# Equilibrium and Kinetic Studies of Biosorption of Methyl Orange dye from Aqueous Solution onto Dodonaea Angustifolia (sand olive) Tree

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## Abstract:

In this study, the removal of Methyl Orange dye by biosorption on Dodonaea leaves has been studied. The effect of operating parameters such as pH, contact time and adsorbent dosage has been investigated. Many kinetic model were applied, the pseudo-second order model was more compatibility with experimental results, as well Langmuir model that suggest monolayer sorption. Results showed that the maximum adsorption capacity were 1.477 mg/g. The values of the separation factors ($R_L$) are in the range of 0-1 which indicates favorable biosorption.

**Keywords**: Biosorption; Dodonaea Leaves; Methyl Orange dye

# 1. Introduction:

A dye is a colored substance which when applied to the fabrics imparts a permanent color and the color is not removed by washing with water, soap or an exposure to sunlight [1]. Color removal has been the target of significant attention in the last few years, not only because of its toxicity but also to its visibility [2]. Textile industry is reported that there are over 100,000 commercially available dyes with a production of over $7 \times 10^5$ metric tons per year [3,4]. Therefore, the decolorization of textile wastewaters has been a major environmental concern for a long time [5]. Many dyes have been used in various dyeing process in textile industry and azo dye is one of them. Azo dyes make up approximately 70% of all dyes used worldwide by weight. They are extensively used in the textile, paper, food, leather, cosmetics and pharmaceutical industries [6]. Also, azo dyes may impart toxicity to aquatic life and may be mutagenic, carcinogenic and may cause severe damage to human beings, such as dysfunction of the kidneys, reproductive system, liver, brain and central nervous system [6, 15].

Methyl orange dye is typically azo-based chromophores combined with different types of reactive groups. Methyl orange (MO) is a commonly used an anionic mono-azo dye in laboratory assays, textiles and other commercial products [2, 3, 8]. It is thought to be toxic if swallowed or inhaled and avoid skin contact with the solution or the solid [7]. The characteristics of these dye compounds have generated some challenging environmental problems, such as increasing the chemical oxygen demand of wastewater, thus reducing the percentage of light penetrating into the water which reduces photosynthesis activity in aquatic media [10, 11]. Methyl orange is sodium 4-[(4-dimethylamino) phenyl diazenyl] benzene

sulfonate is shown in figure 1. It is also called C.1. Acid orange 52. Its properties are summarized as in table 1.
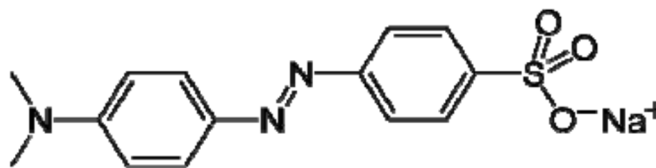


**Figure1. Chemical structural of Methyl Orange dye.**

**Table1. Properties of methyl orange dye.**

| Parameter | Value |
|---|---|
| Chemical formula | $C_{14}H_{14}N_3NaO_3S$ |
| Molecular weight(g/mol) | 327.33 |
| Physical form | Orange powder |
| Density (g/Cm$^3$) | 1.28 |
| $\lambda_{max}$ (nm) | 463 |
| pH | < pH 3.1 red color |
| | >pH 4.4 orange color |

The removal of MO dye from effluents is essential not only to protect human health but also for the protection of water resources. Currently, there is several treatment technologies used in the removal of dyes from waste effluents such as chemical precipitation, adsorption, ion exchange, biodegradation, membrane filtration, coagulation and flocculation [9, 12, 13]. Among the various technologies for removal of methyl orange dye molecules from effluents, biosorption is an alternative eco-friendly technology for removal of azo dyes from aqueous solutions, due its simplicity of design, ease of operation, insensitivity to toxic

substances and complete removal of pollutants, even from dilute solutions [14].

In recent years, many studies have shown that methyl orange dye can be removed using various natural materials such as activated carbon modified by silver Nanoparticles [8], dragon fruit foliage (DFF) [9], activated carbon prepared from Date Stones [12], rice husk [16], chitosan intercalated montmorillonite [17], bentonite-supported nanoscale zero-valent iron [18], Iron (II) crosslinked chitin-based gel beads [19] Calcium Alginate/Multi-walled Carbon Nanotubes [20] and modified halloysite nanotubes [21] have been used and investigated adsorbent.

*Dodonaea angustifolia* is a variable shrub or tree, usually 2-8 m tall; branchlets rusty red and resinous; bark dark grey, fissured and peeling [34]. *D. angustifolia* has not yet been tested for the adsorption of dyes from aqueous solution and therefore its ease of availability, non-toxic nature, and cheapness. Based on the above mentioned fact, the present study was undertaken to explore the adsorption behavior of dodonaea leaves (DL) towards Methyl orange dye, to determine the suitable adsorption isotherms and to determine kinetic models. The effect of parameters such as initial solution pH, adsorbent dosage and contact time was studied.

## 2. Experimental:
### 2.1. Preparation of Methyl Orange dye solutions:

All the chemicals used were of analytical reagent (AR) grade and were used without further purification. Stock solution of 1000 mg/L MO was prepared from Methyl Orange dye (MO), using distilled water. Desired test solutions of MO were prepared using appropriate subsequent dilutions of the stock solution. The range of concentrations of MO prepared from standard solution varies between 5 and 20 mg/L. Before mixing the

adsorbent, the pH of each test solution was adjusted to the required value with 0.1 M NaOH or 0.1 M HCl.

## 2.2 Preparation of Dodonaea Leaves (DL):

The Dodonaea leaves were cleaned with distilled water to remove dust and soluble materials. Then it was allowed to dry at room temperature. The dried leaves were grounded to a fine powder in a grinding mill and sieved to get size fraction 150 μm and then dried in an oven at 60°C for 24 h.

## 2.3 Adsorption experiments:

Batch adsorption experiments were carried out in 100 ml conical flask containing the aqueous MO dye solution of the desired concentration and the known amount of DL. Batch experiments were performed at different biosorbent dosage in the range of 0.05g to 0.8g, initial dye concentration in the range of 5 to 20 mg/l and pH varying from 2 to10. Initial pH was adjusted to the desired level with 0.1 M NaOH or 0.1 M HCl solutions. The solution was agitated at constant speed of 240 rpm and at 21±1°C temperature till the equilibrium condition was reached. Dye concentrations in the aqueous solutions were determined by using UV-VIS spectrophotometer (Jenway Ltd models 4600). Concentrations of dye were estimated from the calibration curve and equations. The amount of methyl orange dye adsorbed at equilibrium, $q_e$ (mg/g), was calculated by:

$$q_e = V(C_0 - C_e)/m \quad \text{………………………………….(1)}$$

where $C_0$ (mg/L) represents the initial MO dye concentration, $C_e$ (mg/L) is the equilibrium concentration of MO dye remaining in the solution, m (g) is

the weight of adsorbent (DL) and V (L) is the volume of the aqueous solution.

Adsorption Efficiency % = $[(C_0-C_e) / C_0] \times 100$ ………………(2)

## 2.4. Factors influencing Adsorption Process:

(A) <u>Effect of contact time</u> : The effect of contact time on the adsorption was studied by using 50 ml of 10 mg/l from MO dye and 0.05g of DL with different time (10-120 min.) at 293K. Agitation was provided at a constant agitation speed of 240 rpm.

(B) <u>Effect of pH:</u> Adsorption experiments were carried out as a function of pH by using 50 ml of 10 mg/l solution from MO dye in different pH- media. NaOH (0.1M) and (0.1 M) HCl were used to adjust the pH in the range (2-10) and at 293K. Agitation was provided for 60 min. contact time at a constant agitation speed of 240 rpm.

(C) <u>Effect of Adsorbent dosage</u>: The effect of adsorbent dosage on the adsorption was studied by using 50 ml of 10 mg/l from MO dye with different weigh of DL (0.05, 0.1, 0.2. 0.4 and 0.8 g) at 293K. The experiment was conducted at pH 6. Agitation was provided for 60 min. contact time at a constant agitation speed of 240 rpm.

## 3. Results and Discussions:
## 3.1 Effect of contact time:

The contact time is one of the most important parameters for practical application. The effect of contact time on the removal adsorption of methyl orange dye is shown in figure 2. At the beginning of adsorption,

the values of percentage removal increased quickly, and then after 60 min., the change turned slow. This was due to the fact that, at the initial stage the number of free adsorption sites was higher, and in the later stage, the remaining vacant sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Similar finding was reported by other researches [7, 9, 12] also.
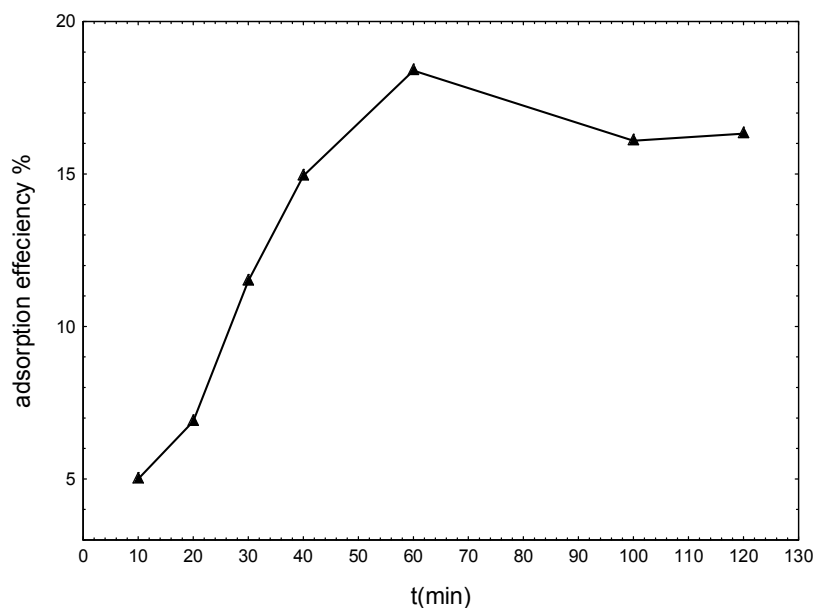


**Figure2. The effect of contact time on MO adsorption**

## 3.2 Effect of pH:

The pH is an important parameter which controls the adsorption process since the pH of the solution influences the surface charge of the adsorbent [9]. The effect of pH on the removal adsorption of methyl orange dye is shown in figure 3, the dye uptake was found to decrease with an increase in pH solution of MO from 10 to 2. It can be explained by the following facts. At acidic pH, the number of positively charged sites

increase, which favors the adsorption of the anions due to electrostatic attraction [7]. Lower adsorption of MO, at alkaline pH is provable due to the competition between anionic dye and excess OH ions in the solution, which may be due to the fact that the high concentration and high mobility OH ions are preferentially adsorbed, compared to dye anions [12]. It can be concluded that the optimum pH for MO biosorption is 6.0 and this pH was used for the rest of the study.
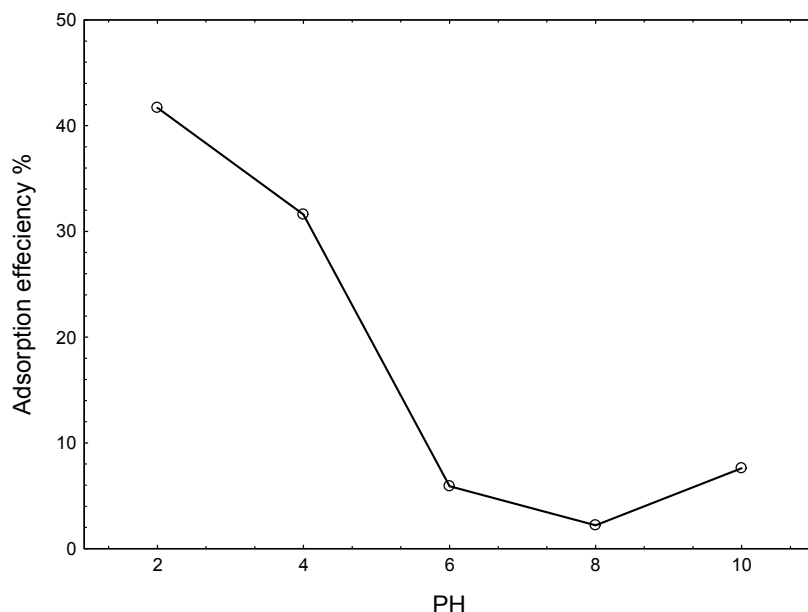


**Figure3. The effect of PH solution on MO adsorption**

## 3.3 Effect of adsorbent dosage:

One of the parameters that strongly affect on the adsorption process in an aqueous solution is the adsorbent dose. Due to it determines the capacity of an adsorbent for a given initial concentration of the adsorbate [22]. The effect of adsorbent dosage on the rate of methyl orange dye uptake onto dodonaea leaves is shown in figure 4. From the figure it also

can be observed that dye uptake decreases with increases in DL dose. But at the same time the overall removal efficiency increases. The removal MO dye at a dose of 0.05 g/L is found to be 45%; removal improves to 62.5% when the adsorbent dosage is increased to 8.0 g/L. The increase in the removal of dyes is due to the increase of number of sites available for adsorption site increases by increasing the adsorbent dose [12], while the decrease in dye uptake value is due to the concentration gradient between adsorbate and adsorbent [23].
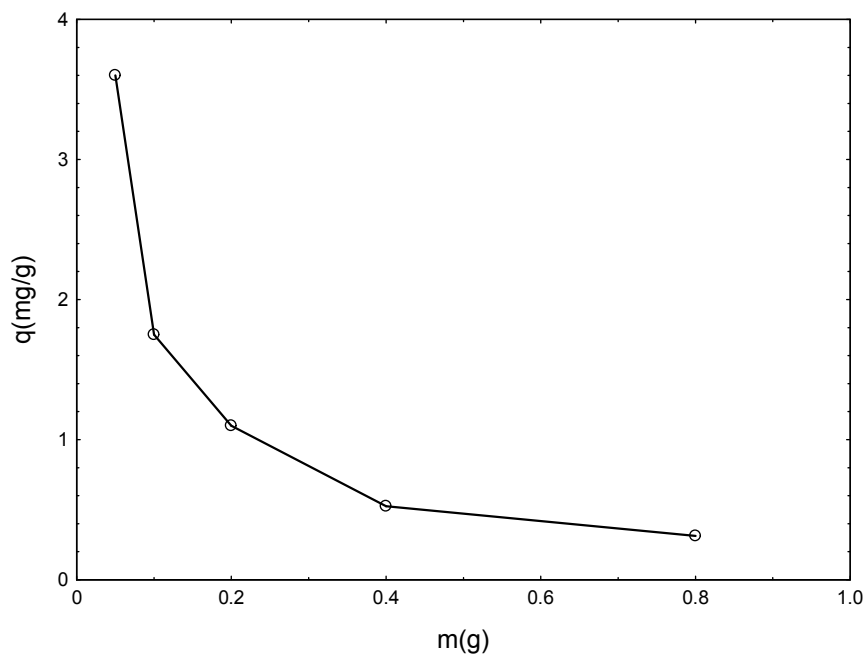


**Figure4. The Effect of adsorbent dosage on MO dye uptake onto DL**

## 3.4 Equilibrium Isotherm Models:

The biosorption isotherms (biosorption equilibrium data) describe how pollutants interact with biosorbent materials [24]. This manner is very important to obtain a model that represents the experimental equilibrium

data. There are several isotherm models available for analyzing experimental sorption equilibrium parameters. However, the most common types of isotherms are Langmuir model [25] and Freundlich model [26]. In this work, Langmuir and Freundlich models were fitted to the experimental data.

### *3.4.1 The Langmuir isotherm:*

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. It is derived by assuming a uniform surface with finite identical sites and monolayer adsorption of the adsorbate. The Langmuir isotherm can be expressed as:

$$C_e/q_e = 1/q_m K_L + 1/q_m \cdot C \quad \text{.................................(3)}$$

Where $q_e$ is the mono-layer adsorption capacity adsorbent (mg/g), $K_L$ is the Langmuir adsorption constant (L/mg) related to the adsorption Equilibrium, $q_m$ is the maximum adsorption capacity of adsorbent (mg/g). Therefore, the linear plot of $C_e/q_e$ versus $C_e$ for the MO dye for Langmuir model is shown in figure 5. From the slope and intercept of the straight line $1/q_m$ and $1/(q_m K_L)$ can be evaluated, respectively. The essential characteristics of the Langmuir isotherm can be expressed by means of '$R_L$' a dimensionless constant referred to as the separation factor or equilibrium parameter [27]. The $R_L$ is defined as:

$$R_L = 1/(1+K_L \cdot C_0) \quad \text{.................................. (4)}$$

This parameter suggests the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). As can be seen from table 2, the $R_L$ values are between 0 and 1.0, indicating that the adsorption of methyl orange dye onto dodonaea leaves is favorable.

**Table2. Values of equilibrium parameter ($R_L$)**

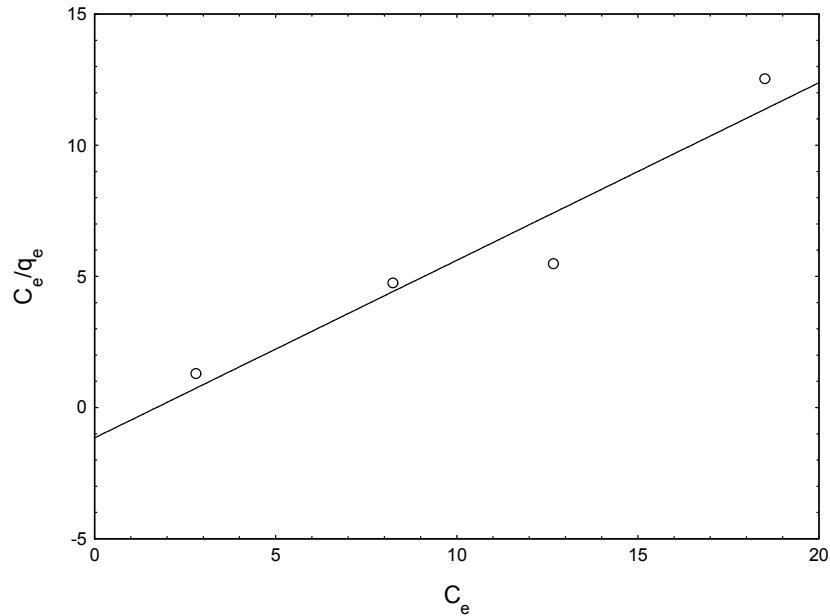| Initial concentration ($C_0$) | 5 | 10 | 15 | 20 |
|---|---|---|---|---|
| Equilibrium parameter ($R_L$) | 0.519 | 0.208 | 0.128 | 0.09 |



**Figure5. The Langmuir isotherm plot of MO onto DL**

### 3.4.2 The Freundlich isotherm:

The Freundlich isotherm is usually adopted for heterogeneous adsorption [28]. One of its limitations is that the amount of adsorbed solute increases indefinitely with the concentration of solute in the solution. This isotherm can be expressed as:

$$ln\ q_e = ln\ K_f + 1/n\ ln\ C_e \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(5)$$

Where $k_f$ is the Freundlich adsorption constants related to the bonding energy, n is the adsorption intensity, and n being a constant representing

the mutual interaction of adsorbed species. Experimental values of n are usually greater than unity and this means that the forces between the adsorbed molecules are repulsive. In addition, the closer the n value of the Freundlich sorption equations is to zero, the more heterogeneous is the system [29]. The linear plot of ln $C_e$ versus ln $q_e$ for the MO dye for Freundlich model is shown in figure 6. From the slope and intercept of the straight line n and $K_f$ can be evaluated, respectively.
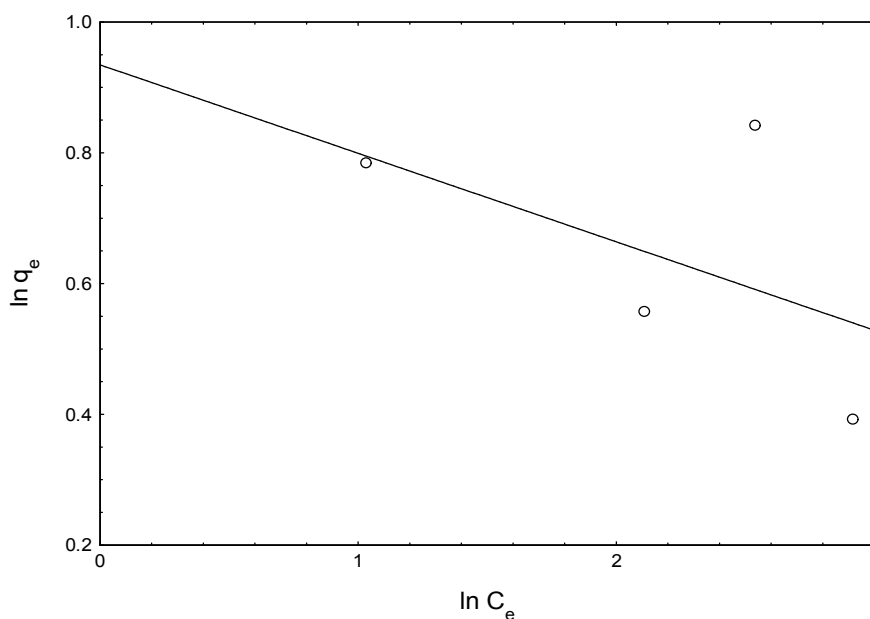


**Figure6. The Freundlich isotherm plot of MO onto DL**

Various parameters obtained from Langmuir and Freundlich isotherm are shown in table 3. From the figures 5 and 6, it was observed that Langmuir isotherm was best fitted with the experimental results. Correlation coefficient ($R^2$) for Langmuir isotherm was 0.917 compared to 0.281 of Freundlich isotherm. This signifies that MO adsorption is taking place through monolayer adsorption. Calculated maximum adsorption

capacity of MO was 1.477 mg/g. The Langmuir isotherm is applicable when there is a strong specific interaction between the solute and the adsorbent. Similar finding was reported by other researches [7, 17, 20] also. Maximum adsorption capacity of some adsorbents for MO dye is presented at table 4.

**Table3. Isotherms models for the adsorption of MO dye onto DL.**

| Adsorbent | Langmuir isotherm | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|
| | $q_m$(mg/g) | $K_L$(L/mg) | $R^2$ | $K_f$(mg/g) | n | $R^2$ |
| Dodonaea leaves (DL) | 1.477 | 0.585 | 0.917 | 2.24 | 7.407 | 0.281 |

**Table4. Recent reported adsorption capacity of some adsorbents for MO dye.**

| No | Adsorbent | $Q_m$ (mg/g) | Reference |
|---|---|---|---|
| 1. | Modified halloysite nanotubes | 94.34 | [21] |
| 2. | Fe(II) cross-linked chitin-based gel beads | 107.5 | [19] |
| 3. | AgNPs-coated AC | 27.48 | [8] |
| 4. | Chitosan intercalated montmorillonite | 70.42 | [17] |
| 5. | CA/MWCNTs composite fiber | 14.13 | [20] |
| 6. | Dragon Fruit Foliage (DFF) | 17.66 | [9] |
| 7. | Moringa Peregrina Ash | 15.43 | [7] |
| 8. | Date Stones Activated Carbon | 3.07 | [12] |
| 9. | NaX zeolite | 1.2678 | [2] |
| 10. | Dodonaea Leaves | 1.477 | Present work |

## 3.5 Adsorption Kinetics:

The kinetic data were analyzed by applying pseudo-first order, pseudo-second order, and intra-particle diffusion models to gain a better understanding of the adsorption process.

### *3.5.1 The pseudo-first order kinetic model:*

The pseudo-first order kinetic model is the earliest known in describing the adsorption rate based on the adsorption capacity [30]. The pseudo-first-order rate is generally expressed as follows:

$$\ln(q_e-q_t) = \ln q_e - K_1 t \ \text{.….…………………………………….}(6)$$

Where $k_1$ (min$^{-1}$) is the rate constant of first-order adsorption. The pseudo-first-order rate constant values were calculated from the slope of figure 7. The linear regression correlation coefficient values show that this model cannot be applied to predict the adsorption kinetic model.
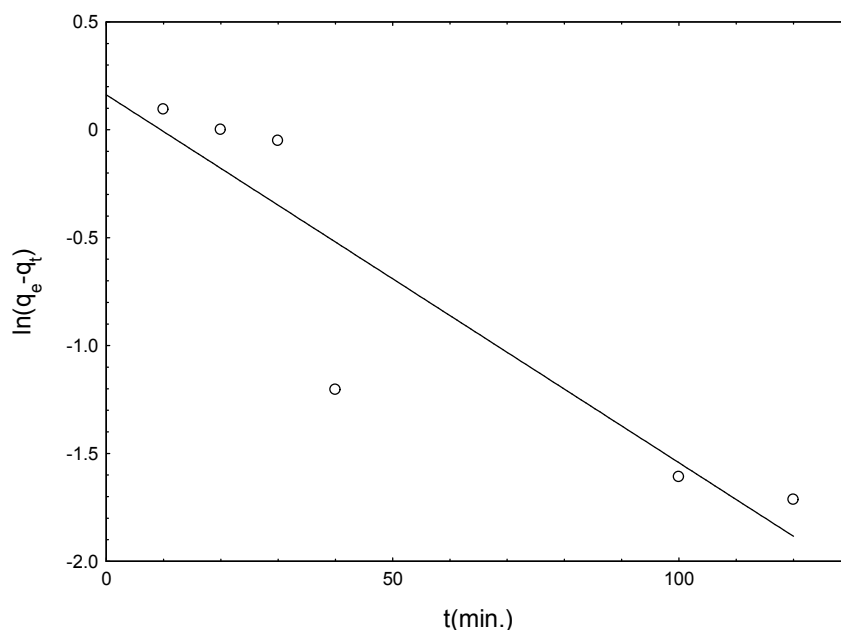


**Figure7. The pseudo-first order plot for removal of MO dye**

### 3.5.2 The pseudo-second order kinetic model:

The pseudo-second order kinetic, which has been applied for analyzing chemisorption kinetics rate [31], is expressed as:

$$t/q_t = 1/K_2 q^2_e + 1/q_e \, t \dots\dots\dots\dots\dots\dots\dots\dots\dots(7)$$

Where $k_2$ (g/(mg.min) is the rate constant of pseudo-second order. The fitting of second-order kinetic expression for the adsorption systems was obtained in which the chemical interaction between the adsorbate-adsorbent on the external surface was the rate-limiting step. From figure 8, the linear regression correlation coefficient $R^2$ values were higher. The higher values confirm that the adsorption data are well represented by pseudo-second order kinetic.
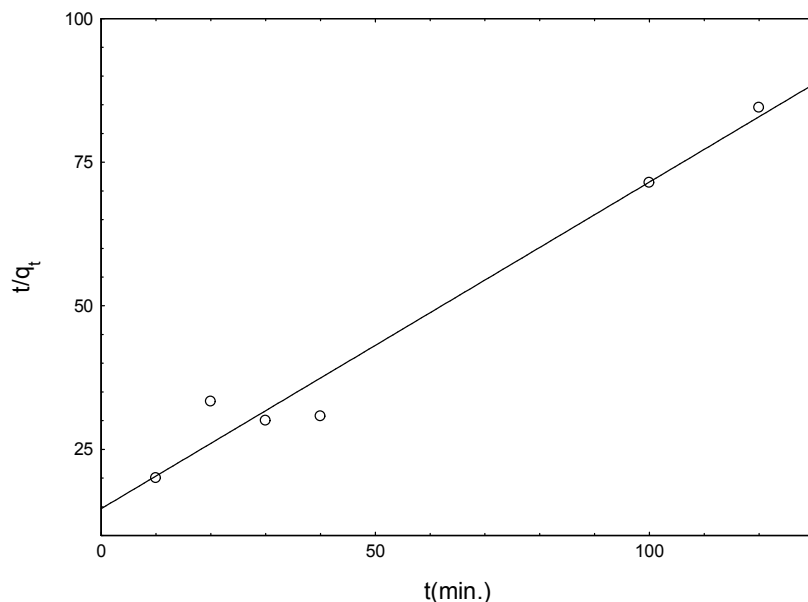


**Figure8. The pseudo-second order plot for removal of MO dye**

### 3.5.3 The intra-particle diffusion model:

The intra-particle diffusion model is assumed that the mechanism for dye removal by adsorption on a sorbent material is taking place through four steps [23]:

1. Migration of dye molecules from bulk solution to the boundary layer film of the adsorbent through bulk diffusion.
2. Diffusion of dye molecules through the boundary layer to the surface of the adsorbent via film diffusion.
3. The transport of the dye molecules from the surface to the interior pores of the particle occur through intra-particle diffusion or pore diffusion mechanism.
4. Adsorption of dye at an active site on the surface of material by chemical reaction via ion-exchange, complexation and/or chelation.

Generally, the diffusion of adsorbate molecules into internal surfaces of pores and capillaries of the adsorbent is the rate limiting step, the intra-particle diffusion model de-signed by Weber and Morris is given in the following equation [32]:

$$q_t = k_i . t^{1/2} + C \ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(8)$$

where $k_i$ (mg/g. $min^{1/2}$) represents the intra-particle diffusion rate constant and $C$ is a constant (mg/g) which gives information about the thickness of the boundary layer. The values of $k_i$ and $C$ are shown in figure 9.

From table 5, based on the high regression coefficient value the adsorption of MO on DL is well-fitted to the pseudo-second order kinetics model compared to the first order and intra-particle diffusion models. Also, in pseudo-second-order kinetic model the values of qe (cal) were very close to qe (exp) values as compared to pseudo-first-order model indicating that

pseudo-second model was better obeyed, it also suggests that the chemisorption process not diffusion-controlled [8, 33].
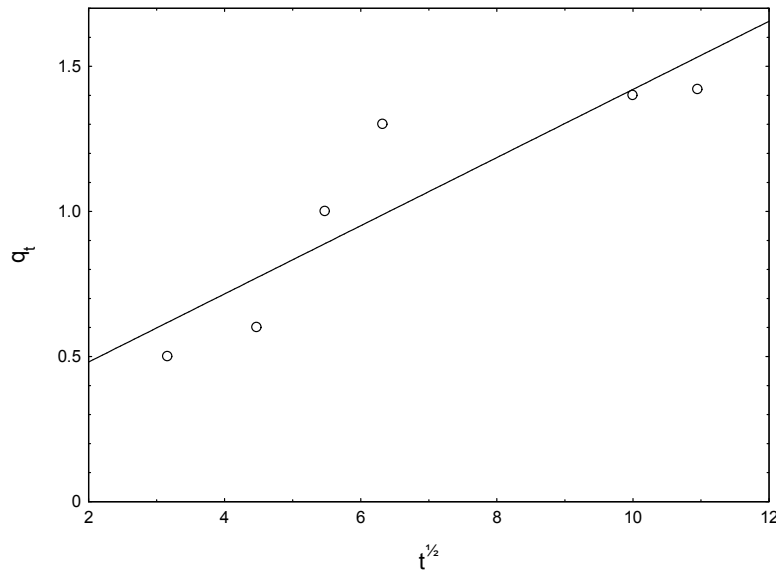


**Figure9. The intra-particle diffusion plot for removal of MO dye**

**Table5. The kinetic data for adsorption of MO dye onto DL.**

| Pseudo-1st order | | | Pseudo-2nd order | | | intraparticle diffusion | | |
|---|---|---|---|---|---|---|---|---|
| $K_1$ | $q_{e(cal)}$ | $R^2$ | $K_2$ | $q_{e(cal)}$ | $R^2$ | $ki$ | C | $R^2$ |
| 0.017 | 1.176 | 0.826 | 0.22 | 1.75 | 0.970 | 0.117 | 0.481 | 0.800 |

## 4. Conclusion:

The potential of dodonaea leaves (DL) for the removal of Methyl orange dye (MO) from aqueous solution was dependent on parameters of biosorption process such as solution pH, adsorbent dose and contact time. The Langmuir adsorption isotherm was best fitted to the experimental data

with a maximum adsorption capacity of 1.477 mg/g. Adsorption kinetics of MO dye adsorption on DL followed the pseudo-second-order kinetic model where the chemisorption process may be the rate-limiting step in the adsorption process. It can be concluded that since the DL is an easily, locally available, low-cost adsorbent and good adsorbent for removal of MO.

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