

Removal of methylene blue from wastewater using Fe₂O₃ as an adsorbent

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ABSTRACT

The removal of methylene blue (MB) from wastewater was studied using ferric oxide (Fe₂O₃) as an adsorbent. The adsorption potential of Fe₂O₃ was investigated in batch adsorption experiment. The adsorption experiments were carried out with variation in contact time, initial pH, and temperature of the solution. The equilibrium time for the adsorption of MB on Fe₂O₃ was found to be about 3 h. Adsorption isotherms were measured at three different temperatures and found to fit Langmuir isotherm. The positive values of estimated enthalpy of adsorption were indicative of activated adsorption. Batch adsorption models, based on the assumptions of the Lagergren pseudo-first-order and the pseudo-second-order model, were applied to predict the kinetics of the adsorption and data fitted very well to the pseudo-second-order kinetic model.

Key words: Adsorption, Adsorbent, Equilibrium, Langmuir isotherm.

1. INTRODUCTION

Wastewater from textile finishing industries commonly contains moderate concentrations (10–200 mg/L) of dyestuffs, to contribute significantly to the pollution of aquatic ecosystems [1]. The introduction of waste products into the environment is a serious problem that has been highlighted by various environmentalist groups [2]. The dyestuffs have a complex chemical structure and are stable to light, heat and oxidation agents [3]. The source of such pollution lies in the rapid increase in the use of synthetic dyes. More than 10,000 chemically different dyes are being manufactured. The world dyestuff and dye intermediates production are estimated to be around 7×10^8 kg/annum [4,5]. Discharging of these dyes into water resources even in a small amount can affect the aquatic life and food web. Dyes can also cause allergic dermatitis and skin irritation. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms [2]. Although some existing technologies, such as chemical coagulation/flocculation, ozonation, cloud point extraction, oxidation processes, nanofiltration, chemical precipitation, ion-exchange, reverse osmosis, and ultrafiltration [2,6-8] may be efficient for the removal of dyestuffs, these techniques are rather expensive. Among treatment technologies, adsorption is rapidly gaining prominence as a method of treating aqueous effluent. Nowadays, numerous numbers of low-cost, commercially available adsorbents are used for the removal of dyes from colored wastewater [9]. However, the adsorption capacities of all the above adsorbents are not satisfactory. Therefore, new effective adsorbents which are low-cost and biodegradable are highly demanded. Basic dyes are the brightest class of dyes and are applied widely in small-scale industries such as textile, carpets, and wood industries whose discharge bearing dyes through effluents are added into natural streams. Methylene blue (MB) is a heterocyclic aromatic chemical compound. It is a cationic dye [10-13].

Fe₂O₃ is available as ore. In general, it is used as a photocatalyst, but it also can be used as an adsorbent to remove dyes. Fe₂O₃ is economically cheaper than other adsorbent. For these reason, Fe₂O₃ was selected as an adsorbent for the present study. Attempts have been made to explore the possibilities for the removal of MB and other dyes from aqueous solution by studying adsorption properties through

laboratory experiments. In the present work, the equilibrium time for adsorption, the adsorption isotherms, isobars, and kinetic parameters were determined. The effects of temperature and pH on adsorption were investigated.

2. MATERIALS AND METHODS

The cationic dye used in this study, MB was purchased from Merck, Germany and used without further purification. The dye stock solution was prepared by dissolving accurately weighed dye in de-ionized double distilled water. The experimental solutions were obtained by diluting the stock solution in accurate proportions to the needed initial concentrations. The other reagents used in this study were of pure analytical grade. The Fe₂O₃ powder (Fluka Chemika, Japan) was used as an adsorbent. Before use, the adsorbent was oven dried at 110°C for 12 h.

2.1. Optimization of pH for the Adsorption Experiment

For the determination of optimum pH, 0.1 g Fe₂O₃ was taken in each of nine bottles. 25.0 mL MB solution was taken in each bottle. The pH of the solution was adjusted in the range from 2.0 to 11.0 (microprocessor pH meter, HANNA Instrument, Romania). The bottles were placed in a thermostatic shaker (HAAKE, 5W B-20 Fisons Ltd., Germany) maintained at 30°C and were shaken continuously for 3 h. The reagent bottles were successively withdrawn after definite time, and the solution was centrifuged. After centrifuge, the pH of the solution was measured. The difference of this pH from initial pH was estimated as ΔpH. The plot of ΔpH versus initial pH produces a curve which intercepts the X-axis on one point.

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2.2. Estimation of the Equilibrium Time

The equilibrium time of the adsorption of MB on Fe_2O_3 was estimated at pH 9.0. 0.1 g of Fe_2O_3 and 25 mL of 3.0×10^{-5} M of MB solution were used in each of 13 bottles. The bottles were shaken in a thermostatic mechanical shaker at 30°C . After a definite interval of time, each bottle was withdrawn from the shaker. The supernatant of the bottle was transferred and centrifuged repeatedly until a clear liquid was obtained. The absorbance of the clear solution was measured spectrophotometrically at λ_{max} 663.0 nm (UV-1650 PC, Shimadzu, Japan). For blank 0.1 g of Fe_2O_3 and 25 mL of de-ionized double distilled water were added in a bottle. The bottle was shaken for 5 h at 30°C . The absorbance of the clear solution was also measured spectrophotometrically. The amount of MB adsorbed at time t (mg/g), q_t , onto Fe_2O_3 was calculated by a mass balance relationship,

$$q_t = (C_0 - C_t) V/m \quad (1)$$

At equilibrium time, the amount of MB adsorbed q_e (mg/g), was calculated by the following relationship,

$$q_e = (C_0 - C_e) V/m \quad (2)$$

Where C_0 is the initial dye concentration in the solution (mg/L); C_t is the residual dye concentration in the solution at any time t (mg/L); C_e is the residual dye concentration in the solution at equilibrium time (mg/L); V is the solution volume (L), and m is the mass of Fe_2O_3 (g). The plot of amount adsorbed, q_t (mg/g) versus the time (min) of adsorption is presented in Figure 1.

2.3. Adsorption Isotherm

Adsorption experiments were carried out on Fe_2O_3 using different initial concentrations of MB from 1.0×10^{-5} to 3.5×10^{-5} M at pH 9.0. 40 mL of each solution was taken in 6 bottles. The bottles were shaken in a thermostatic mechanical shaker at 30°C for 3 h. The bottles were withdrawn at the stipulated time from the shaker and supernatant was transferred to the centrifuge tube for centrifugation. The absorbance of the clear solution was measured spectrophotometrically. The relationship between the amount of MB adsorbed q_e (mg/g) and the residual dye concentration in the solution at equilibrium time C_e (mg/L) was calculated by the following Langmuir (Langmuir, 1916) and Freundlich (Freundlich, 1906) isotherms,

$$\text{Langmuir equation: } C_e/q_e = 1/V_m b + C_e/V_m \quad (3)$$

Where, Equation (3) represents a linear equation. Plots of (C_e/q_e) versus C_e give a straight line of line slope $1/V_m$ and intercept $1/V_m b$. Hence, V_m and b can be estimated.

$$\text{Freundlich equation: } x/m = k C_e^{1/n}$$

$$\log x/m = \log k + 1/n \log C_e$$

$$\log q_e = \log k + 1/n \log C_e \quad (4)$$

Where, q_e = amount of adsorbed species, C_e = equilibrium concentration of the solution, k and n are constant for a given adsorbate-adsorbent system.

2.4. Effect of Temperature

To determine the effect of temperature on adsorption isotherms at pH 9.0, adsorption experiments were performed at three different temperatures, namely 30°C , 40°C , and 50°C following the same procedure as discussed in the previous section.

3. RESULTS AND DISCUSSION

3.1. Determination of Optimum pH

Before measuring the equilibrium time for the adsorption of MB on Fe_2O_3 , it was important to determine the optimum pH of the solution to

be used for adsorption experiments. Figure 2 shows that the optimum pH was 9.0 at which minimum variation of solution pH was observed during the adsorption process. Optimization of solution pH is very important because if the solution pH is changed with adsorption time, it will be difficult to identify the sorption pH as well as the amount adsorbed. During the determination of the effect of pH on adsorption of MB on Fe_2O_3 , pHs of solutions were varied from 8 to 10 where the initial pH of solution did not change. The optimum pH for the adsorption experiment was found to be 9.0 for MB solution. The present study investigated the adsorption of MB on Fe_2O_3 at pH 9.0 and 30°C temperature.

3.2. Influence of pH on Adsorption

In general, surface charges of adsorbent and adsorbate are pH dependent. The zero point charge [14] (pH_{zpc}) of Fe_2O_3 is 7.9. Hence, at lower pH the concentration of H^+ ions present in the solution competes with the cationic dye MB for exchange sites and as such removal is less at below pH 7.9. Above this pH, the concentration of H^+ ion decreases where the concentration of MB solution remains constant, consequently the removal of MB increases at higher pH values. At pH 9.0, adsorption increases due to the electrostatic force of attraction between negatively charged surface and cationic dye. Since MB is cationic in nature, it may interact more with Fe_2O_3 surface at higher pH. This interaction gradually increases with the increase of pH of the solution. About 94% of dye concentration is removed by Fe_2O_3 at around pH 9.0 as shown in Figure 3. Therefore, the solution of pH 9.0 is suitable for adsorption study with Fe_2O_3 .

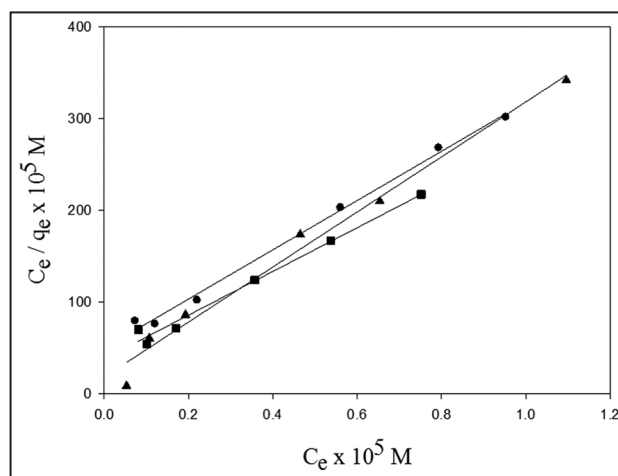


Figure 1: Langmuir isotherm for the adsorption of MB on Fe_2O_3 at 30°C , 40°C , and 50°C at pH 9.0 (\bullet = 30°C , \blacktriangle = 40°C , and \blacksquare = 50°C).

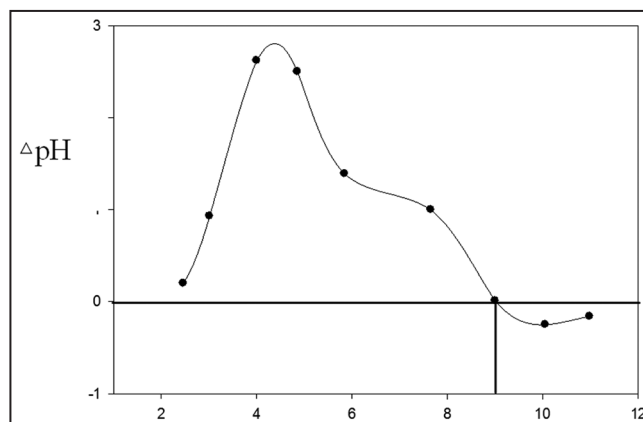


Figure 2: Determination of optimum pH for MB solution.

3.3. Estimation of Equilibrium Time

The time at which the rate of adsorption is equal to the rate of desorption. It is very important for batch adsorption study. The amount of MB adsorbed on Fe_2O_3 is shown as a function of time in Figure 4. It shows that the required contact time to reach the equilibrium of MB is 120 min. The contact time curve shows that the dye removal rate was rapid in the first 5 min due to surface adsorption. The curve of contact time is single, smooth, and continuous leading to saturation due to the intraparticle diffusion process. This curve indicates the possible monolayer coverage of dye [15] on the surface of Fe_2O_3 . During estimating the equilibrium time, it was observed that the removal of MB on Fe_2O_3 was found to be about 96.31 % within 3 h for all concentrations (Figure 5).

3.4. Adsorption Isotherm

Adsorption isotherms were determined at three different temperatures using MB solutions of pH 9.0, as shown in Figure 1. Under all conditions, amount adsorbed increased with the increase of equilibrium concentration.

3.6. Effect of Temperature

The effect of temperature on adsorption showed that the amount adsorbed increased with increasing temperature. The isotherms at 30°C, 40°C, and 50°C suggest that chemical interaction occurred between MB and Fe_2O_3 (Figure 5).

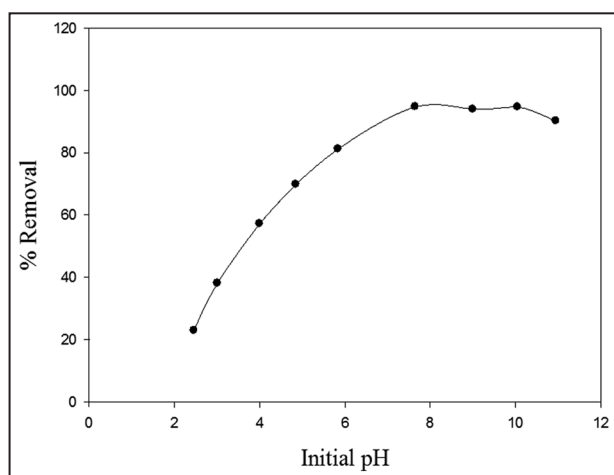


Figure 3: A plot of % removal versus initial pH of MB solution.

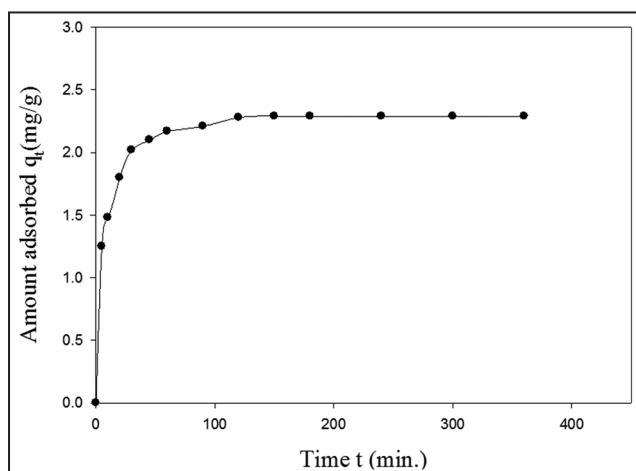


Figure 4: Estimation of equilibrium time for adsorption of MB on Fe_2O_3 (temperature: 30°C; pH 9.0; initial concentration of MB: 3.0×10^{-5} M).

3.7. Nature of Isotherms

The plot of C_e/q_e versus C_e shows a straight line shown in Figure 6. The values of R^2 for Freundlich isotherms and Langmuir isotherms were shown in Table 1. The regression values (R^2) for Langmuir isotherms were closer to one comparing to those of Freundlich isotherms. Hence, the isotherms were fitted in Langmuir isotherms.

3.8. Thermodynamic Parameters

A plot of adsorption capacity as a function of temperature shows that the amount of MB adsorbed on Fe_2O_3 increased with increasing temperature from 30°C to 50°C to indicates that adsorption capacity depends on temperature (Figure 7). The increase in sorption with temperature suggests that the chemical interaction occurred between adsorbate and adsorbent. Gibbs free energy, enthalpy, and entropy changes (ΔG , ΔH , and ΔS) for the adsorption process could be obtained from experiments carried out at different temperatures. The values of ΔH and ΔS could be determined from the slope and intercept of the linear plots of $\ln(q_e/C_e)$ versus $1/T$ Figure 8. ΔG was calculated from the values of ΔH and ΔS [16]. The value of differential enthalpy of adsorption for definite amount adsorbed 2.0 mg/g is 21.23 kJ/mol. As the values of ΔH are relatively lower and positive, the process is an

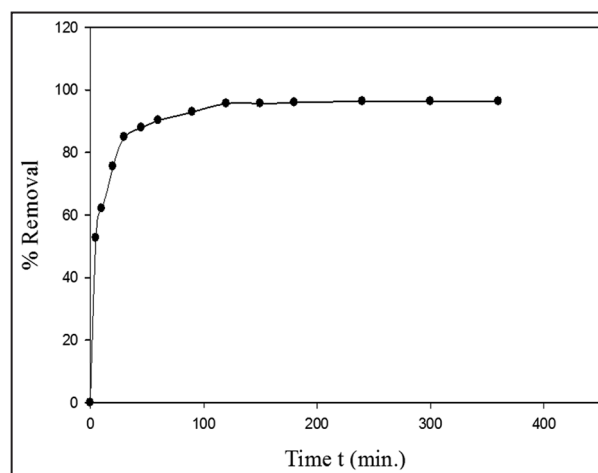


Figure 5: Percent removal of MB with time for adsorption on Fe_2O_3 (temperature: 30°C; pH 9.0; initial concentration of MB: 3.0×10^{-5} M).

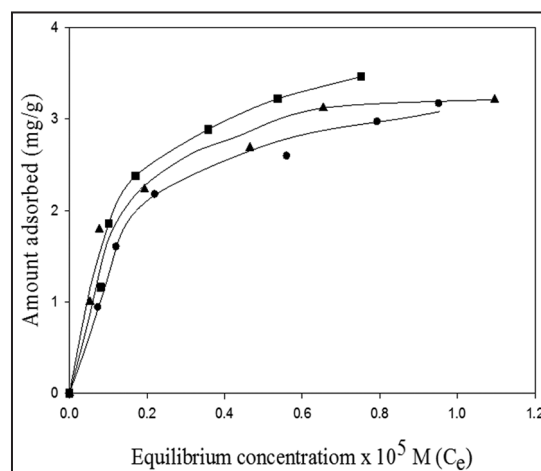


Figure 6: Adsorption isotherm for the adsorption of MB on Fe_2O_3 at 30°C, 40°C and 50°C at pH 9.0 (● = 30°C, ▲ = 40°C, and ■ = 50°C).

endothermic one and favored activated chemical interaction between adsorbent and adsorbate. The values of Gibbs free energy change is negative and increases with increases in temperature. The values of entropy were calculated as listed in Table 2.

Table 1: Langmuir and Freundlich parameters of adsorption of MB on Fe₂O₃ at different temperatures.

Temperature, (°K)	Freundlich, R ²	Langmuir		
		R ²	V _m (mg/g)	b
303	0.9096	0.9908	3.70	5.32
313	0.8649	0.9954	3.54	8.99
323	0.8661	0.9872	4.20	6.26

Table 2: Thermodynamic parameters for adsorption of MB on Fe₂O₃.

Temperature, (°K)	ΔH (kJ/mol ⁻¹)	ΔS (J/K/mol ⁻¹)	ΔG (kJ/mol)
303			-17.42
313	21.23	127.55	-18.69
323			-19.97

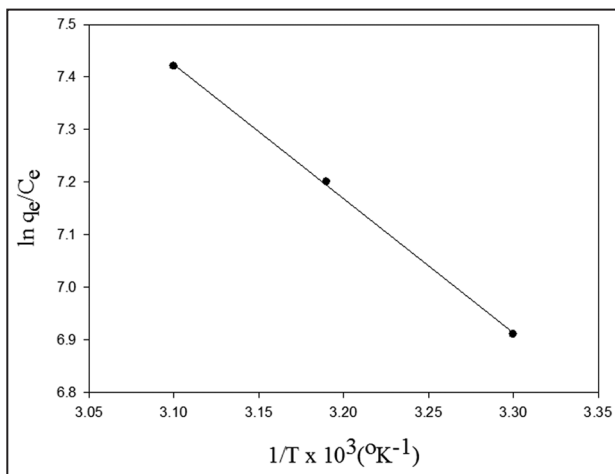


Figure 7: A plot of $\ln(q_e/C_e)$ versus $1/T$ to determine the heat of adsorption for definite surface coverage.

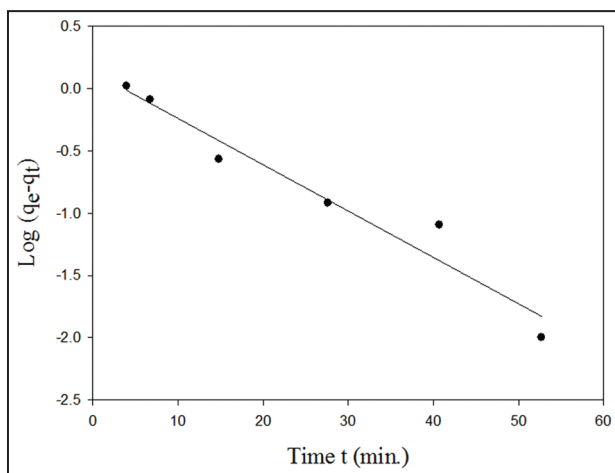


Figure 8: Pseudo-first-order kinetics plots for adsorption of MB on Fe₂O₃.

3.9. Adsorption Kinetics

To investigate the mechanism of adsorption kinetics, Lagergren's pseudo-first-order equation [17] and Ho's pseudo-second-order equation [18] were used to study the biosorption kinetic onto Fe₂O₃.

$$\text{Pseudo-first-order: } \log(q_e - q_t) = \log q_e - (k_1/2.303) t \quad (5)$$

$$\text{Pseudo-second-order: } t/q_t = 1/(2k_2q_e^2) + (1/q_e)t \quad (6)$$

Where, q_e and q_t are the amount of adsorbate adsorbed (mg/g) at equilibrium time and at any time t , k_1 and k_2 are the rate constants of pseudo-first-order adsorption (min⁻¹) and pseudo-second-order adsorption (mg/g/min). The pseudo-first-order and pseudo-second-order kinetic plots using equations (5) and (6) are shown in Figures 8 and 9. The values of the rate constants, regression coefficients and percentage deviation comparing of q_e values obtained experimentally with those obtained from the first- and second-order plots. However, it was seen that the experimentally obtained q_e value did not match those determined from the Lagergren plot as shown in Figure 8 and very large deviation existed. The experimental and plotted q_e values match each other with small deviation for pseudo-second-order equation (Table 3). It can be stated that pseudo-second-order kinetic model provides a good correlation for the adsorption of MB onto Fe₂O₃ in contrast to pseudo-first-order kinetic model.

3.10. Intraparticle Diffusion

The adsorbate species are most probably transported from the bulk of the solution into the solid phase through an intraparticle diffusion

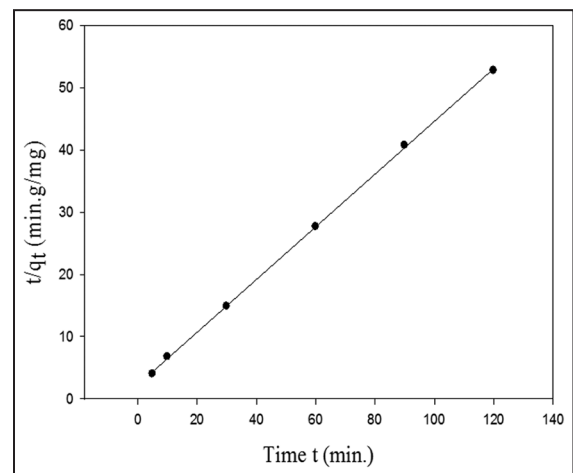


Figure 9: Pseudo-second-order kinetics plots for adsorption of MB on Fe₂O₃.

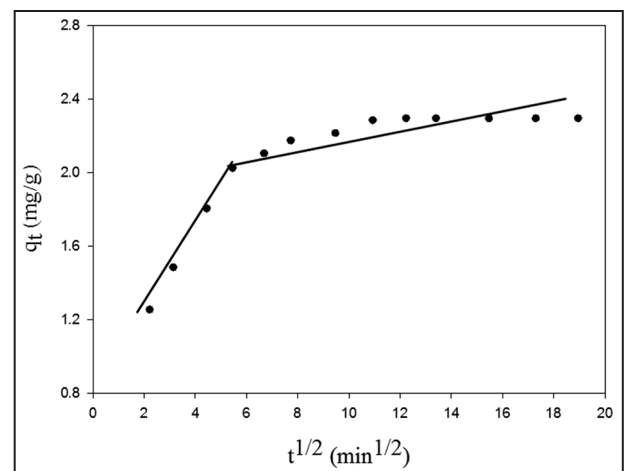


Figure 10: Intraparticle diffusion plot for the adsorption of MB.

Table 3: Kinetic parameters for biosorption of MB on Fe₂O₃.

Conc. (mg/L) × 10 ⁵ M	q _{e, exp} (mg/g)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model			
		Rate const. k ₁ (min ⁻¹) × 10 ²	Regression coefficient R ²	q _{e, cal} (mg/g)	Deviation (%)	Rate const. k ₂ (mg/g/min) × 10 ²	Regression coefficient R ²	q _{e, cal} (mg/g)	Deviation (%)
3.0	2.29	1.67	0.9554	0.23	89.95	3.68	0.9998	2.38	3.93

process, which is often the rate-limiting step in many adsorption processes. The possibility of intraparticle diffusion was explored using the intraparticle diffusion model [19]. An empirically functional relationship, common to adsorption processes defines the process, and the uptake varies almost proportionally with $t^{1/2}$, the Weber-Morris plot, rather than with the contact time t [20].

$$q_t = k_i t^{1/2} + C \quad (7)$$

Where q_t is the amount of MB adsorbed (mg/g) at time t , k_i is the intraparticle diffusion rate constant (mg/g min^{1/2}), and C is the intercept. Theoretically, the plot k_i versus $t^{1/2}$ should show at least four linear regions that represent boundary layer diffusion. At the beginning of adsorption, there is a linear region representing the rapid surface loading, followed by a curved portion where the overall rate is controlled by both film-diffusion and pore diffusion, then a linear region representing pore diffusion and finally, a horizontal linear region representing equilibrium (Figure 10).

4. CONCLUSION

This study investigates the removal of MB, a cationic dye from simulated wastewater using Fe₂O₃ as an adsorbent. The amount of adsorption of MB increases with the increase in temperature and the equilibrium time and optimum pH for adsorption are 3 h and 9.0, respectively. The experimental data have been analyzed using Langmuir and Freundlich isotherm models and the Langmuir provided the best fit. The kinetic data fit very well to the pseudo-second-order kinetic model.

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