034	0.036	92.76

Table-6. Different concentrations of Methyl Red before adsorbing vs after adsorption.

	Initial Concentration (mg/L)	Absorbance (nm)	Concentration After Adsorption (mg/L)	% Removal
Best Initial Concentration	0.1	0.008	0.008	91.39
	0.2	0.02	0.021	89.24
	0.3	0.032	0.034	88.52
	0.4	0.054	0.058	85.47
	0.5	0.07	0.075	84.93

3.4 Effect of Changing the Adsorbent Dose

Adsorbent dose experiments were performed at different levels of adsorbent dose and under the following fixed conditions; contact time 90 min, pH = 4, initial Methylene Blue concentration of 0.3 mg/L and initial Methyl Red concentration 0.1 mg/L. The best adsorbent dose was at the lowest concentration of Methylene Blue after adsorption process. The adsorption efficiency of Methylene Blue and Methyl Red increased from 79.77 to 93.61 % and from 69.86 to 91.6 %, respectively with increasing in the adsorbent dose from 0.25 to 2 g/L. This happened due to increasing in the available active sites for dye adsorption with increasing in the adsorbent dose which resulted in increasing in the adsorption efficiency. Tables 7 and 8 represented the effect of changing the adsorbent dose on the removal efficiencies of Methylene Blue and Methyl Red.

Table-7. Data of adsorption dose vs concentration of Methylene Blue after adsorption.

	Adsorbent dose (g/L)	Absorbance (nm)	Concentration After Adsorption (mg/L)	% Removal
	0.25	0.057	0.06	79.77
	0.5	0.048	0.051	82.97
	1	0.042	0.044	85.10
	1.5	0.031	0.033	89.00
Best Adsorbent Dose	2	0.018	0.019	93.61

Table-8. Data of adsorption dose vs concentration of Methyl Red after adsorption.

	Adsorbent dose (g/L)	Absorbance (nm)	Concentration After Adsorption (mg/L)	% Removal
	0.25	**0.028**	**0.030**	**69.87**
	0.5	0.025	0.027	73.1
	1	0.02	0.021	78.48
	1.5	0.014	0.015	84.93
Best Adsorbent Dose	2	0.0078	0.0084	91.60

4. ADSORPTION KINETICS

Adsorption kinetics is important factor which must be understood before using of any adsorbent. There are two types of kinetics analysis linear or non-linear that is applied into each adsorption process, where coefficient of correlation is applied to reach the best model. Adsorption kinetics consist of curve or line which describes the rate of retention or immunity of solute molecules from an aqueous medium to solid- phase interface at curtained adsorbents dose, pH, temperature and aqueous flow rate.[8]. Pseudo First Order (PFO) kinetic model is called also Lagergren model. In the Pseudo Second Order kinetic model (PSO) rate of solute adsorption is proportional to the available sites on the adsorbent, where the amount of solute on solid phase interface of adsorbent is the driving force of the reaction that is proportional to the number of active sites available on the adsorbent. The following equations represent the PFO and PSO kinetic models;

$$\text{PFO: } \text{Log}\,(qe - q) = \text{Log}\,(qe) - \frac{k1 * t}{2.303} \quad (1)$$

$$\text{PSO: } \frac{t}{qt} = \frac{1}{k2 * qe^2} + \left(\frac{1}{qe}\right) * t \quad (2)$$

Where q_e and q_t are the amounts of nitrate adsorbed by adsorbent at equilibrium and at time (t), respectively. k_1, k_2 are rate constants for Pseudo first order and Pseudo second order, respectively [9], [10], [11].

4.1 Methylene Blue

The adsorption kinetics of Methylene Blue by Chitosan was studied at the following conditions; initial pH = 4, initial Methylene Blue concentration = 0.3 mg/L, temperature = 25 ºC, contact time = 90 min and adsorbent dose = 2 g/L. Figure-1 represented the PSO kinetic model for adsorption of Methylene Blue using Chitosan.

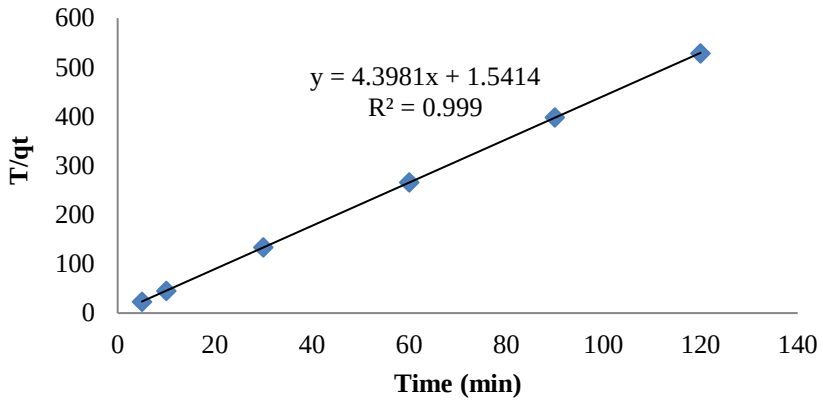

Figure-1. Pseudo second order kinetics model for Methylene Blue removal by the Chitosan.

Table-9 represented the parameters of kinetic models for Methylene Blue and Methyl Red; the correlations coefficients (R^2), initial adsorption rate (h), k_1 and k_2 are rate constants for Pseudo first order and Pseudo second order kinetic models, respectively.

Table-9. Pseudo first order and Pseudo second order kinetic models parameters for Methylene Blue.

Kinetic model	Parameters	Methylene Blue	Methyl Red
PFO	**q_e (exp) (mg/g)**	**0.227**	**0.237**
	q_e (calculated) (mg/g)	106.43	0.023
	k_1 (min^{-1})	0.023	0.044
	R^2	0.774	0.859
PSO	q_e (exp) (mg/g)	0.227	0.237
	q_e (calculated) (mg/g)	0.648	0.31
	k_2 (mg/g. min)	0.54	2.47
	R^2	0.999	0.999

The results in Table-9 concluded that the PFO model was not suitable for the Methylene Blue and Methyl Red adsorption by Chitosan as the calculated values of adsorption capacity at equilibrium (q_e) showed higher difference with the experimental values than the PSO model. Also, the PFO model showed lower correlation coefficient values for Methylene Blue and Methyl Red adsorption than the PSO model where (R^2 = 0.999) for both dyes. Therefore, the Methylene Blue and Methyl Red adsorption by Chitosan could be well represented by the PSO kinetic model. It was observed that adsorption rate constant k_2 values in PSO model 0.54 and 2.47 mg/g.min for Methylene Blue and Methyl Red, respectively are higher than that of PFO model 0.023 and 0.044 min^{-1} for Methylene Blue and Methyl Red, respectively. This also ensured that the best fit model is PSO model due to the higher rate of Methylene Blue and Methyl Red adsorption from an aqueous solution using Chitosan.

As the Methylene Blue and Methyl Red adsorption by Chitosan suggested model was the PSO kinetic model which indicated that a chemisorption process occurred so, the rate limiting step for these systems were determined by the intra-particle diffusion model and Byod plot. The intra-particle diffusion model could be represented by the following equation [12], [11]:

$$qt = kdiffusion * T^2 + Ci \quad (3)$$

Where qt is the amount of nitrate adsorbed at time (t) and C_i is the thickness of layer and $k_{diffusion}$ is the adsorption rate constant of intra-particle diffusion model. The Byod plot was determined using the following equations [12]:

$$F = \frac{qt}{qmax} \quad (4)$$

Where the q_{max} is the maximum adsorbed amount of solute and F is the fraction of the adsorbed solute at any time (t).

The Bt values could be calculated at different contact times through the following equation [12]:

$$Bt = -0.4977 - \text{Ln}\,(1 - \text{F}) \quad (5)$$

Where B_t is the mathematical function of F.

Figure 2 represented the intra-particle diffusion model plot where the first linear portion represented the occurrence of film diffusion followed by another linear portion which represented the occurrence of intra-particle diffusion.

Byod plot is used to predict the actual limiting step involved in the adsorption process by plotting the B_t values vs. time (t) [12].

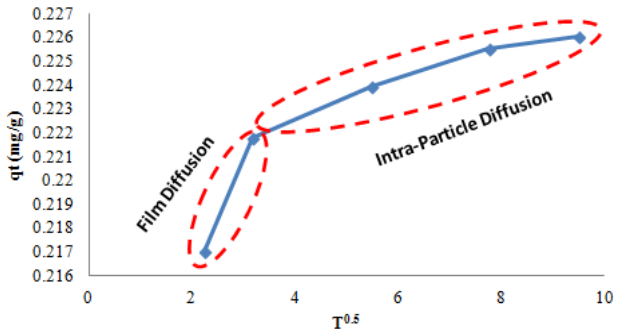

Figure-2. Intra-particle diffusion model for Methylene Blue removal by Chitosan.

Byod plot suggested that the actual slowest step was the film diffusion as the plot was linear and didn't pass through the origin as represented in Figure-3.

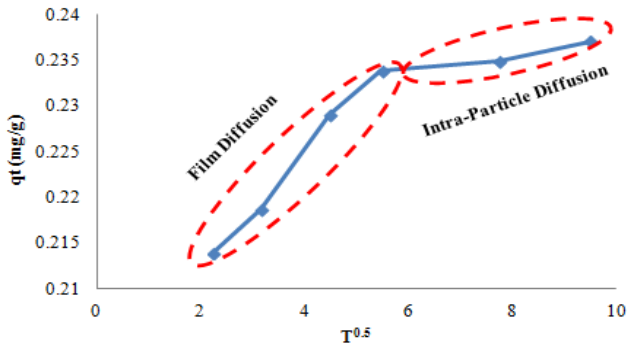

Figure-3. Byod Plot for Methylene Blue removal by Chitosan.

4.2 Methyl Red

Figure-4 represented the intra-particle diffusion model plot for Methyl Red adsorption by Chitosan where the first linear portion represented the occurrence of film diffusion followed by another linear portion which represented the occurrence of intra-particle diffusion.

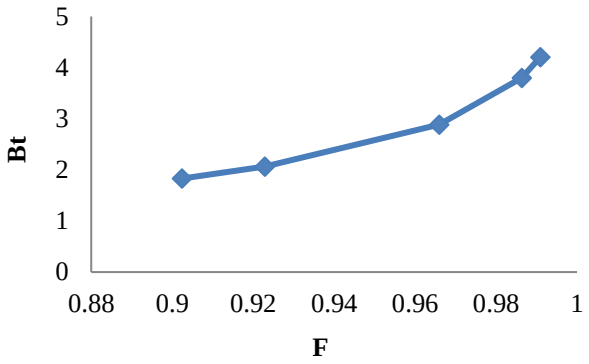

Figure-4. Intra-particle diffusion model for Methyl Red removal by Chitosan.

Byod plot suggested that the actual slowest step was the film diffusion as the plot was linear and didn't pass through the origin as represented in Figure-5.

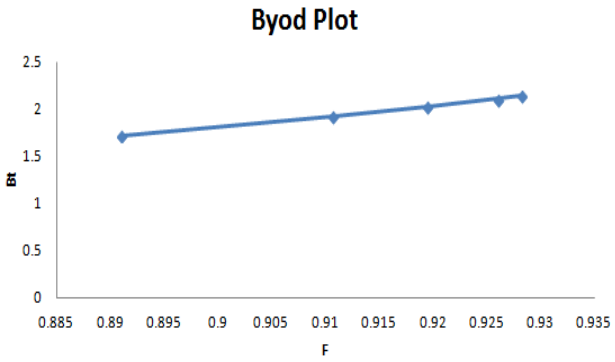

Figure-5. Byod Plot for Methylene Blue removal by Chitosan.

5. ADSORPTION ISOTHERM STUDIES

Two and three parameters isotherm models were studied to fit the experimental data obtained from the effect of Methylene Blue initial concentration from 0.1 to 0.5 mg/L on adsorption and under the following fixed conditions; pH = 4, contact time = 90 min and adsorbent dose = 3 g/L . Three parameters isotherm models are accurate than two parameters isotherm models because, they have three constants in their equations.

5.1 Two Parameters Isotherm Models

5.1.1 Langmuir

Langmuir isotherm model is concept of the monomolecular adsorption on homogeneous surfaces.

Langmuir is represented by the following equation [10], [13], [14]:

$$\frac{Ce}{qe} = (\frac{1}{qm}) * Ce + \frac{1}{qm*KL} \quad (6)$$

Where C_e and q_e represent the concentrations of nitrate at equilibrium (mg/L) in solution and in solid phase, respectively. q_m is the maximum monolayer adsorption capacity (mg/g) and K_L is the Langmuir constant which indicates the adsorption energy (L/mg). The values of q_m and K_L can be determined from the linear plot of C_e/q_e versus C_e.

5.1.2 Freundlich

This model is used to give information of the adsorption characteristics for the heterogeneous surface. Freundlich isotherm is represented by the following equation:

$$Log\ qe = Log\ KF + \frac{1}{n} * Log\ Ce \quad (7)$$

Where K_F (L/mg) and n are the Freundlich constants that indicate the adsorption capacity and adsorption intensity, respectively [10], [14].

5.1.3 Halsey

Halsey isotherm is used for multilayer adsorption system and heterogeneous surfaces for adsorption of metal ions at a relatively large distance from the surface [14]. Halsey isotherm is represented by the following equation:

$$Ln\ qe = \frac{1}{nH} * Ln\ KH - \frac{1}{n} * \ln\frac{1}{Ce} \quad (8)$$

Where K_H and n_H are the Halsey constants. Figures 4 and 5 represented the Halsey isotherm kinetic model for adsorption of Methylene Blue and Methyl Red adsorption by Chitosan.

5.1.4 Dubinin-Radshkuvich

Dubinin-Radushkevich isotherm model is an empirical adsorption model that expresses the adsorption mechanism using Gaussian energy distribution on heterogeneous surfaces [15]. This model is suitable only for intermediate range of adsorbate concentrations as it displays unrealistic behavior that does not predict Henry's laws at a low pressure. Dubinin-Radushkevich isotherm model:

$$\ln q_m = \ln q_e - \beta E^2 \quad (9)$$

$$\epsilon = RT \ln(1 + \frac{1}{C_e}) \quad (10)$$

$$E = \frac{1}{\sqrt{2B}} \quad (11)$$

Where ϵ is Polanyi potential, β is Dubinin-Radushkevich constant, R is the gas constant (8.31 $Jmol^{-1}$ k^{-1}), E is the mean adsorption energy and T is absolute temperature.

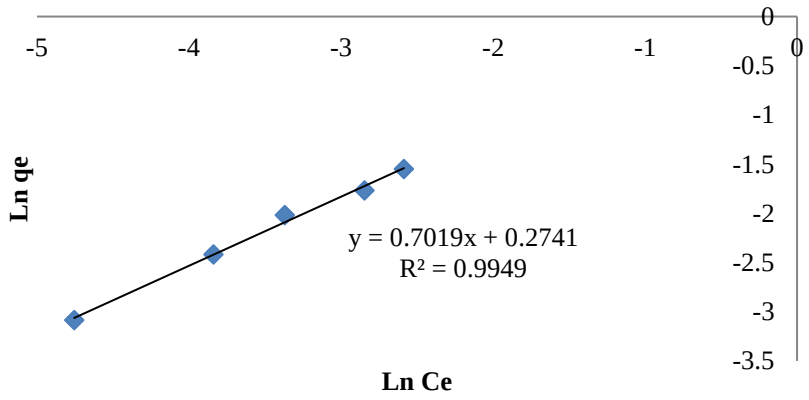

Figure-6. Halsey isotherm model for Methylene Blue adsorption by Chitosan.

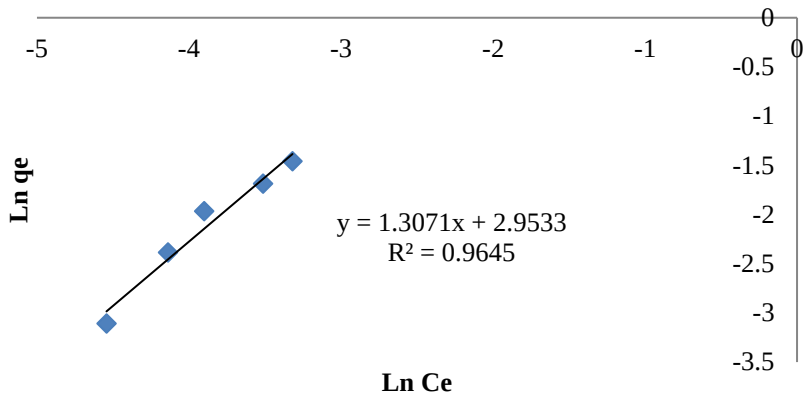

Figure-7. Halsey isotherm model for Methyl Red adsorption by Chitosan.

5.2 Three Parameters Isotherm Models

5.2.1 Langmuir-Freundlich

Langmuir-Freundlich isotherm characterizes the distribution of the adsorption energy onto the adsorbent's heterogeneous surface. Langmuir-Freundlich isotherm could be expressed by the following equation:

$$q_e = [q_m.(K_L.C_e)^n] / [1 + (K_L.C_e)^n] \quad (12)$$

Where q_m is maximum adsorption capacity (mg/g), K_L is equilibrium constant for heterogeneous adsorbent and n is heterogeneous parameter which lies in between 0 and 1. Non-linear regression method can be used to determine these parameters [15].

5.2.2 Koble-Carrigan

The Koble-Carrigan isotherm model is a combination of Langmuir and Freundlich isotherms which is used to represent the equilibrium adsorption data. Koble-Carrigan isotherm is expressed by the following equation:

$$q_e = A.C_e^n / (1 + B.C_e^n) \quad (13)$$

Where A $(L^n.mg^{1-n}/g)$, B $(L/mg)^n$ and n are the Koble-Carrigan constants, n is exponent that lies between 0 and 1 and q_e is the amount of pollutant which is adsorbed on the sorbent at equilibrium (mg/g) [14], [15], [10].

5.2.3 Redlich-Petreson

The Redlich-Petrson isotherm model is applicable for either heterogeneous or homogenous adsorption systems due to its characterization. Redlich-Petrson isotherm is expressed by the following equation:

$$q_e = A.C_e / (1 + B.C_e^{\beta}) \quad (14)$$

Where B is a constant (L/mg), A is the Redlich-Peterson isotherm constant (L/g), Ce is the equilibrium concentration (mg/L), β is exponent that lies between 0 and 1 and q_e is the amount of pollutant which is adsorbed on the sorbent at equilibrium (mg/g) [14], [10], [15].

Table-10 represented the results of the Two-Parameter and Three-Parameter isotherm models for Methylene Blue and Methyl Red adsorption by Chitosan. The best fitted isotherm models were Freundlich and Halsey as they had the greatest correlation coefficient values. This indicates that the surface heterogeneity of the adsorbent and the adsorption process operated under multilayer adsorption. It was found that the Halsey isotherm model is an excellent model to describe the multi-layer behaviour of adsorption [14] [14] [14] [14] [13] [12] [11] [10] [10] [9] [9] [8] [7] [6]. Dubinin-Radushkevich model indicated that the adsorption type of Methylene Blue and Methyl Red was a Chemisorption process because; the values of activation energy (E) for Methylene Blue (4248.64 kJ/mol) and for the Methyl Red (5630.77 kJ/mol) were higher than 8 kJ/mol. The higher value of K_F for Methylene Blue 19.17 L/mg than that of Methyl Red 1.31 L/mg indicated that Chitosan adsorbed Methylene Blue amounts higher than Methyl Red. The values of q_{max} for Methylene Blue and Methyl Red 0.424 mg/g and 0.354 mg/g, respectively indicates that Chitosan adsorbed higher Methylene Blue amounts than Methyl Red and this result was consistent with the values of the Freundlich constant K_F for Methylene Blue and Methyl Red. The higher value of the equilibrium constant (K_L= 16.44 L/mg) for Methylene Blue than the value of K_L for Methyl Red = 14.35 L/mg indicated that there was a stronger bonding between Methylene Blue and Chitosan than Methyl Red.

For three parameters isotherm models; Koble-Corrigan isotherm model was the best fitted with the experimental results of Methylene Blue as it had the lowest value of SSE = 0.0001 than the Redlich-Petrson and Langmuir-Freundlich isotherm models. Koble-Corrigan isotherm model was the best fitted with the experimental results of Methyl Red as it had the lowest value of SSE = 0.006 more than the Redlich-Petrson and Langmuir-Freundlich isotherm models. The value of parameter "n" in Koble-Carrigan isotherm model were 0.35 and 0.55 for Methylene Blue and Methyl Red, respectively which were closed zero, this indicated that the

equilibrium isotherm model was approaching to Freundlich equation [16].

Table-10. Results of the two-parameter and three-parameter isotherm models for Methylene Blue and Methyl Red adsorption by Chitosan.

		Parameters	Methylene Blue	Methyl Red
Two-Parameter Models	**Freundlich**	**R^2**	**0.964**	**0.995**
		1/n	1.3	0.7
		n	0.765	1.42
		K_F (L/mg)	19.17	1.31
	Halsey	R^2	0.964	0.995
		n_H	0.765	0.274
		K_H (L/mg)	2.26	0.377
	Langmuir	R^2	0.953	0.967
		Q_{max} (mg/g)	0.424	0.354
		K_L (L/mg)	16.44	14.35
	Dubinin-Radushkevich	R^2	0.960	0.994
		B (mol^2/J^2)	2.77E-08	1.57E-08
		E (KJ/mol)	4248.64	5630.77
		Q_{max} (mg/g)	1.65	2.5
Three-Parameter Models	Langmuir - Freundlich	SSE	0.001	0.007
		q_{MLF} (mg/g)	3.65	6.76
		M_{LF}	0.854	1.25
		K_{LF}	3.33	2.58
	Koble - Corrigan	SSE	0.0001	0.006
		A ($L^n.mg^{1-n}/g$)	1.68	7.9
		B $(L/mg)^n$	-0.5	-1.5
		n	0.35	0.55
	Redlich - Peterson	SSE	0.001	0.131
		A (L/g)	6.28	24.36
		B (L/mg)	-0.119	-1.52
		β (mg/g)	4.02	7.96

6. CONCLUSIONS

Pseudo Second Order kinetic model was the best model to describe the Methylene Blue and Methyl Red adsorption by Chitosan which indicated that a chemisorption process occurred between each dye and Chitosan. The rate limiting step was determined using intraparticle diffusion model and Byod plot which illustrated that film diffusion was the rate limiting step for adsorption system of Methylene Blue using Chitosan and for adsorption system of Methyl Red using Chitosan. Freundlich and Halsey isotherms were the best fitted model to describe the both adsorption systems. The values of q_{max} for Methylene Blue and Methyl Red 0.424 mg/g and 0.354 mg/g, respectively indicated that Chitosan adsorbed higher Methylene Blue amounts than Methyl Red. The maximum Methylene Blue removal 93.6 % was achieved at pH = 4, adsorbent dose 2 = g/L, initial Methylene Blue concentration = 0.3 mg/L and contact time = 90 min. The maximum Methyl Red removal 91.6 % was achieved at pH = 4, adsorbent dose 2 = g/L, initial Methyl Red concentration = 0.1 mg/L and contact time = 90 min.

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