

Modeling of experimental data for the adsorption of methyl orange from aqueous solution using a low cost activated carbon prepared from *Prosopis juliflora*

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This paper presents the feasibility for the removal of methyl orange (MO) dye from aqueous solution using an activated carbon prepared from *Prosopis juliflora* bark. Batch adsorption experiments were carried out as a function of pH, contact time, adsorbate concentration, adsorbent dosage and temperature. The commonly applicable isotherms namely Freundlich and Langmuir equations are used for the prediction of isotherm parameters. A comparison of linear least-square method and a trial-and-error non-linear method are examined in Freundlich and Langmuir (Four forms) isotherms. The nature of adsorption isotherm feasibility was evaluated with dimensionless separation factors (R_L). The dynamics of adsorption process was analyzed with Lagergren's Pseudo-first order and Pseudo-second order kinetic equations. Thermodynamic parameters like the change in enthalpy (ΔH°), change in entropy (ΔS°) and change in Gibbs free energy (ΔG°) were evaluated and ΔG° shows a negative value whereas ΔH° shows the positive value indicating that the adsorption process was spontaneous and endothermic in nature. The functional group characterization of the adsorbent was done using Fourier transform infrared spectroscopy (FTIR). The thermal stability of activated carbon was analyzed using Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA).

Keywords: activated carbon, adsorption, isotherm, kinetics and methyl orange.

INTRODUCTION

Pollution of aquatic environment is mainly due to the disposal of effluents from the industries. The various industries such as textile, paper, rubber, plastics, paints, printing, leather and food processing industries¹ discharge an enormous amount of colored effluents in to the water bodies, which cause water pollution and serious problems to the environment². Synthetic dyes are extensively used in the textile industry because of their favorable characteristics of bright color, being easily water soluble, cheaper to produce and easier to apply with natural fibers like wool, cotton, silk and synthetic fibers like polyesters, acrylic, rayon³. The synthetic dyes have complex molecular structures, which make them more stable and difficult to biodegrade^{4, 5}. The dyes are designed to be resistant to fading by chemicals and light⁶. They are stable to high temperatures and enzyme degradation resulting from the detergent washing. Therefore biodegradation of dyes is typically a difficult process. Several research reports revealed that very small quantities of dyes are highly toxic which causes acute disorders in aquatic organisms⁷. Uptake of textile effluents through food chain in aquatic organisms and human beings may cause various chromosomal fractures, respiratory, mutagenic and carcinogenic problems⁸⁻¹⁰. Therefore, the wastewater containing dyes must be properly treated before being discharged into the water bodies. A variety of conventional methods are used to remove the color from industrial effluents including coagulation, floatation, biological treatment, hyper filtration and oxidation. However, these technological processes have significant disadvantages, including incomplete dye removal, requirement of expensive equipments and monitoring systems, high reagent or energy requirements or generation of toxic sludge and other waste products.

Adsorption is the most versatile technique and widely used by many researchers¹¹⁻¹⁵, because of its inexpensive nature and ease of use. Various research works have been undertaken for the removal of different pollutants using a large number of materials as adsorbents¹⁶⁻³⁴. The advantage and disadvantage of adsorption techniques have been extensively reviewed by Lorenc et al.³⁵ and Cooper³⁶. Adsorption on the activated carbon was found to be an effective process for dye removal, although the commercially available activated carbon is too expensive and has high usage costs. This has led many researchers to search for inexpensive and locally available materials which are used for the preparation of activated carbon to make the process economically viable.

A detailed literature survey shows that *Prosopis juliflora* bark carbon has not been tried as an adsorbent material for the removal of MO dye. The *Prosopis juliflora* is a fast growing small tree in India. It is mainly cultivated and consumed for timber and furniture industries of the developing nations. This tree is widely grown in dry lands, arid regions and other parts of India. It is one of the most tolerant species for saline, alkaline soils and also capable of growing in water logged areas. *Prosopis juliflora* bark carbon (PJBC) can be used as a low-cost adsorbent material for the removal of methyl orange from wastewater. The objectives of the present study are to remove methyl orange from aqueous solution by batch mode adsorption studies. In batch studies, the dynamic behavior of the adsorption was investigated on the effect of adsorbate concentration, temperature, adsorbent dosage, contact time and pH. Adsorption data used for modeling by the linear least-square method and a trial-and-error based non-linear method of two commonly used isotherms (Langmuir and Freundlich), were examined at different temperatures over the entire concentration ranges. From the adsorption measure-

ments the first and second order kinetic equations are evaluated. The functional group of the adsorbent was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The thermal stability of activated carbon was analyzed using Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA).

MATERIALS AND METHODS

Preparation of adsorbent

Activated carbon was prepared from *Prosopis juliflora* bark. It was collected on the premises of University College of Engineering Pattukottai. The material was washed in hot distilled water to remove the earthy matter, cut into small pieces and dried. It was impregnated with 1:1 sulphuric acid then the charred material was washed several times with distilled water until the pH of the washings become neutral and dried in hot air oven about 393 K for 24 hours. The dried carbon was placed in a muffle furnace at 723 K for the complete carbonization of the material. Finally, the activated carbon was ground and sieved using 180–300 μ m standard sieves. Commercially available analytical grade other reagents (Merck, India and SD-fine, India) were used in this study.

Adsorbate

A stock solution of adsorbate was prepared by dissolving an exact and calculated quantity of methyl orange ((p-dimethylamino-azobenzene sulfonic acid), molecular formula is $C_{14}H_{14}N_3NaO_3S$ and Formula weight is 327.34) in double distilled water which was used throughout the experiments. Figure 1 shows the structure of methyl orange.

Experimental Methods

25 mL of a known concentration of methyl orange dye solution and 100 mg of the adsorbent was taken in a 100 mL glass-stoppard flask at 303 ± 0.5 K and the mixture was stirred on a mechanical shaker for 50 min. The samples were withdrawn with preset time intervals, and the adsorbent was separated from the solution by centrifugation process with the speed of 4500/min for 5 minutes. The absorbance of the supernatant solution was measured before and after adsorption in a double beam spectrophotometer (λ_{max} : 450 nm). All experiments were carried out in twice, and the concentrations are given

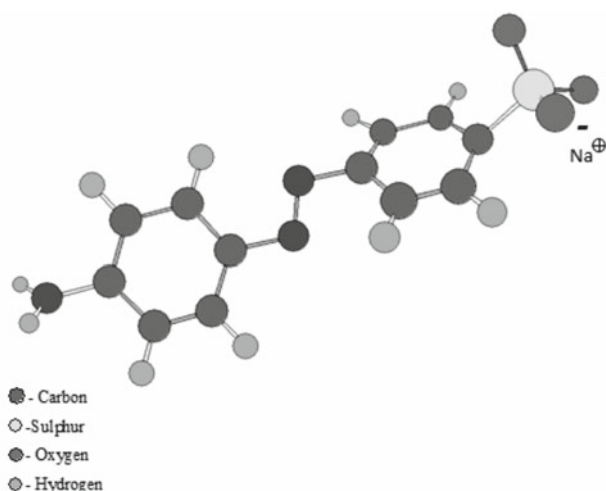


Figure 1. Structure of methyl orange

an average values. The initial dye concentration in the test solution and the adsorbent dosage were varied to investigate their effect on the adsorption kinetics. The effect of pH was observed by studying the adsorption of dye over the pH range from 2 to 10. The pH of the dye solution was adjusted by using 0.1 M NaOH or 0.1 M HCl solution using pH meter. The sorption studies were carried out at different temperatures (303, 313, 323, 333 and 343 K). This study helps an evaluation of various thermodynamic parameters with the effect of temperature. The amount of sorption at time t , q_t (mg/g) was calculated using the following equation:

$$q_t = (C_0 - C_t) \frac{V}{M} \quad (1)$$

where, C_0 is initial concentration of dye, C_t is the concentration at a given time t , V is the volume of the dye solution in L and M denotes weight of activated carbon in g.

The percentage of dye removal was calculated using the following equation,

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

Analytical studies

The presence of various functional groups in the adsorbent material was analyzed using Fourier Transform Infrared Spectroscopy (FTIR) with the wavelength of 4000 cm^{-1} to 400 cm^{-1} . The temperature refractoriness of the adsorbent was analyzed using the Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA).

RESULTS AND DISCUSSION

Characterization of the adsorbent

Activated carbons are widely used as an adsorbent material for the removal of various hazardous products in the water matrices due to their high efficiency of adsorption, high surface area and porous structure. The sorption activity of the activated carbon mainly depends on its chemical nature and pore structure. Table 1 shows the various physiochemical properties of activated carbon prepared from *Prosopis juliflora* bark. The ash content of the carbon gives very low value, this indicates that the low quantity of inorganic matter and high quantity the carbon content. The presence of larger surface area in

Table 1. Physiochemical properties of *Prosopis juliflora* bark carbon

Parameter	Value
pH	6.62
pHzpc	4.2
Moisture Content (%)	2.9
Bulk density (g/ml)	0.4957
Solubility in water (%)	1.0526
Solubility in 0.25M HCl (%)	3.6114
Porosity (%)	81.983
Specific gravity	1.7183
Volatile matter (%)	12.53
Ash content	4.56
Fixed Carbon	83.44
Sodium (ppm)	34
Potassium (ppm)	3.2
Conductivity (mS)	13.37
Surface area (m^2/g)	658

a carbon is responsible for the higher adsorption rate of the adsorbate. The low bulk density value shows that the carbon has a large number of pores. The presence of acid soluble matter in the carbon reveals the presence of carboxyl groups in the pore spaces.

The determination of zero point charge (pHzpc) was done to investigate the surface behaviour of adsorbent and the influence of pH in an adsorption process. It was estimated by using titration method. In this method 50 mL of NaCl solution was taken in a series of six stop-pearl Erlenmeyer flasks. The pH values of NaCl solution are adjusted between 2 and 10 by adding 0.1 M HCl or 0.1 M NaOH solution. 100 mg of PJBC was added into each flask with constant shaking for 1 hour and the contents are allowed to attain equilibrium for 48 h then the pH value of each flask was measured by using a pH meter. A graph was plotted between pH_{final} and pH_{initial} and the point at which they intersect each other and subsequently that point was recorded as pHzpc of the surface of PJBC. The pHzpc value of PJBC was found to be 4.2.

FTIR studies

The presence of functional groups in an adsorbent material is significantly enhancing the adsorption process; therefore it is essential to find out which type of functional is present in it. The FTIR spectrum is used for the prediction of type and nature of functional group present in an adsorbent material. In this study the FTIR spectrum of carbon and dye loaded carbon is presented in Fig. 2. From the figure, the dotted line (carbon) shows that the peaks in the range of 3868.15 cm^{-1} , 3763.59 cm^{-1} , 3432.81 cm^{-1} , 2161.28 cm^{-1} , 1591.51 cm^{-1} , 1359.46 cm^{-1} and 1146.85 cm^{-1} . The peak position at 3868.15 cm^{-1} , 3763.59 cm^{-1} and 3432.81 cm^{-1} are indicates the stretching vibration of OH group involves in the inter-molecular or intramolecular hydrogen bonding of the moisture present in either carbon or KBr³⁷. The peaks at 2161.28 cm^{-1} , 1591.51 cm^{-1} , 1359.46 cm^{-1} and 1146.85 cm^{-1} shows the presence of alkyl group, C=C bond in aromatic conjugation, C-N peptide bond and S=O interaction respectively. The methyl orange loaded spectrum of FTIR shows that the broader and slight change in peak position (3845.65 cm^{-1} , 3735.12 cm^{-1} , 3419.45 cm^{-1} ,

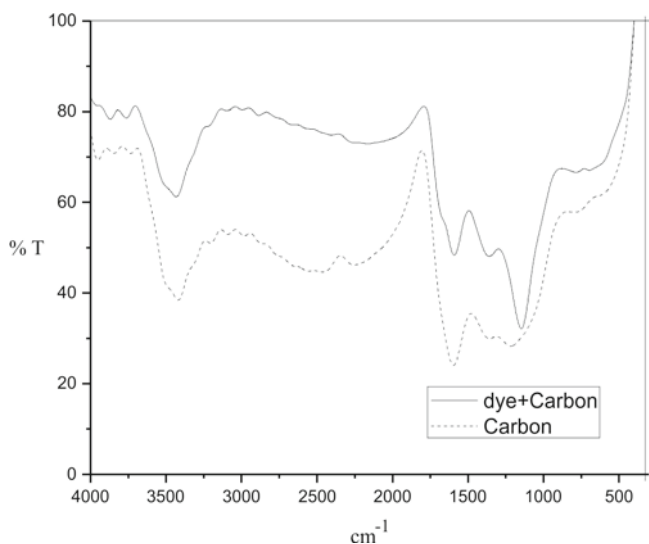


Figure 2. FTIR spectrum of carbon and Methyl orange loaded carbon

3089.79 cm^{-1} , 2462.90 cm^{-1} , 2255.33 cm^{-1} , 1596.51 cm^{-1} and 1217.93 cm^{-1}) reveals that the adsorbent containing functional groups are physically bound with methyl orange dye and the adsorption of dye was effective on the surface of the adsorbent.

TGA and DTA studies

The thermal stability of the activated carbon was evaluated using Thermo Gravimetric Analysis and Differential Thermal Analysis. The TGA and DTA curve of the PJBC is presented in Fig. 3. The analysis was carried out with increasing the temperature of 10 K/min with nitrogen flow rate 10 mL/min. In TGA Analysis, the curve shows that by increasing the temperature from 313 to 473 K, there was a slight reduction in the weight of the activated carbon. This may be the removal of moisture content in the carbon and the temperature beyond 473 to 773 K the significant weight loss appears due to the decomposition of surface groups and the formation of CO and CO₂. The residual carbonization product was obtained in the range of 773 to 1073 K. In TGA and DTA curve implies that the observed weight loss is due to the presence of volatile materials and some intermediate product was obtained, there by a significant reduction in weight was seen in the temperature of 473 to 773 K. The presence of hydroxyl group, carbonyl group and free hydrogen were responsible for the total reduction of the weight loss of the material. At higher temperature (above 873 K), the obtained intermediate involves further decomposition there by the formation of residual products like tar and char.

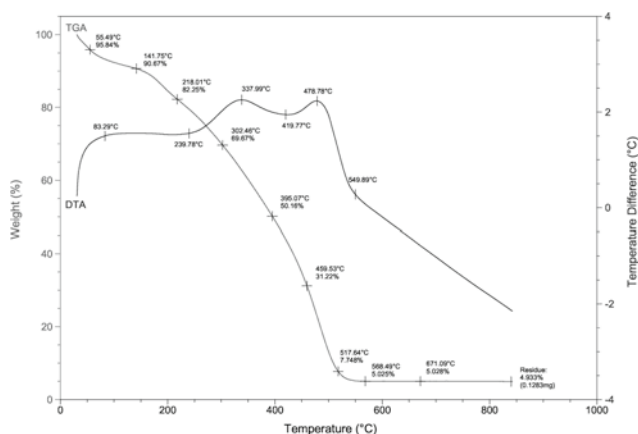


Figure 3. TGA and DTA of activated carbon

Effect of pH

The pH of the solution plays an important role that highly influencing the adsorption capacity of the adsorbent. Therefore the investigation of the effect of pH is essential to determine the optimisation of the operational parameter in actual application of the work. The effect of pH on the removal of methyl orange is shown in Fig. 4. The adsorption efficiency of the activated carbon increased from pH value of 2 to 4 because the surface activated carbon may contain a large number of active sites. Therefore dye uptake capacity can be related to the active sites and also the interaction of the solute in the solution. For the determination of effect of pH of MO dye, 120 mg/L of concentration was used. The adsorption of dye on the activated carbon was decreased over the pH range of 4 to 10. At higher pH value, the

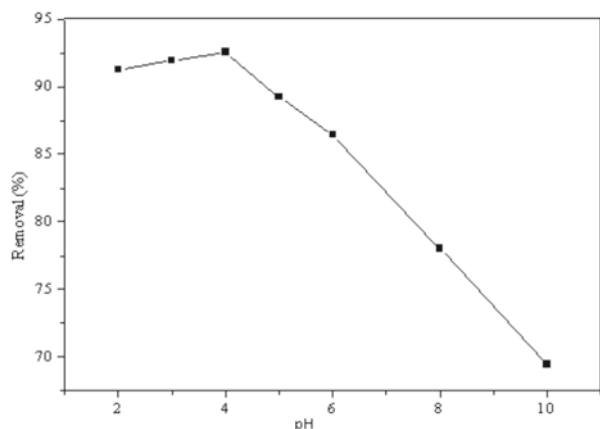


Figure 4. Effect of pH for the removal of MO onto PJBC

particles present on the adsorbent surface may become negatively charged, which enhances the positively charged ions through electrostatic forces of attraction³⁸ thereby the rate of adsorption for MO dye decreases in higher pH values. The experimental results have shown that the effect of pH was significantly influencing the adsorption rate. From Fig. 4, the optimum pH for the removal of methyl orange was found to be 4.0.

Effect of dye concentration

The effect of dye concentration was evaluated using the concentration ranges from 20–160 mg/L with the increment of 20 mg/L. The dye concentration increased from 20 to 100 mg/L, the sorption capacity was rapidly increased up to the equilibrium (120 mg/L) but after reaching the adsorption equilibrium the sorption capacity is not so rapid (140 to 160 mg/L). This is due to the non availability of the active site in the surface of adsorbent. Fig. 5 indicated that 120 mg/L was the optimum concentration for the removal of methyl orange than the other concentrations.

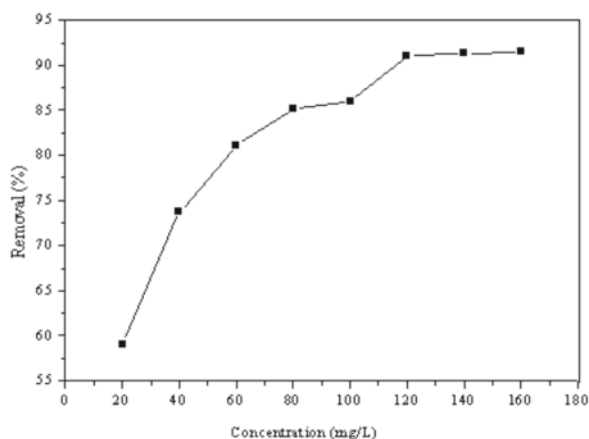


Figure 5. Effect of initial concentration of MO onto PJBC

Effect of adsorbent dose

Figure 6 shows the removal of methyl orange dye by varying the quantity of the adsorbent from 50 mg to 1000 mg with the increment of 50 mg of the adsorbent. The removal efficiency was increased with an increase in the adsorbent dosage. The experimental result showed that 100 mg of adsorbent dosage was the optimum quantity for the removal of methyl orange.

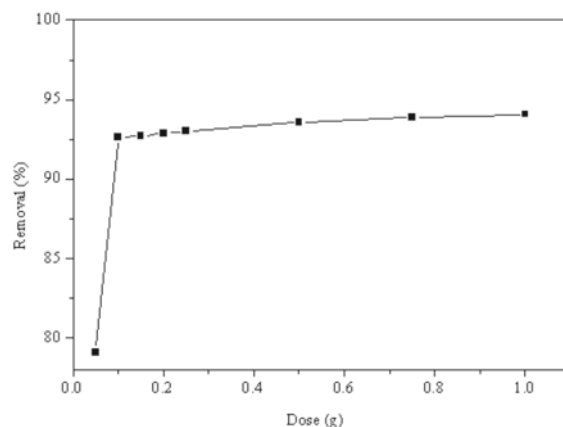


Figure 6. Effect of Dose for the removal of MO onto PJBC

Effect of temperature

The effect of temperature was investigated in different temperature ranges from 303 K to 343 K with the increment of 10 K range. Fig. 7 shows that 303 K was the optimum temperature for the effective removal of methyl orange. The effect of temperature has not significantly increased the adsorption process. This decrease in adsorption with increasing the temperature is mainly due to the enhancement of the desorption step in the sorption process. The temperature may weaken the physical forces of attraction between the active sites on the activated carbon and the dye species and also between adjacent dye molecules on the adsorbed phase.

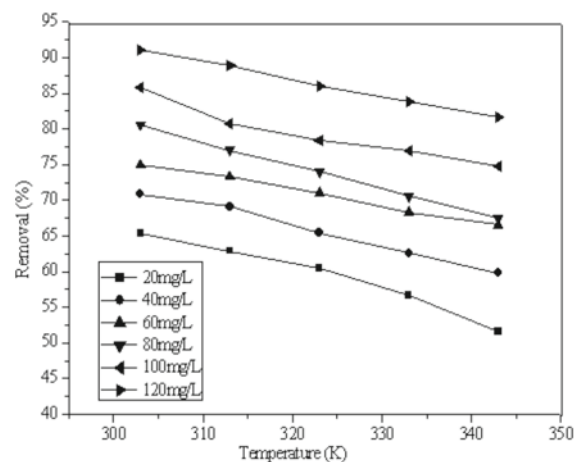


Figure 7. Effect of temperature for the removal of MO onto PJBC

Effect of contact time

The effect of contact time was investigated using various time intervals as 10 to 90 minutes with the increment of 10 minutes range. Figure 8 shows that initially the adsorptive removal of methyl orange increases with increasing the time to certain limit. About 40 minutes of the contact time gave higher percentage removal. Then the removal percentage decreases with time which indicates that active sites are unavailable in the adsorbent surface.

Isotherm studies

The adsorption data were analyzed with two adsorption isotherm models, namely Freundlich and Langmuir. Various forms of Langmuir and Freundlich isotherm equations were tested with the linear and the non-linear

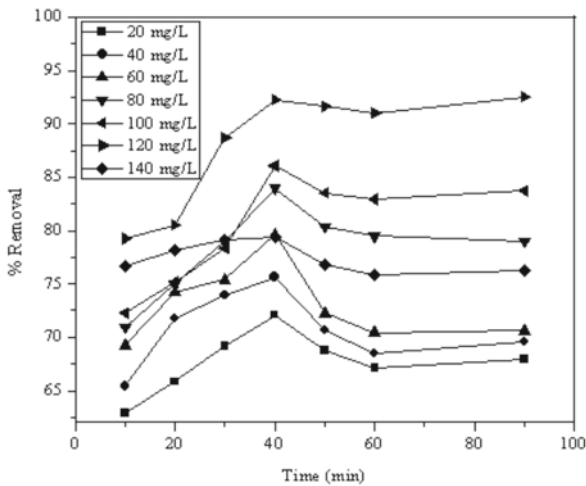


Figure 8. Effect of contact time for the removal of MO onto PJBC

method. The Langmuir adsorption model is based on the assumption that the adsorption process involved the monolayer of the solute molecules on the surface of the adsorbent²⁵. The mathematical expression is

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (3)$$

where, q_e (mg/g) and C_e (mg/L) are the amounts of dye adsorbed per unit mass of the sorbent and unadsorbed dye concentration in the solution, q_m is maximum amount of dye adsorbed per unit mass of sorbent at complete monolayer on surface bound, and K_a (L/mg) is a constant related to the affinity of the binding sites. Various forms of the Langmuir and Freundlich isotherms of linear and non-linear models are presented in Table 2.

The Langmuir isotherm possesses the linear forms as Langmuir-1, Langmuir-2, Langmuir-3 and Langmuir-4 and the values of Langmuir constants are obtained by plotting a graph between various parameters such as C_e vs. C_e/q_e , $1/C_e$ vs. $1/q_e$, q_e vs. q_e/C_e and q_e/C_e vs. q_e which are shown in Fig. 9. The Freundlich isotherm constant was calculated by plotting $\ln(C_e)$ vs. $\ln(q_e)$, and is shown in Fig. 10. The non-linear forms of Langmuir and Freundlich isotherm constant parameters were calculated by

plotting C_e vs. q_e with their corresponding temperatures of 303, 313, 323, 333 and 343 K are presented in Fig. 11.

The correlation co-efficient (r^2) values of the non-linear method (Table 4) shows higher value compared to the linear regression (Table 3) method. With the use of various temperatures, the highest r^2 value (nearer to unity) was shown in the temperature of 303 K compared to the other temperature. In the Langmuir isotherm, the correlation co-efficient (r^2) value obtained in the temperature 303 K is 0.9991 and other temperatures like 313, 323, 333 and 343 K are gave the values 0.9908, 0.9946, 0.9888 and 0.9833 respectively. Freundlich isotherm shows the correlation co-efficient (r^2) value lower when compared to the Langmuir values. The Freundlich isotherm shows r^2 values 0.9840, 0.9851, 0.9833, 0.9874 and 0.9746 with the temperatures 303, 313, 323, 33 and 343 K, respectively.

The q_m and K_a values were predicted from the other linearized forms of Langmuir equations, it was observed that the Langmuir constants varied for different forms of linear Langmuir equations. This is because depending on the way the isotherm is linearized, the error distribution changes either for worse or better⁴⁴.

The Freundlich²⁶ isotherm equation is expressed as

$$q_e = K_F C_e^{1/nF} \quad (4)$$

where, K_F (mg/g) (L/g) is an indicator of the adsorption capacity, $1/n$ is the adsorption intensity. The magnitude of the exponent $1/n$, shows the favorability of adsorption, $1/n$ value was $n > 1$ represents favorable adsorption condition⁴¹.

From the experimental results, Langmuir-1 shows best correlation coefficient (r^2) value compared to the other Langmuir and Freundlich forms. The higher q_m value of Langmuir-1 confirms that the maximum quantity of adsorption (120 mg/L) at 303 K. The equilibrium data were further analyzed using the linearized form of the Freundlich equation using the same set of the experimental data. The calculated Freundlich isotherm parameters and the corresponding r^2 values were shown in Table 3. It was observed that in all the temperatures the Freundlich isotherm correlation coefficient (r^2) values

Table 2. Isotherms and their forms

Isotherms	Non-linear	Linear	Plot	Reference
Freundlich	$q_e = K_F C_e^{1/nF}$	$\log(q_e) = \log(K_F) + \frac{1}{nF} \log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$	26
Langmuir-1	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{q_e}$ vs. C_e	25
Langmuir-2		$\frac{1}{q_e} = \left(\frac{1}{K_a q_m} \right) \frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$	
Langmuir-3		$q_e = q_m - \left(\frac{1}{K_a} \right) \frac{q_e}{C_e}$	q_e vs. $\frac{q_e}{C_e}$	
Langmuir-4		$\frac{q_e}{C_e} = K_a q_m - K_a q_e$	$\frac{q_e}{C_e}$ vs. q_e	

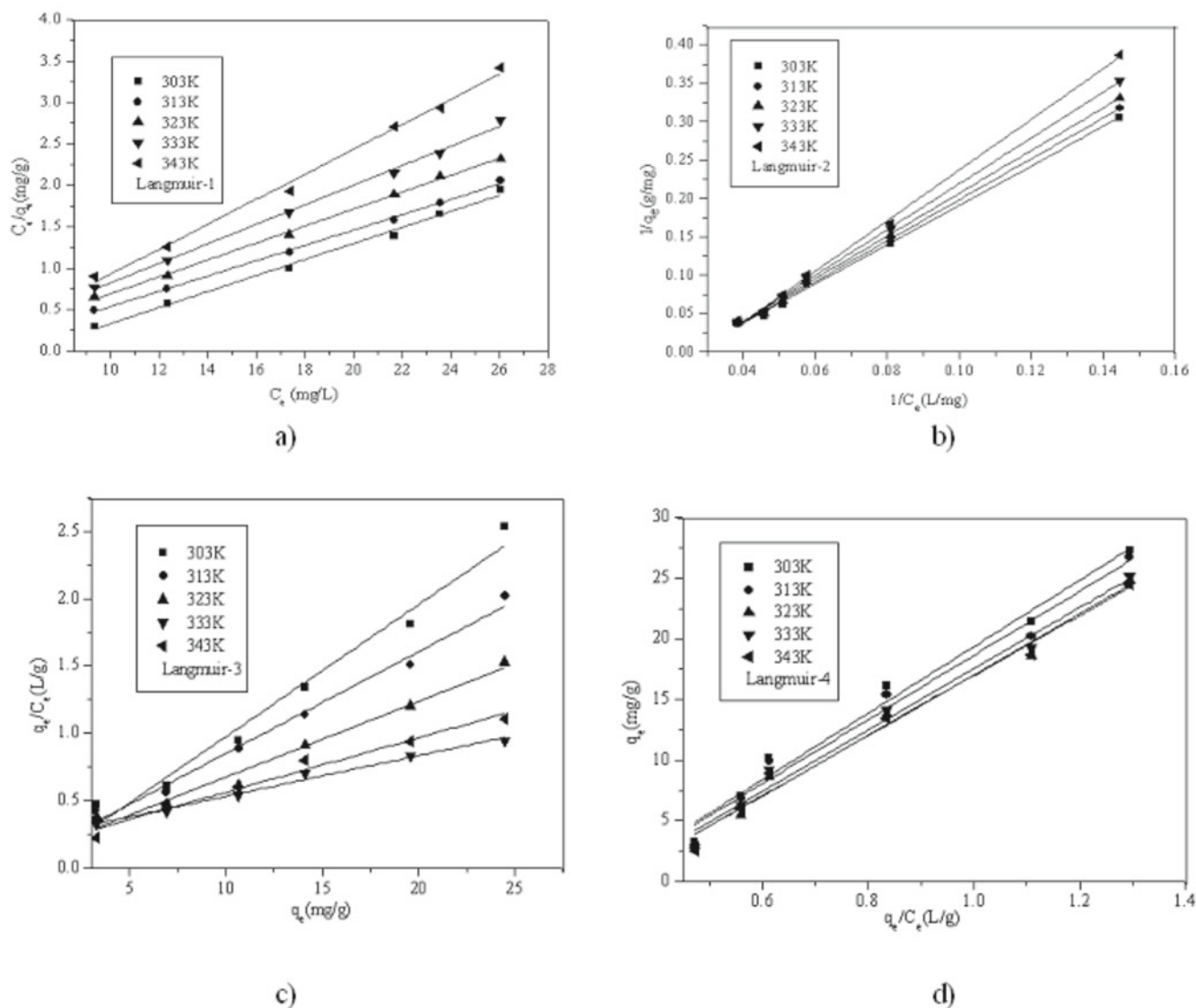


Figure 9. a) Langmuir isotherm-1 plot for the adsorption of MO onto PJBC, b) Langmuir isotherm-2 plot for the adsorption of MO onto PJBC, c) Langmuir isotherm-3 plot for the adsorption of MO onto PJBC, d) Langmuir isotherm-4 plot for the adsorption of MO onto PJBC

Table 3. Isotherm parameters using linear method at various temperatures

Isotherm		Temperature(K)				
		303K	313K	323K	333K	343K
Langmuir 1	q_m (mg/g)	10.2976	10.7980	9.7570	9.4653	9.6212
	K_a (L/mg)	0.0094	0.0086	0.0105	0.0140	0.0228
	r^2	0.9925	0.9976	0.9974	0.9959	0.9936
Langmuir 2	q_m (mg/g)	0.3751	0.3592	0.3351	0.3028	0.3896
	K_a (L/mg)	0.1680	0.1822	0.1993	0.2365	0.3074
	r^2	0.9905	0.9952	0.9945	0.9924	0.9909
Langmuir 3	q_m (mg/g)	0.6459	0.5863	0.7805	0.4006	0.9361
	K_a (L/mg)	17.2072	17.2433	17.8190	18.9815	18.7770
	r^2	0.9713	0.9859	0.9759	0.9866	0.9708
Langmuir 4	q_m (mg/g)	0.3071	0.3141	0.2950	0.2958	0.3184
	K_a (L/mg)	25.2561	24.7267	27.4349	26.4534	25.0048
	r^2	0.9791	0.9786	0.9776	0.9746	0.9819
Freundlich	1/n	1.4619	1.4566	1.4652	1.4914	1.5340
	K_F (mg/g)(L/g)	0.5230	0.5354	0.5714	0.6336	0.7173
	r^2	0.9775	0.9768	0.9762	0.9738	0.9742

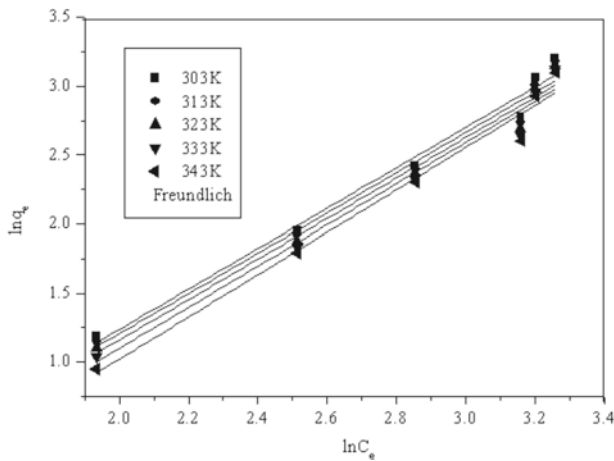


Figure 10. Freundlich isotherm plot for the adsorption of MO onto PJBC

were found to be relatively less than that of the best fit linearized Langmuir isotherm. This suggests that the Langmuir isotherm is a more appropriate isotherm than the Freundlich isotherm for the present system. For the comparison of the linear and the non-linear method⁴⁴, a good agreement of correlation co-efficient (r^2) values of both Langmuir and Freundlich isotherm was found in the experiments. The results implied that the non-linear method was the best fitted method compared to the linear form.

The essential characteristics of the Langmuir isotherm can be also expressed in terms of a dimensionless constant separation factor R_L that is given by³⁸.

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

The value of R_L represents the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The calculated R_L values at different initial concentrations of methyl orange have shown in Fig. 12, the values of R_L lie between 0 and 1, thereby confirming that the adsorption is a favorable process. In addition, the low R_L values reveals that the interaction between dye molecules and the PJBC might be relatively strong³⁹.

Kinetic studies of adsorption

The equilibrium kinetics are characterized in order to determine the rate limiting steps involved in the process of sorption of methyl orange dye onto PJBC. The mechanism of adsorption is generally considered to involve three steps, one or any combination of which can be the rate-controlling mechanism: mass transfer across the external boundary layer film of liquid surrounding the outside of the particle; adsorption at a site on the surface (internal or external) and the energy will depend on the binding process (physical or chemical); this step is often assumed to be extremely rapid; diffusion of the adsorbate molecules to an adsorption site either by a pore diffusion process through the liquid filled pores or by a solid surface diffusion mechanism⁴⁰. The Lagergren's pseudo- first order (Eq. (6)) and the pseudo-second order (Eq. (7)) kinetic models were applied^{24, 27, 42}.

$$\log(q_e - q) = \log(q_e) - \frac{K_1 t}{2.303} \quad (6)$$

Table 4. Isotherm parameters using non-linear method, at various temperatures

		Temperature (K)				
		303	313	323	333	343
Non-linear Langmuir	q_m	0.1521	0.1656	0.2163	0.1728	0.2025
	K_a	0.9073	0.8712	0.4112	0.3558	0.2319
	r^2	0.9991	0.9908	0.9946	0.9888	0.9833
Non-linear Freundlich						
	$1/n$	2.2586	2.5901	2.1986	2.8501	2.1440
	K_F	0.0357	0.0300	0.0474	0.0390	0.0393
	r^2	0.9840	0.9851	0.9833	0.9874	0.9746

Table 5. Pseudo-first order and second order kinetic equations and their forms

Type	Non-linear	Linear	Plot	Reference
Pseudo-first order	$q = q_e (1 - e^{-K_1 t})$	$\log(q_e - q) = \log q_e - \frac{K_1 t}{2.303}$	$\log(q_e - q) \text{ vs. } t$	24
Pseudo-second order	$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$	$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	$\frac{t}{q} \text{ vs. } t$	42

Table 6. Pseudo-first order and second order kinetic parameters using linear method

C_0	Pseudo-first order			Pseudo-second order			
	K_1	q_e	r^2	$q_e \text{ .exp}$	K_2	$q_e \text{ .cal}$	r^2
20	0.0093	0.6567	0.9226	6.25	0.4813	3.0245	0.9903
40	0.0085	0.4979	0.7776	9.74	0.0543	4.3100	0.9742
60	0.0103	0.4390	0.8567	11.96	0.0345	4.8468	0.9361
80	0.0180	0.4482	0.9105	16.80	0.0719	5.6870	0.9537
100	0.0208	0.4883	0.9612	21.52	0.0112	8.1031	0.9656
120	0.0184	0.2323	0.8734	24.30	0.0019	10.2093	0.9760
140	0.0202	0.2268	0.9371	28.90	0.0127	14.9120	0.9904

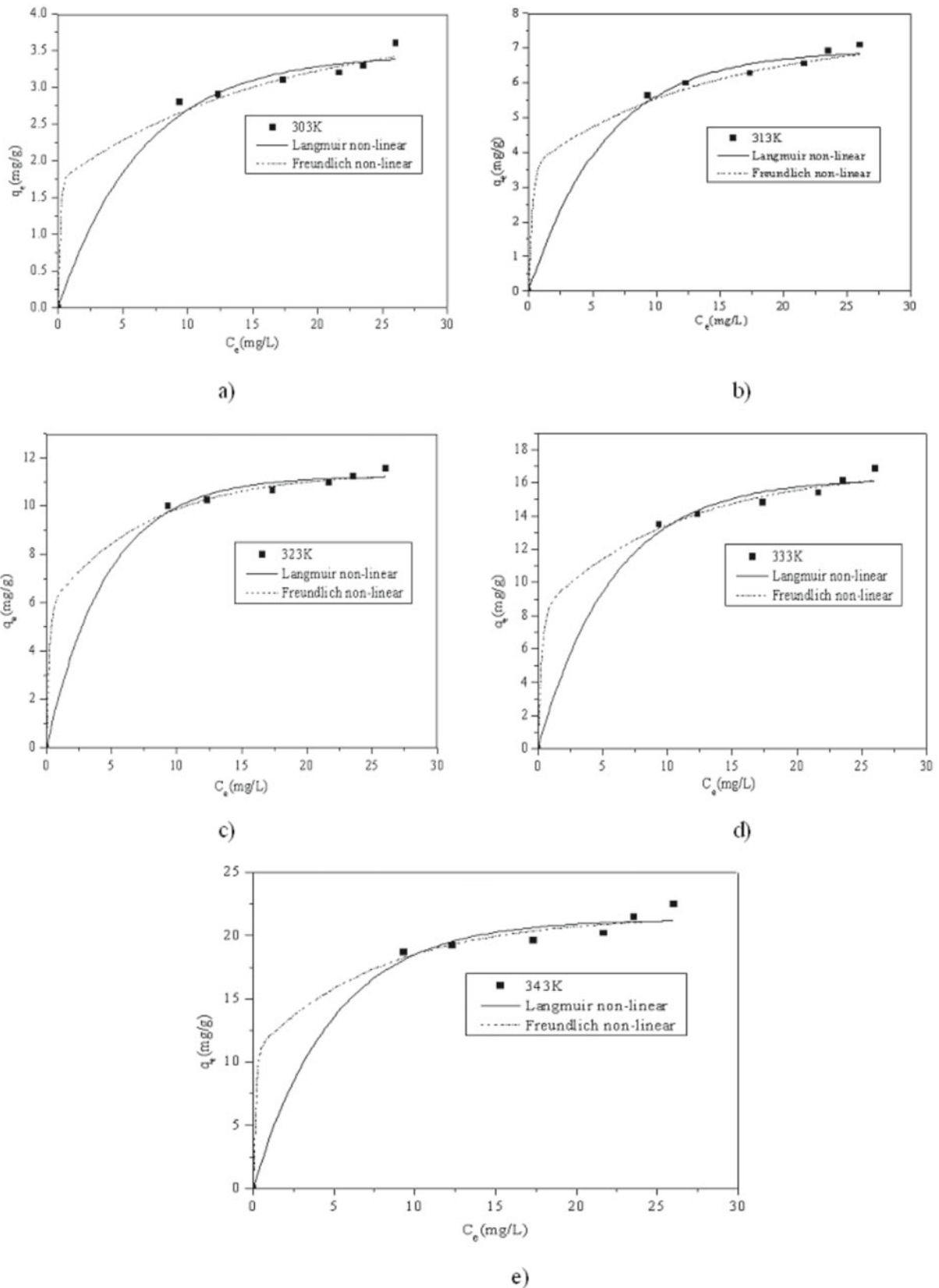


Figure 11. a) Adsorption isotherm of MO onto PJBC at 303 K, b) Adsorption isotherm of MO onto PJBC at 313 K, c) Adsorption isotherm of MO onto PJBC at 323 K, d) Adsorption isotherm of MO onto PJBC at 333 K, e) Adsorption isotherm of MO onto PJBC at 343 K

where, K_1 is the pseudo first order adsorption rate constant, q_e is the amount of dye adsorbed on the PJBC at equilibrium (mg/g), q_t is the amount of methyl orange adsorbed on the PJBC at any time t (mg/g).

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where, K_2 is the pseudo second order adsorption rate constant, q_e is amount of dye adsorbed on the PJBC at equilibrium (mg/g), q_e^2 is the pseudo second order adsorption rate constant (mg/g/min). Various forms of Lagergren's kinetic equations of linear and non-linear are presented in Table 5. The experimental results were

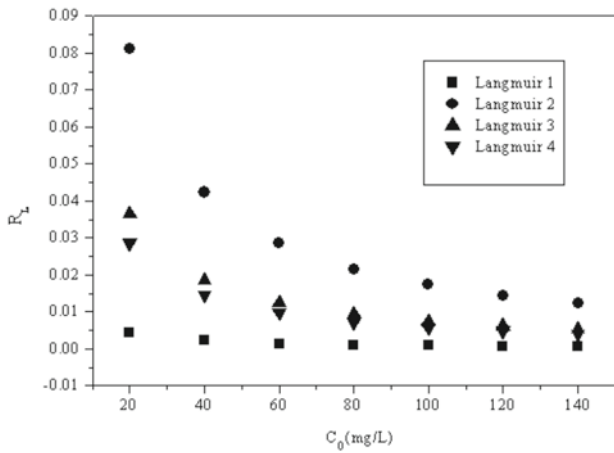


Figure 12. Separation factor R_L versus initial concentration C_0 for the adsorption of MO onto PJBC

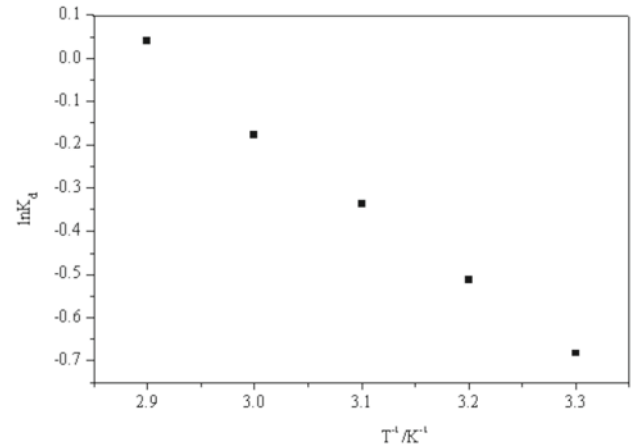


Figure 15. Van't Hoff plot for the adsorption of MO on to PJBC

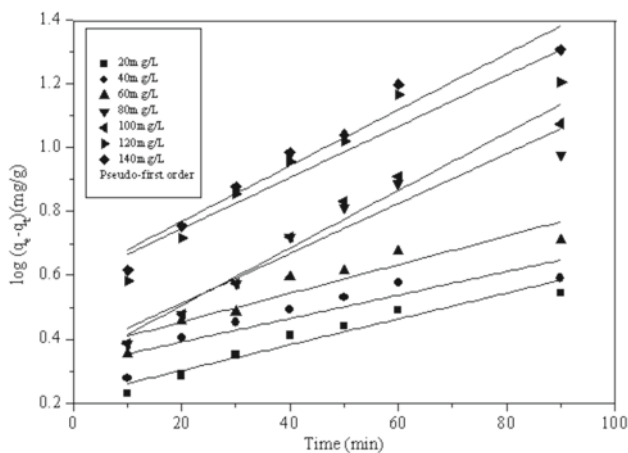


Figure 13. Pseudo-first order kinetic model for the adsorption of MO onto PJBC

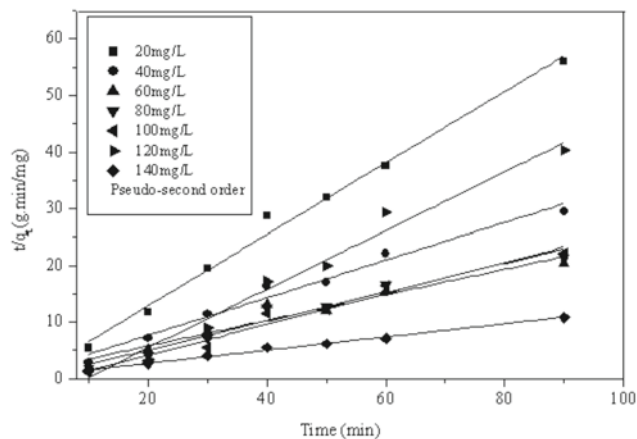


Figure 14. Pseudo-second order kinetic model for the adsorption of MO onto PJBC

used for the prediction of the Pseudo-first order and the Pseudo-second order kinetics parameters like r^2 , K_1 , K_2 and q_m . By plotting a graph between t vs. $\log(q_e - q_t)$ and t vs. t/q_t and it was shown in Fig. 13 and Fig. 14, respectively. The calculated value of the pseudo-first order rate constant (K_1), the pseudo-second order rate constant (K_2), equilibrium uptake capacity (q_e) and their corresponding regression coefficient (r^2) were presented in Table 6. From the table the coefficient values of the pseudo-first order rate constant and the obtained q_e values are very low.

Table 7. Thermodynamic parameters for the adsorption of MO onto PJBC

T(K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol.K)
303	-0.1	4.1	43.1
313	-0.4		
323	-0.9		
333	-1.3		
343	-1.4		

On the other hand the obtained values of the pseudo-second order kinetics show that the correlation coefficient values are 0.9903 and 0.9904. This indicates that the sorption process follows the second order kinetic mechanism rather than the first order mechanism. That means that the rate of the adsorption process does not only depend on the concentration factor (Pseudo-first order) and also depends both on concentration as well as time (Pseudo-second order).

Adsorption Thermodynamics

The thermodynamic parameters provide the in-depth information of the inherent energetic changes that are associated with adsorption. The thermodynamic parameters, such as standard Gibbs energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), were determined by using the following equations⁴³.

$$K_d = \frac{q_e}{C_e} \quad (8)$$

$$\Delta G = -RT \ln K_d \quad (9)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

where, K_d is the distribution coefficient, T is the temperature, and R is the gas constant ($8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), respectively. ΔS° and ΔH° were calculated from the slope and intercept of Van't Hoff plots of $\ln K_d$ vs. $1/T$ (Fig. 15).

The calculated values of thermodynamic parameters are given in Table 7. The negative ΔG° values at different temperatures imply the spontaneous nature of the adsorption of MO onto the PJBC. The more negative value shows that the amount adsorbed at equilibrium must be increased. The value of ΔH° is found to be positive in the temperature range of 303 K to 343 K. It reveals that the adsorption process was endothermic in nature. Moreover, adsorption in the liquid phase is

a complex phenomenon in which the solute and the solvent compete for the solid surface. Adsorption and desorption of the solute and the solvent molecules take place simultaneously, and the adsorption process involves energy changes that could result in a positive ΔH^0 . In addition, the positive⁴⁵ value of ΔS^0 confirms that the good affinity⁴⁶ of MO towards the activated carbon and the increased randomness at the solid-solution interface during the adsorption process of MO on to PJBC.

CONCLUSION

From the experimental and statistical data obtained in the present study, we may conclude that the activated carbon prepared from *Prosopis juliflora* bark can be used as a potential adsorbent, abundant, eco-friendly and cheap one for the removal of methyl orange from an aqueous solution. The acidic pH significantly enhances the adsorption process. The highest percentage removal of dye was observed in room temperature (303K). Various forms of the Freundlich and the Langmuir isotherm models were evaluated using linear and non-linear regression analysis. The correlation coefficient value shows that Langmuir has best fitted performance than the Freundlich isotherm. The R_L value shows that the adsorption process was favourable. The pseudo second-order kinetic model fits very well with the dynamic adsorption behaviour of dye that shows the chemical adsorption involved. From the thermodynamic study, the negative values of ΔG^0 and positive value of ΔH^0 indicated that the dye adsorption process is a spontaneous and endothermic in nature. In addition, the positive value of ΔS^0 reveals a good affinity at the solid-solution interface during the adsorption process. The FTIR spectrum implies that the principal functional sites take part in the sorption process including carboxyl, hydroxyl and other functional groups. The TGA and DTA studies indicated the decomposition of surface groups and formation of various gaseous products.

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