

## Cholestyramine as an Adsorbent for Methyl Orange from Aqueous Solution

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### Abstract

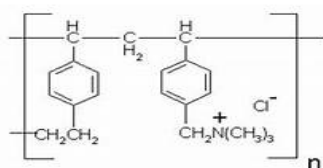
The removal of methyl orange (MO) from aqueous solution by adsorption on cholestyramine resin was evaluated by batch mode. The experiments were performed as a function of initial dye concentration, stirring rate, ionic strength, adsorbent dosage, pH and temperature. Adsorption process was attained to the equilibrium within 40 minutes. The adsorption capacity of MO increased with increasing initial dye concentration, stirring rate, and decreased with increasing ionic strength, pH, adsorbent dosage and temperature. The experimental data were analyzed by Langmuir and Freundlich isotherm models and fitted well to Langmuir model with a value of adsorption capacity of ( $Q_0$ ) 200 mg/g of MO. The effect of temperature on removal capacity was examined and was found to be an exothermic process. Thermodynamic parameters such as change in free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) were determined.  $\Delta H$  value was -17.85 kJ/mol confirming that adsorption was mainly physisorption. The negative values of  $\Delta G$  reflected the spontaneous nature of adsorption process and the negative values of entropy change  $\Delta S$  (-103.2 J/mol) imply an increase of randomness at the solid–solution interface through the adsorption at low temperatures.

**Keywords** cholestyramine, methyl orange, adsorption, isotherm models

### 1. Introduction

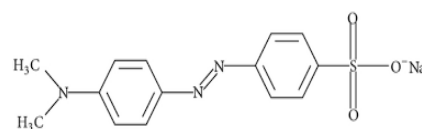
Cholestyramine is a large anionic exchange hydrophilic resin, insoluble in water. The functional group of the anion exchange resin is a quaternary ammonium group attached to an inert styrene-divinylbenzene copolymer (Fig. 1). Its chloride salt is intended for oral administration as a cholesterol-lowering agent for patients of primary hypercholesterolemia.

As a strong ion-exchanger, it can exchange its chloride ions with anionic bile acids in the gastrointestinal tract and bind strongly to them in the resin matrix acids forming an insoluble complex, which could be eliminated with the feces [1]. Serum cholesterol and low-density lipoproteins are reduced as a result of that binding.



**Fig (1)** Chemical structure of cholestyramine

Methyl orange (MO) is a pH indicator used in neutralization titrations because of its clear and distinct colour change. Unlike a universal indicator, methyl orange does not have a full spectrum of colour change, but has a sharper end-point. Methyl orange shows a red colour in acidic medium and a yellow colour in basic medium.



**Fig (2)** Chemical Structure of methyl orange

Water pollution by dyes is a serious problem owing to the toxicity of these compounds. Textile dyeing wastewater is recognized as one of the root causes of environmental pollution. The presence of high concentrations of dyes in water bodies stop the reoxygenation capacity of the receiving water and cut-off sunlight, which upsetting biological activities in aquatic life. It affects also the photosynthesis process of aquatic plants or algae. The polluting effects of dyes against aquatic environment can also be result of toxic effects due to their long-time presence in environment and accumulation in sediments. Organic dyes, which are usually carcinogenic or mutagenic, are very resistive to biodegradation and accumulate in fishes and other aquatic life forms.

Many techniques have been developed to find an economic and effective way to treat wastewater polluted with organic compounds, especially dyes. Many countries have enacted strict emissions standards but there is no uniform standard currently, Waste minimization is of great importance in decreasing pollution load and production costs.

Biological treatment [2], coagulation [3], flocculation [4], electrochemical [5], photo catalytic degradation [6] and ion-exchange [7] have been applied to remove dyes from wastewater. The application of such techniques depends on cost,

effectiveness and environment impact. Beside these techniques, adsorption appears to be an attractive method for treatment of dye effluents due to its low cost, simplicity of operation and efficiency for variety of pollutants [8].

Adsorption is a procedure by which a dissolved substance is transferred from the liquid phase to the surface of a solid material to bind via physical and/or chemical interactions. Adsorbent surfaces and dyes molecules can interact via a variety of mechanisms such as Van der Waals forces, hydrogen bonding and electrostatic attraction [9]. Some of the most effective adsorbents used for wastewater treatment are activated carbon, natural polymers as chitosan and chitin, synthetic polymers, agricultural wastes and ash. The efficiency of adsorption process depends mainly on the nature of adsorbent material, chemical structure of dye and the operating conditions as temperature, pH and ionic strength [10].

Several works have been reported for methyl orange removal from aqueous solutions utilizing different materials activated carbon [11-13], agricultural wastes [14,15], natural polymers [16,17], clays [18,19], colloids [20,21], and composites [22,23].

The purpose of this work is to examine the ability of cholestyramine to remove methyl orange from aqueous solution. To determine the optimum conditions for dye removal, the effect of various factors affecting the adsorption efficiency including contact time, pH, ionic strength, temperature, initial dye concentration and adsorbent dose.

## 2. Materials and methods

The anion exchanger cholestyramine was obtained from Pharco Pharmaceutical Company, Egypt and used as received. Methyl orange dye was obtained from Sigma-Aldrich Co. (Switzerland). Its molecular formula is  $C_{14}H_{14}N_3NaO_3S$  with a molar mass of 327.334.

All reagents were of analytical grade and used without further purification. pH adjustments were performed with HCl (1 M) and NaOH (1 M) solutions. A stock solution of MO dye was prepared in deionized water and various concentrations (50, 75, 100 and 125 mg/L) were prepared by proper dilution with water. De-colorization experiments were performed by using batch mode by 25 ml of dye solution was equilibrated and stirred (at 200 rpm) with definite amount of the adsorbent for 40 minutes. The dye solution was then centrifuged to remove the adsorbent prior to analysis. The concentration of the dye was analysed by monitoring the absorbance of the dye solution at maximum absorbance value ( $\lambda_{max} = 464$  nm) before and after attainment of equilibrium with cholestyramine using UV-Vis Spectrophotometer. The removal percentage of the dye was calculated using the following equation:

$$Removal \% = \frac{C_0 - C_e}{C_e} \times 100 \quad (1)$$

where  $C_0$  is the initial concentration of the dye and  $C_e$  is the equilibrium dye concentration in mg/L.

The mass of the sorbent used in calculations of the sorption capacity at equilibrium ( $q_e$ ) at time  $t$  and ( $q_0$ ) was 0.4 g/L. The sorption capacity values are presented in mg of dye per g of sorbent as:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where  $V$  is the volume of the solution (L); and  $W$  is the dry weight of sorbent (g).

## 3. Results and Discussion

### 3.1 Effect of contact time and dye concentration

The contact time is a fundamental parameter in all transfer phenomena such as adsorption. The effect of contact time on the removal percent of MO dye adsorbed on cholestyramine at room temperature ( $25 \pm 1^\circ\text{C}$ ) was examined at dye concentration 50 mg/L with 0.4 g/L cholestyramine dose. As seen in Fig. 3, the percent of dye removal reached 96.95% after 40 min of continuous stirring of the solution. This value corresponds to 121.18 mg dye adsorbed on one gram of adsorbent. The equilibrium time was attained in about 40 min.

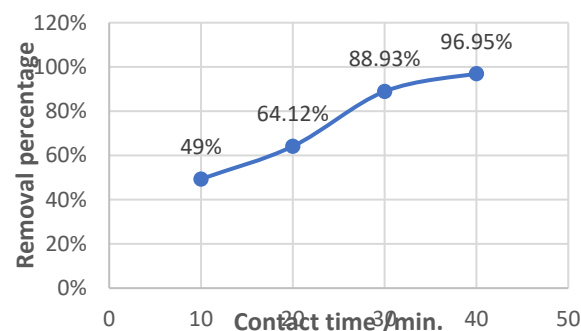
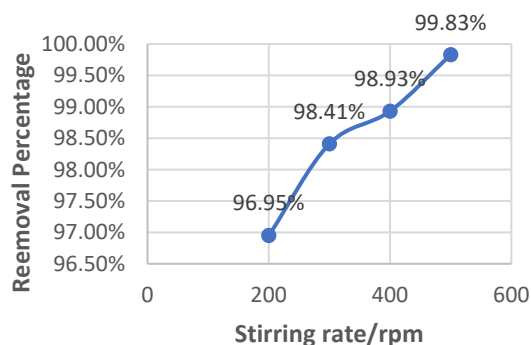


Fig (3) Effect of contact time on adsorption of MO on cholestyramine

### 3.2 Effect of stirring rate

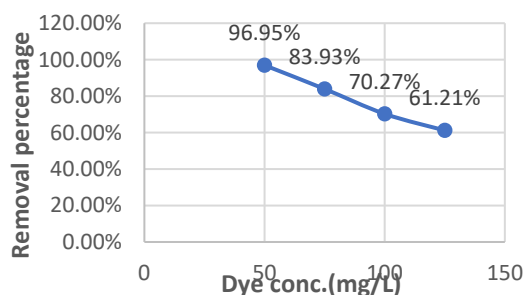
The effect of stirring speed was studied in the range of 200-500 rpm at 50 mg/L and 0.4 g/L adsorbent, and the results are shown in Fig. 4. According to the result, as the stirring speed increased from 100 to 500 rpm, removal efficiency of MO increased from 96.9% to 99.8%. This behavior may be explained by the fact that when the stirring speed increases, all particles are kept in suspension in solution, which enhances the chance of adsorbate contact with the adsorbent [24]. When contact surface solid/liquid increase, the transfer of dye molecules to the surface of adsorbent will be favourable [25]. In this study, the optimum stirring rate was considered as 500 rpm.



**Fig (4)** Effect of stirring rate on adsorption of MO on cholestyramine

### 3.3 Effect of dye concentration

It could be seen from Fig. 5 that the removal percent decreases with increasing dye content. The removal percent was 96.95% at 50 mg/L dye and dropped to 62.21% at dye concentration 125 mg/L. This can be explained by the fact that the film resistance to mass transfer surrounding the adsorbent particles is decreased by the agitation rate [26]. The dye loaded to the cholestyramine at equilibrium decreased with increasing initial dye concentration. This value increased from 121.18 mg/g at 50 mg/L of dye to 191.28 mg/g at initial dye concentration 125 mg/L.

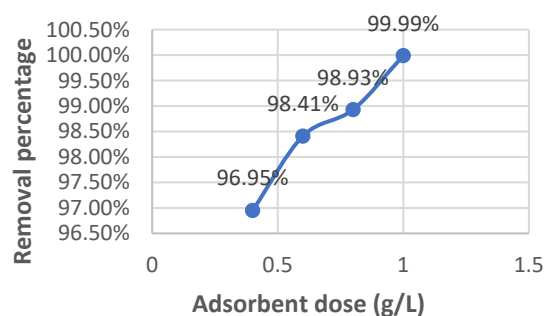


**Fig (5)** Effect of initial dye concentration on 3.4 adsorption of MO on

### Effect of cholestyramine dose

The effect of cholestyramine dose on removal percent of MO was examined at different doses (0.4, 0.6, 0.8 and 1.0 g/L). The resulted relationship is presented in Fig. (6). As shown, increasing cholestyramine dose caused a consequent increase in dye removal percent. At adsorbent dose 0.4 g/L, a percent dye removed is 96.95% (121.18 mg/g) and at 1.0 g/L it is 99.99% (124.99 mg/g). The increase in dye removal percentage with increasing adsorbent dose can be attributed to increased surface area of the adsorbent and consequently the availability of more adsorption sites. The remarkable decrease in removal capacity with dose may be attributed to overlapping or aggregation of adsorption sites leading to decrease in total adsorbent surface area

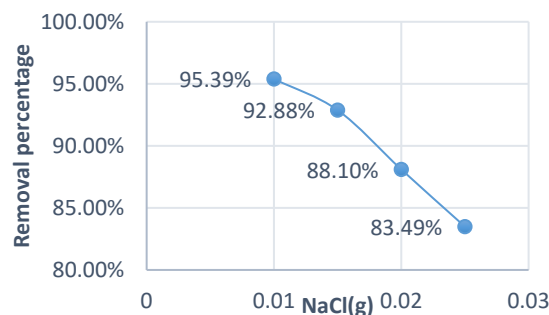
available to the dye and an increase in diffusion path length [27].



**Fig (6)** Effect of cholestyramine dose on removal percent of MO

### 3.5 Effect of ionic strength

The effect of ionic strength on dye removal was studied by adding NaCl to the working solutions in different doses (0.4, 0.6, 0.8, 1.0 g/L). It seems that the presence of NaCl in the medium of MO screened the anions exchange between Cholestyramine and ionized MO, and so resulted in decreasing the removal efficiency. It has been stated that, when the electrostatic forces between the adsorbent surface and adsorbate ions were highly attractive, an increase in ionic strength will lead to decrease the adsorption capacity. On the contrary, when the electrostatic attraction is repulsive, an increase in ionic strength will increase adsorption [28,29]. This trend could be attributed to inhibition for the nearness of dye molecules and sorption sites.



**Fig (7)** Effect of salinity on adsorption of MO on cholestyramine.

### 3.6 Effect of initial pH

The effect of initial pH on adsorption of MO on cholestyramine was studied in the range 5.5 to 10.3 and the results are shown in Fig. 8. As could be seen, with the increase of pH value of the solution, the removal percent gradually decreased. The highest removal percent was detected at pH 5.5 (97.26%), while the lowest one was at pH 10.3 (78.97%). This behaviour has been observed in other published works dealing with the adsorption of MO on various adsorbents [30-32]. In acidic conditions, cholestyramine was combined with  $\text{MO}^-$  ions

through electrostatic interaction due to the protonation of surface functional groups. With the increase of pH, the degree of protonation decreased and the electrostatic effect weakened, resulting in a decline of adsorption quantity. In addition, OH<sup>-</sup> started competing with MO<sup>-</sup> for the active points on cholestyramine when pH was greater than 7.0, which further weakened the adsorption effect.

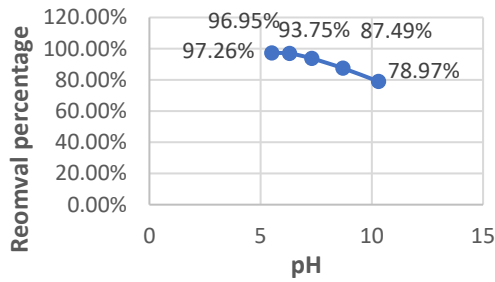


Fig (8) Effect of pH on adsorption of MO on cholestyramine.

3.7 Effect of temperature

The effect of temperature on MO adsorption initial concentration (50 mg/L) was studied in the temperature range of 25-55 °C (298–328 K), and the results were shown in Fig. 9. It was observed that the adsorption capacity of MO decreased with increase in temperature, indicating exothermic nature of the adsorption of MO onto cholestyramine. In this case, higher temperature may decrease the adsorptive forces between the dye molecules and the active sites on the adsorbent surface [33].

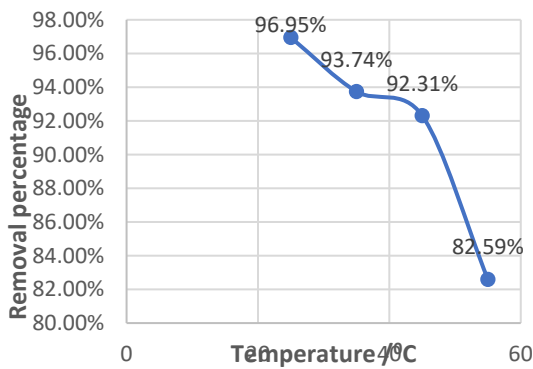


Fig (9) Effect of temperature on adsorption of MO on cholestyramine.

The thermodynamic parameters of the adsorption of MO was conducted by changing the temperature of the working solution and the results are shown in Table 1. The thermodynamic parameters such as change in free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) were determined using the following equations [34]:

$$\Delta G = -RT \ln K_d \tag{3}$$

$$K_d = \frac{q_e}{C_e} \tag{4}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{5}$$

where  $K_d$  is the equilibrium constant, T is the solution temperature (K) and R is the ideal gas constant (8.314 J/mol·K).  $\Delta H$  and  $\Delta S$  were calculated from the slope and intercept of van't Hoff plots of  $\ln K_d$  vs.  $1/T$  (Fig. 10). The negative values of  $\Delta G$  and negative value of  $\Delta H$  indicate that the adsorption of MO on cholestyramine is spontaneous and an exothermic process. These behaviours seem to be explained by the ionic-nature of the dye MO-cholestyramine interaction. Furthermore, the positive value of  $\Delta S$  indicates the good binding affinity of the adsorbent with Cr(VI) ion and increased randomness at the adsorbent-adsorbate interface during metal ion adsorption [35].

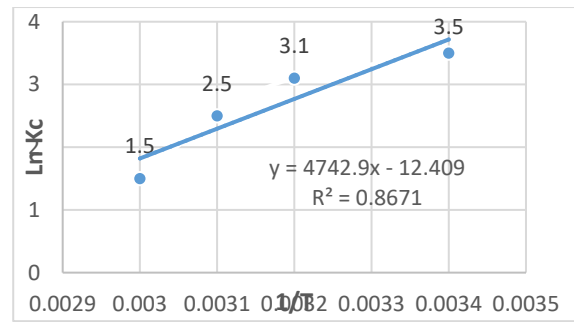


Fig (10) Thermodynamics of MO on cholestyramine

Table (1) Adsorption thermodynamic parameters of MO on cholestyramine

T (K)	$\Delta G$ (KJ/mol)	$\Delta H$ (KJ/mol)	$\Delta S$ (J/mol)
298	-8.74		
308	-7.71		
318	-6.67	-39.43	-103.2
328	-5.65		

3.8 Adsorption isotherms

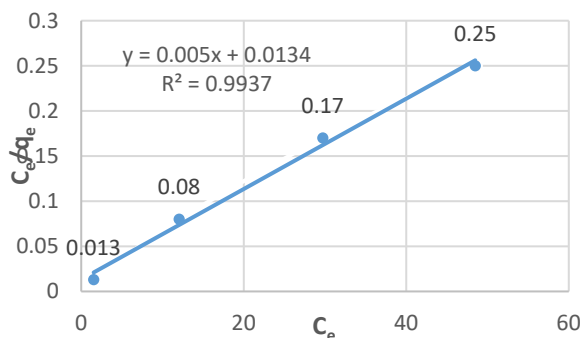
Adsorption isotherms describe the equilibrium between adsorbent and adsorbate, or in other words, the relationship between the quantity of material adsorbed and that remaining in the solution at a fixed temperature after equilibrium. In order to optimize the design of an adsorption system to remove MO dye, it is important to establish the most appropriate correlation for the equilibrium data. Two isotherm models: Langmuir and Freundlich were applied to the adsorption process.

The Langmuir isotherm model states that the adsorption process on the adsorbent surface occurs as a monolayer coverage where molecules being adsorbed per binding site with no interaction till a saturation is happened.

The Langmuir model is represented by linearized equation as following [36]:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (6)$$

Where  $C_e$  (mol/L) is the equilibrium concentration of solute,  $q_e$  (mol/g) is the amount of solute adsorbed per unit mass of adsorbent,  $b$  (L/mol) is a constant related to the heat of adsorption and  $Q_0$  (mol/g) is the maximum amount of adsorbate to establish a homogenous monolayer on the adsorbent surface. By representing the data as a linear plotting of  $C_e/q_e$  versus  $C_e$ ,  $Q_0$  and  $b$  can be obtained from the slope and the intercept, respectively (Fig. (11)).



**Fig (11)** Langmuir isotherm of MO on cholestyramine

The equilibrium parameter or separation factor ( $R_L$ ) is an essential characteristic of Langmuir model, which is obtained from the next equation [37]:

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

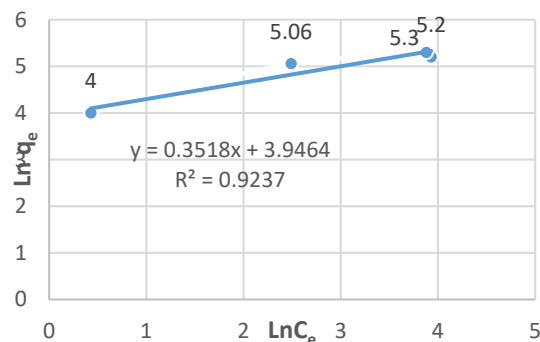
Calculating the value of  $R_L$  gives an idea about the nature of the adsorption process whether it is unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). The sorption process of MO onto Cholestyramine has been between zero and one, reflecting that the process is favourable [38].

The Freundlich isotherm describes the adsorption process as a heterogenous multilayer adsorption with interaction between adsorbed molecules. This model assumes that the dye concentrations on the sorbent increases with raising the dye concentration in the solution. The linear form of this model can be obtained from the following equation [39]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

where  $q_e$  (mol/g) is the amount of solute adsorbed per unit mass of adsorbent,  $C_e$  (mol/L) is the equilibrium concentration of solute,  $K_F$  (mol<sup>(1/n)</sup>L<sup>(1/n)</sup>/g) is the Freundlich constant that related to the adsorption capacity of the adsorbent and  $1/n$  is another constant (heterogeneity factor). Plotting  $\ln q_e$  against  $\ln C_e$  as a linear relation gives the values

of  $K_F$  and  $\frac{1}{n}$  from the slope and the intercept; fig. (12). The value of  $\frac{1}{n}$  is between zero and 1; the surface is more heterogeneous when the value of  $\frac{1}{n}$  is closer to zero. The data of Langmuir and Freundlich isotherms constants are shown in Table (2).



**Fig (12)** Freundlich isotherm of MO on cholestyramine

**Table (2)** Langmuir and Freundlich isotherms constants for adsorption of MO on cholestyramine.

Langmuir Isotherm Parameters			
$Q_0$ (mg/g)	$b$ (L/mg)	$R_L$ (L/mg)	$R^2$
200	0.37	0.021 - 0.051	0.994
Freundlich Isotherm Parameters			
$K_F$	$1/n$	$R^2$	
114.32	0.352	0.924	

From the previous data, the best-fit adsorption isotherm is Langmuir isotherm indicating that adsorption occurs as a monolayer covering the surface of adsorbent.

### 3.9 Adsorption Kinetics

The study of adsorption kinetics illustrates how the solute removal rate which controls the residence time of the adsorbate at the solution interface. The data of adsorption kinetics help to understand the dynamics of adsorption process in terms of the rate constant order. The adsorption rate is important in designing the adsorption system and it can be calculated from kinetic studies [40]. The adsorption kinetics was studied at 50 mg/L, and the adsorption rate was monitored by studying the contact time up to 40 min. The experimental data obtained for various contact time were analysed using two kinetic models, namely, pseudo-first-order and pseudo-second order.

#### 3.9.1 Pseudo-first order model

Thus, the kinetic of MO adsorption onto Cholestyramine surface was analysed according to



pseudo-first-order and pseudo-second-order kinetic models. The rate constant of adsorption is determined from the pseudo-first-order equation [41]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{9}$$

where  $q_e$  and  $q_t$  are the amounts of adsorbed MO (mg/g) at equilibrium, (t) is time (min), and  $K_1$  ( $\text{min}^{-1}$ ) is the adsorption rate constant. A plot of a linear relationship between  $\log(q_e - q_t)$  versus time would give the value of  $k_1$  from the obtained slope, from the slope and intercept of the plot, respectively (Fig. 13).

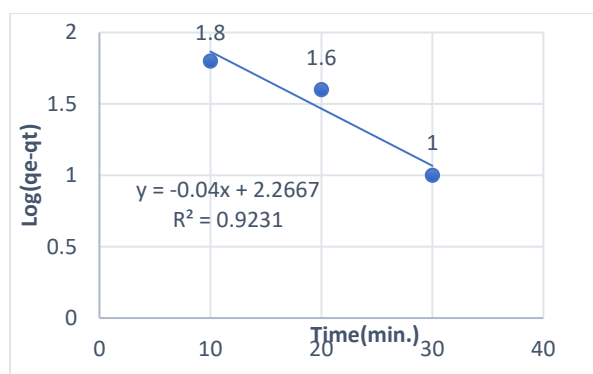


Fig (13) Pseudo-first order kinetics for the adsorption of MO on Cholestyramine

### 3.9.2 Pseudo-second order model

The pseudo-second-order kinetic model is summarized as following equation [42]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

Where  $h$  is the initial adsorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ ) and  $K_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is rate constant of second-order adsorption. The plot of  $\frac{t}{q_t}$  versus  $t$  should show a linear relationship. Values of  $K_2$  and  $q_e$  (equilibrium adsorption capacity) were calculated from the obtained intercept and slope of the plot.

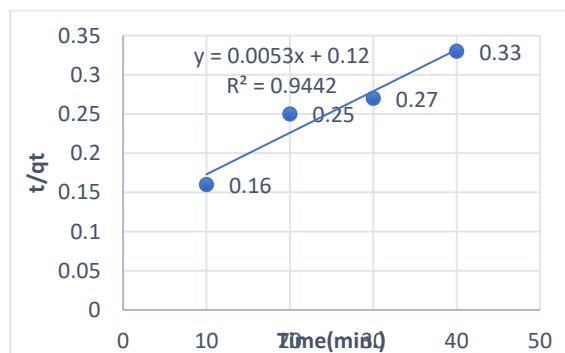


Fig (14) Pseudo-second order kinetics for the adsorption of MO on Cholestyramine

Table (3) Kinetic parameters for pseudo-first and pseudo-second order models applied for adsorption of MO on cholestyramine.

Pseudo 1 <sup>st</sup> order model			Pseudo 2 <sup>nd</sup> order model		
$K_1$	$q_e$	$R^2$	$K_2$	$q_e$	$R^2$
0.09	184.8	0.9231	$2.3 \times 10^{-4}$	188.7	0.9442

From the values of correlation coefficients resulted from application of the two kinetic modes, it could be stated that the adsorption of MO dye on cholestyramine follows pseudo second-order kinetics with a rate constant  $2.3 \times 10^{-4}$  (Table 3).

### Conclusion

Cholestyramine resin shows significant adsorption capacity for the removal of methyl orange dye from dye effluent under suitable experimental conditions. The removal process was optimized, and the maximum dye removal of 99.99% was achieved at optimum conditions of 1.0 g/L adsorbent, 40 min contact time, and 200 rpm agitation speed. The best-fit adsorption isotherm was achieved with the Langmuir model with an adsorption capacity of 200 mg/g, indicating that adsorption occurs by monolayer coverage. The negative value of enthalpy confirms the exothermic nature of the adsorption. The negative values of free energy change indicate that it is a spontaneous process. Cholestyramine is an effective adsorbent for anionic dyes, it is cheap, easy to apply and timesaving.

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