

# Thermodynamics and Adsorption Study of Methyl Orange onto Fired Bricks

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**Abstract:** In this study, fired bricks (FB) was used as an adsorbent to remove an anionic dye, methyl orange (MO), from an aqueous solution by the batch adsorption technique. Various conditions were evaluated, including initial dye concentration, adsorbent dosage, contact time, solution pH, agitation speed and temperature. The adsorption isotherms of the FB were studied using the Freundlich, Tekman and Langmuir models. The experimental data obtained with FB fits best to the Langmuir isotherm model and exhibited a maximum adsorption capacity ( $q_{max}$ ) of 2.3mg/g. The intra particle diffusion studies revealed that the adsorption rates were not controlled only by the diffusion step. The thermodynamic parameters, such as the changes in enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ), and Gibbs free energy ( $\Delta G$ ), showed that the adsorption is endothermic, random and nonspontaneous at high temperature. The results indicate that FB adsorbs MO efficiently and could be utilized as a low-cost alternative adsorbent for the removal of anionic dyes in wastewater treatment.

**Keywords:** adsorption – methyl orange – fired bricks

## 1. Introduction

Water pollution is one of the most undesirable environmental problems in the world and it requires solutions. Textile industries produce a lot of wastewater, which contains a number of contaminants, including acidic or caustic dissolved solids, toxic compounds, and any different dyes, many of the organic dyes are hazardous and may affect aquatic life causing various diseases and disorders. [1] Synthetic dyes are extensively used in various branches of the textile industry, paper printing, color photography, pharmaceutical, leather, cosmetics, plastic, and other industries. The discharges of industrial wastewater containing dyes cause areal environmental problem because of its high toxicity and possible accumulation in the environment [2, 3]. Synthetic dyes are a group of most dangerous pollutants in water [4-6]. The presence of even very low concentrations of dyes in water reduces light penetration through the water surface, precluding photosynthesis of the aqueous flora [7].

Many of these dyes are carcinogenic, mutagenic, and teratogenic and also toxic to human beings, fish species, and microorganisms. Hence, their removal from aquatic wastewater becomes environmentally important [8]. A great varieties of synthetic dyes are produced on a daily basis in dyestuff, textile, leather, paper and food industries [9].

The methods of color removal from industrial effluents include biological treatment, coagulation, oxidation, hyper filtration and adsorption [10-14]. Among the treatment options, adsorption appears to have considerable potential for the removal of color from industrial effluents [15, 16]. Adsorption can perform many separations that are impossible or impractical by conventional techniques such as distillation, absorption and even a membrane based system [17]. Applications for adsorption have been expanded rapidly because of sharply rising environmental or quality requirements and advances in adsorption quality have made it possible to many of those demands [18, 19].

The best known application of adsorption is the purification of municipal water at low cost level [20, 21]. The most important attributes of adsorbent to application of adsorption are capacity, selectivity, regenerability, kinetics, compatibility and cost [22]. Adsorption is used for water and wastewater treatment to remove hazardous organic compounds and those that impart odor or taste [23].

At present, there is a growing interest in using low cost sorbents for dye sorption. If a sorbent is inexpensive and ready for use, the sorption process will be a promising technique. Activated carbon is the most widely used adsorbent for this purpose because of its extended surface area micro-porous structure, high adsorption capacity and, high degree of surface reactivity [24, 25]. However, commercially available activated carbons are very expensive and the laboratory preparation of activated carbons also accompanied by a number of problems such as combustion at high temperature, pore blocking and hygroscopicity. This has led to search for cheaper and simplest substituents.

In this work, crushed fired brick was used as an adsorbent to remove Methyl orange dye from aqueous solution. The effect of adsorption parameters such as pH, adsorbent concentration, contact time and initial dye concentration adsorbed was studied. The purpose of the present work was to utilize new low cost sorbent for enhancing the treatment of environmental pollution and reducing the cost of pollution treatment.

## 2. Experimental

### 2.1. Materials

The fired brick (FB) was collected and ground to fine size, then washed with distilled water, after that dried and used directly.

Analytical grade methyl orange ( $C_{14}H_{14}N_3NaO_3S$ ; molecular weight 327.33 g/mol) was obtained from Merck and was

used as received (Figure 1). The dye solution was prepared at the desired concentration using distilled water



**Figure 1:** Chemical structures of methyl orange

## 2.2. Batch adsorption experiments

Adsorption measurements on FB were carried out in batches. A desired amount of the adsorbent was added to 20mL of the MO solution (various concentrations). The desired pH was achieved by adjustment with 0.1M HCl or 0.1M NaOH. The mixture was stirred magnetically at room temperature and 400 rpm, and samples were withdrawn from the experimental flask at pre-determined time intervals until the adsorption equilibrium was reached. Next, the dye solution was separated from the adsorbent by filtration. The supernatants were filtered to ensure that the solutions were free of adsorbent particles prior to measuring the residual dye concentration.

## 2.3. Dye concentration and removal capacity

The concentration of methyl orange (MO) was determined spectrophotometrically using a UV-visible spectrophotometer (UV-1800, SHIMADZU UV SPECTROPHOTOMETER) by taking measurements at the absorbance maximum (478nm). A calibration curve was plotted between the absorbance and the concentration of the MO solution to obtain the absorbance-concentration profile. The amount of MO uptake per unit of adsorbent ( $q$ ) was calculated using the following equations:

$$q = (C_i - C_e) \times \frac{V}{m} \quad (1)$$

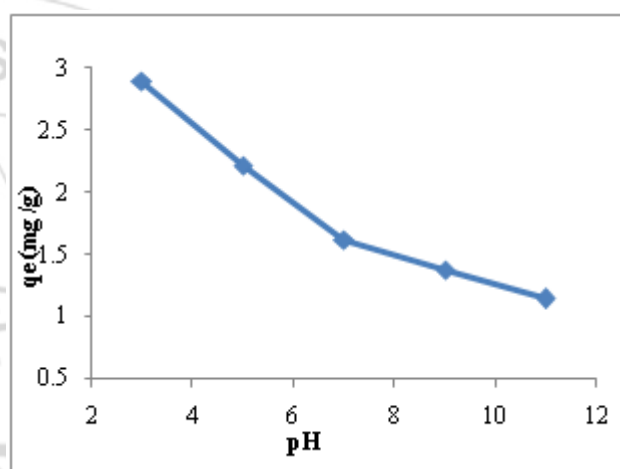
Where  $C_i$  is the initial MO concentration ( $\text{mg L}^{-1}$ ),  $C_e$  is the MO concentration at the adsorption equilibrium ( $\text{mg L}^{-1}$ ),  $V$  is the volume of MO solution (L), and  $m$  is the weight of the FB (g).

## 3. Result and Discussion

### 3.1 The effect of pH

The pH of the solution is one of the most important process parameters for controlling the adsorption. Figure 2 shows the effect of pH value (in the range of pH= 3–11) on the adsorption of MO onto FB. The maximum adsorption capacity ( $2.9 \text{ mgg}^{-1}$ ) was attained at pH 3. The major

constituents of FB are  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , which develop charges when in contact with water [26]. Protonation of the silica present in FB likely occurred, facilitating diffusion and providing a more active FB surface.  $\text{Al}_2\text{O}_3$ , a typical amphoteric oxide, dissolves in a strong acid to give  $\text{Al}^{3+}$  ions which then attracted to more stable negatively charged MO molecules, resulting in greater adsorption. However, the adsorption capacities decreased significantly when the pH of the system was increased. The higher pH value reduced the number of positively charged sites and raised the number of negatively charged sites, creating electrostatic repulsion between the negatively charged surface of the FB and the anionic MO molecules. As a result, there was in a significant reduction in the removal of MO from the solution. Moreover, the presence of some alkali metal oxides in FB also provided an abundance of hydroxyl anions when the material was in contact with water and these anions competed with the anionic MO molecules for the adsorption sites, which resulted in lower adsorption of MO [27].



**Figure 2:** Effect of pH on adsorption of MO on FB (adsorbent dosage  $4.0 \text{ g L}^{-1}$ , initial MO concentration  $20 \text{ mg L}^{-1}$ )

### 3.2 The effect of initial MO concentration

Experiments were carried out at different initial concentrations of MO while the other parameters were kept constant. As shown in Figure 3, the adsorption capacity improved with increased initial dye concentrations. A higher initial dye concentration led to an increase in the mass gradient between the solution and the FB, which then functions as a driving force for the transfer of dye molecules from bulk solution to the FB surface [26]. At an MO concentration of 20 ppm, the maximum adsorption capacity was  $2.9 \text{ g/g}$  after a contact time of 60min.

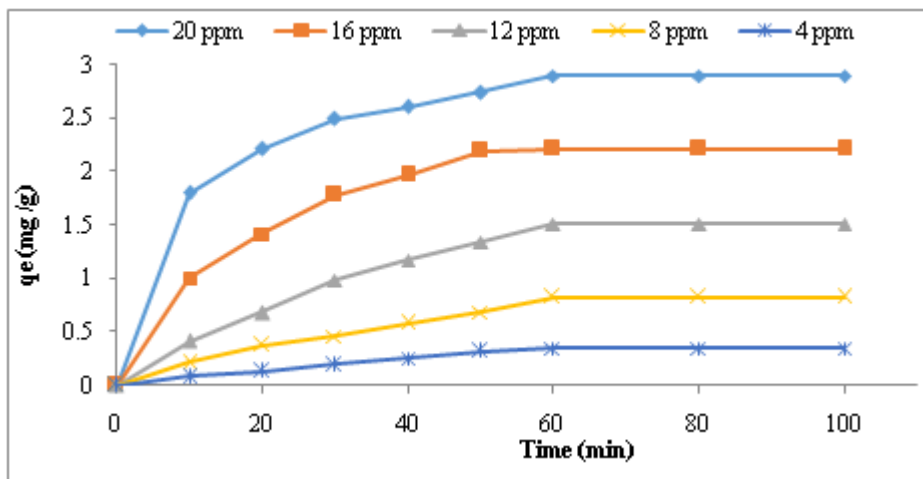


Figure 3: Effect of initial concentration of the MO on LVM (adsorbent dosage 4 g L<sup>-1</sup>, initial pH 3)

### 3.3 The effect of adsorbent dosage

Figure 4 shows the effect of varying the adsorbent dosage from 1 to 4g/L of FB. The adsorption capacity of MO increased with increasing adsorbent dosage, and the highest adsorptive capacity (2.9g/g) was achieved using 4 g/ L of

FB. A higher adsorbent dosage means that a large overall total surface area of FB is exposed, and hence, more MO anions were adsorbed onto the surface per gram unit of FB, which led to the higher adsorption capacity.

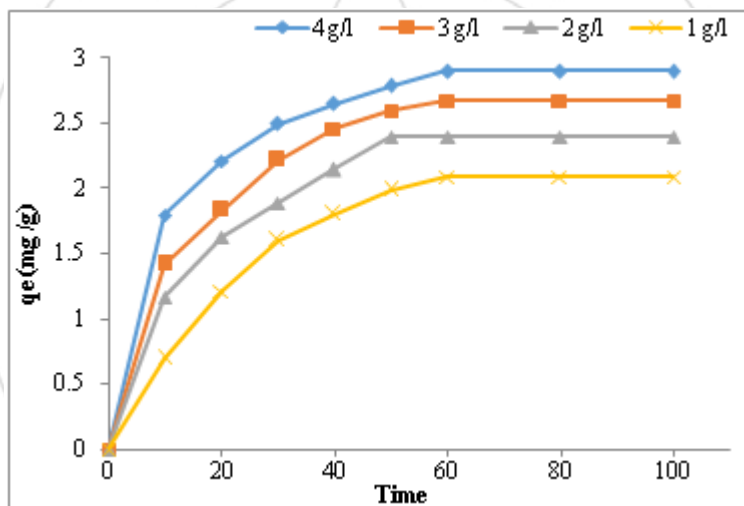


Figure 4: Effect of FB dosage (initial concentration 20 mgL<sup>-1</sup>, initial pH 3)

### 3.4 Effect of Agitation Speed

Agitation speed is an important parameter in sorption phenomena, which has a serious action on the distribution of the solute in the bulk solution and the formation of the external boundary film. The effect of agitation on the uptake of MO by FB was studied at different agitation speeds (100-400 rpm). From Figure 5, it can be observed that agitation speed significantly affects the sorption of MO, thus confirming that the influence of external diffusion on the sorption kinetic control plays a significant role. The percent of dye adsorbed was found to increase successfully from 39.7 to 64.3% with increased in agitation speed from 100 rpm to 500 rpm, thus confirming that the influence of external diffusion on the sorption kinetic control plays a significant role. With increasing the agitation speed, the rate of diffusion of dye molecules from bulk liquid to the liquid boundary layer surrounding the particle becomes higher because of an enhancement of turbulence and a decrease of thickness of the liquid boundary layer.

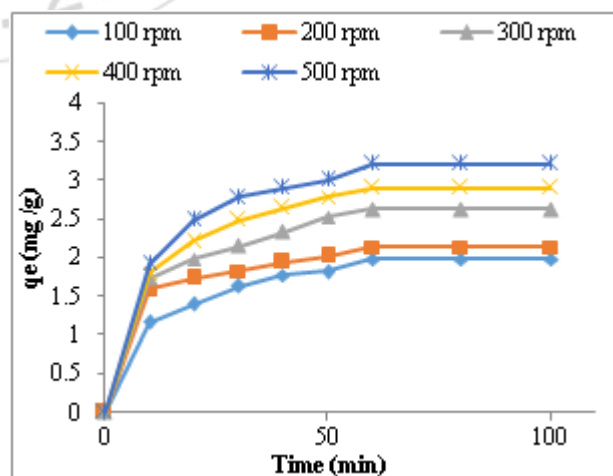
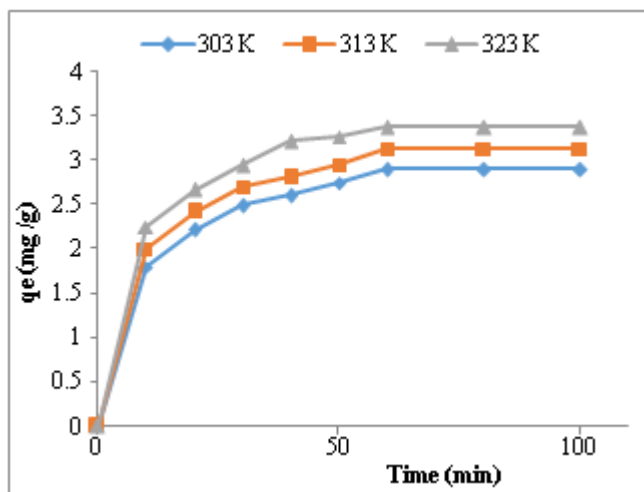


Figure 5: Effect of agitation speed for adsorption of the MO on FB (adsorbent dosage 4 g L<sup>-1</sup>, initial pH 3)

### 3.5. Effect of temperature

Figure 6 illustrates the adsorption capacity of the FB increased with an increase of the temperature from 303 to 323 K. It can be seen that higher temperatures were favorable for adsorption. The equilibrium adsorption capacity was affected by temperature, especially, with the amount of MO adsorbed increasing from 2.9 to 3.3 mg/g when the temperature was raised from 303 to 323 K. It has been well-documented that temperature has two major effects on the adsorption process. An increase in temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles as a result of the decreased viscosity of the solution [28].



**Figure 6:** Effect of temperature on adsorption of MO onto FB (initial concentration  $20\text{mgL}^{-1}$ , initial pH 3, adsorbent dosage  $4\text{g L}^{-1}$ , contact time 1 h).

### 3.6. Adsorption isotherms

In this study, three commonly used models, the Freundlich, Langmuir, and Temkin isotherm isotherms were applied to understand the dye-fired brick interaction. The Freundlich isotherm is an empirical equation that assumes that the adsorption surface becomes heterogeneous during the course of the adsorption process. The heterogeneity arises from the presence of different functional groups on the surface and from the various adsorbent-adsorbate interactions. The Freundlich isotherm is expressed by the following empirical equation:

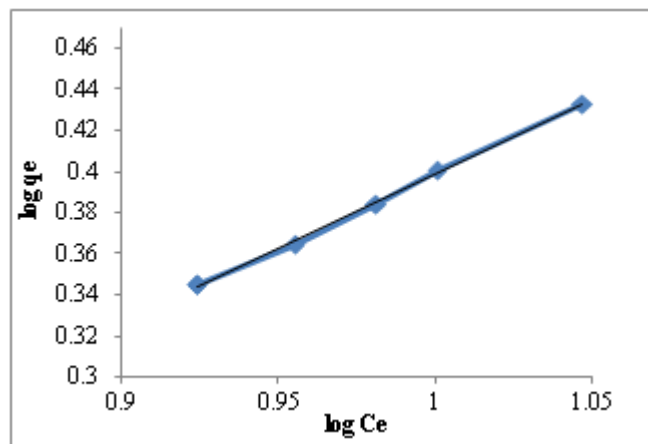
$$q_e = k_f C_e^{1/n} \quad (2)$$

In logarithmic form, Eq. (2) can be represented as:

$$\log q_e = \log k_f + 1/n \log C_e \quad (3)$$

where  $q_e$  is the amount of MO adsorbed per unit of adsorbent at equilibrium ( $\text{mg/g}$ ),  $C_e$  is the concentration of the dye solution at equilibrium ( $\text{mg/L}$ ),  $K_F$  and  $n$  are Freundlich adsorption isotherm constants, which indicate the extent of the adsorption and the degree of nonlinearity between the solution concentration and the adsorption, respectively. The values of  $K_F$  and  $n$  can be calculated from the intercept and slope of the linear plot between  $\log C_e$  and  $\log q_e$  (Figure 7) and are listed in Table 1. In general, as the  $K_F$  value increases, the adsorption capacity of the adsorbent for a given adsorbate also increases. The value of the Freundlich

exponent  $n$  (1.38) is in the range of  $n > 1$ , indicating that the adsorption process is favorable [29].

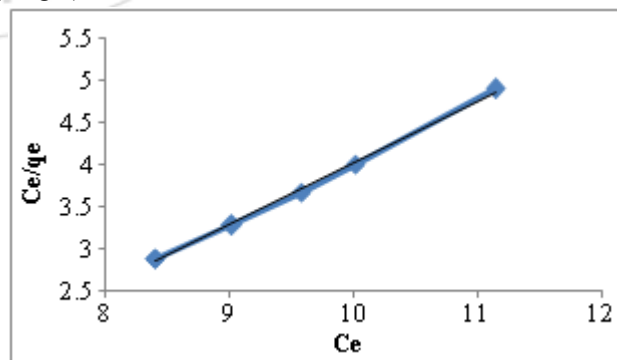


**Figure 7:** Freundlich adsorption isotherm for adsorption of MO on FB (adsorbent dosage  $4\text{gL}^{-1}$ , initial pH 3) :

The Langmuir isotherm is based on the assumption that the adsorption process takes place at specific homogeneous sites within the adsorbent surface and that once a dye molecule occupies a site, no further adsorption can take place at that site, which concluded that the adsorption process is monolayer in nature [30]. The equation of Langmuir isotherm is represented as follows:

A well-known linear expression for the Langmuir isotherm is represented as:

where  $C_e$  is the concentration of dye solution at equilibrium ( $\text{mg L}^{-1}$ ),  $q_e$  is the amount of MO adsorbed per unit of adsorbent at equilibrium ( $\text{mg g}^{-1}$ ),  $q_m$  is the maximum amount of adsorption with complete monolayer coverage on the adsorbent surface ( $\text{mg g}^{-1}$ ), and  $K_L$  is the Langmuir constant, which is related to the energy of adsorption ( $\text{Lmg}^{-1}$ ).



**Figure 8:** Langmuir adsorption isotherm for adsorption of MO on FB (adsorbent dosage  $4\text{gL}^{-1}$ , initial pH 3)

The Langmuir constants  $K_L$  and  $q_m$  can be determined from the intercept and slope of the linear plot of  $C_e/q_e$  versus  $C_e$  (Figure 8) and are presented in Table 2. The essential characteristics of the Langmuir isotherm can be expressed in



terms of a dimensionless constant separation factor  $R_L$ , which is given by Eq. (6)

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

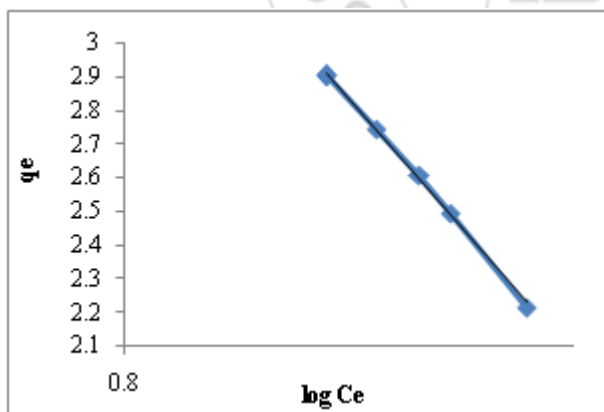
where  $C_0$  ( $\text{mgL}^{-1}$ ) is the highest initial concentration of adsorbent, and  $K_L$  ( $\text{Lmg}^{-1}$ ) is the Langmuir constant. The parameter  $R_L$  indicates the nature of shape of the isotherm accordingly:

- $R_L > 1$  Unfavorable adsorption
- $0 < R_L < 1$  Favorable adsorption
- $R_L = 0$  Irreversible adsorption
- $R_L = 1$  Linear adsorption

Table 2 shows that the value of  $R_L$  is 0.05 at  $30^\circ\text{C}$ , indicating that the adsorption of MO on FB is favorable at the temperature studied. The  $R^2$  values of the Langmuir and Freundlich isotherms are 0.997 and 0.998, respectively, indicating that the equilibrium sorption data fits best with the Freundlich isotherm.

**Table 1:** Isotherm parameters for adsorption of methyl orange on fired brake at  $30^\circ\text{C}$

isotherm	parameters
Freundlich	
$K_f$	0.322
$n$	1.38
$R^2$	0.998
Langmuir	
$q_m$ ( $\text{mg g}^{-1}$ )	2.3
$K_L$ ( $\text{L mg}^{-1}$ )	0.313
$R^2$	0.997
$R_L$	0.05
Temkin	
$A$ ( $\text{L/mg}$ )	5.5
$B$	7.99
$R^2$	0.9982



**Figure 9:** Temkin adsorption isotherm for adsorption of MO on FB (adsorbent dosage  $4\text{gL}^{-1}$ , initial pH 3)

Temkin isotherm takes into account the effects of indirect adsorbate-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 [31]. The linear form of Temkin isotherm is expressed as:

$$q_e = B \ln A + B \ln C_e \quad (7)$$

where  $B$  is the Temkin constant related to heat of adsorption and  $A$  is the equilibrium binding constant ( $\text{L/mg}$ ). The

constant  $A$  and  $B$  can be determined by a plot of  $q_e$  versus  $\ln C_e$ .

The correlation coefficient,  $R^2$  value and the constant obtained from the isotherm model are summarized in Table 1. The Temkin isotherm model gave the highest  $R^2$  values which were greater than 0.9982 at the temperature studied, showing that the adsorption of dyes on FB was best described by this model.

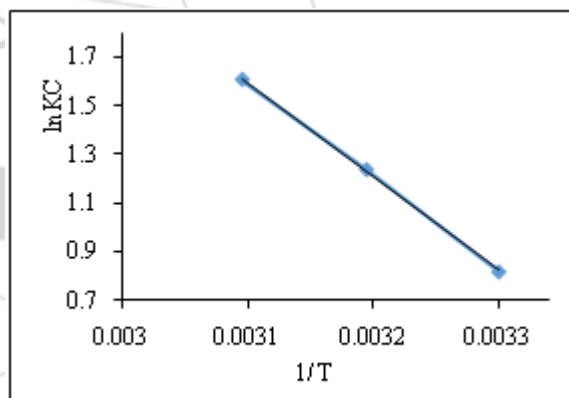
The maximum monolayer adsorption capacity,  $q_m$  has been widely used to compare the efficiency of an adsorbent. Table 1 indicates that the fired brake used in this work had a relatively large adsorption capacity of  $3.27 \text{ mg/g}$  at  $323\text{K}$ . The large adsorption capacity could be attributed to its relatively high surface area and its mesoporous structure. A value for  $1/n$  was found to range between zero and one, indicating that the adsorption condition was favorable.

### 3.7 Thermodynamic analyses of the adsorption isotherm data

Thermodynamic parameters such as the changes in the standard free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) can be calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_C \quad (8)$$

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ T \quad (9)$$



**Figure 10:** Plot of  $\ln K_C$  versus  $1/T$  for estimation of thermodynamics parameters for the adsorption of MO onto FB.

**Table 2:** Thermodynamic parameters for the adsorption of methyl orange on Fired brake at different temperatures

$T$ (K)	$\ln K_C$	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol/K)
303	0.81921	4.05		
313	1.23605	3.21	3.87	13.6
323	1.60944	3.19		

where  $K_C$  is the equilibrium constant of the adsorption, which obtained from Eq. (10)

$$K_C = \frac{K_C(\text{adsorbent})}{K_C(\text{solution})} \quad (10)$$

where  $C_e$  (adsorbent) and  $C_e$  (solution) are the equilibrium concentration of the dye ions on adsorbent and in solution, respectively. Eqs. (8) and (9) then give the van't Hoff equation as:

$$\ln K_C = \frac{\Delta}{R} - \frac{\Delta}{RT} \quad (11)$$

As shown in Figure 10, the plot of  $\ln K_C$  versus  $1/T$  gives a straight line with a slope of  $\Delta H^\circ$  ( $\text{kJ mol}^{-1}$ ) and an intercept of  $\Delta S^\circ$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ). The values of these thermodynamic parameters (studied at three different temperatures) are listed in Table 5. The positive value of  $\Delta G^\circ$  at different temperatures showed that the adsorption was not a spontaneous and that the system gained energy from an external source [32]. The positive  $\Delta H^\circ$  value indicates the endothermic nature of the adsorption; this feature may also indicate that monolayer adsorption is taking place [33].

The positive values of  $\Delta S^\circ$  suggest that there is increased randomness at the solid–solution interface during the adsorption of MO in aqueous solution on FB. Also, the positive value of  $\Delta S^\circ$  indicates that some structural changes may have taken place as a result of interactions between the MO molecules and the functional groups on the FB surface [34].

#### 4. Conclusion

The present study investigated the adsorption of MO from aqueous solutions by using an adsorbent of fired bricks FB has been demonstrated to be highly effective for the removal of the anionic dye MO with an adsorption equilibrium time of less than 60 min. The best-fit adsorption isotherm was achieved with the Langmuir model, indicating that adsorption occurs by monolayer coverage. The positive enthalpy change for the adsorption process confirms the endothermic nature of the adsorption. The low price and abundance of FB make this material particularly promising for the removal of anionic dyes in industrial wastewater treatment.

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