

**Research Article** 

Chemical Review and Letters journal homepage: www.chemrevlett.com ISSN (online): 2645-4947 (print) 2676-7279



# Adsorption of Orange 3R by chitosan modified montmorillonite nanocomposite

Simin Arabi 1, \*

<sup>1</sup> Department of Chemistry, Safadasht Branch, Islamic Azad University, Tehran, Iran

# ARTICLE INFO

#### ABSTRACT

Article history: Received 1 March 2023 Received in revised form 20 April 2023 Accepted 12 May 2023 Available online 20 June, 2023

Keywords: Adsorption kinetics Isotherm models Chitosan–montmorillonite magnetic Orange 3R Thermodynamic parameter The objective of this research is to adsorbe Orange 3R dye by a new catalyst chitosan-montmorillonite magnetic (CTS-MMT-Fe<sub>3</sub>O<sub>4</sub>) was used as an effective adsorbent for the adsorption of anions. In this research, the adsorption of Orange 3R dye as an anionic sulphonated reactive azo dye, from aqueous solution by CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> nanocomposite was investigated. The synthesized nanocomposite was characterized by FTIR (Fourier transform infrared), XRD (X-Ray diffraction) and SEM (Scanning Electron Microscopy) to evaluate the surface morphology. Adsorption experiments were conducted at room temperature in batch system. The effects of pH, initial concentration of dye, contact time and adsorbent dosage were investigated. Kinetic and equilibrium sorption parameters were evaluated pseudofirst and pseudo-second order rate models and Langmuir and Freundlich isotherms. The results indicated that the adsorption of dye onto adsorbent was better described by the pseudo second-order compared to by the pseudo-first-order. Also, the experimental data were better fitted to the Langmuir model with high R<sup>2</sup> value  $(R^2=0.99)$  than Freundlich model for adsorption. The thermodynamic studies showed that the adsorption is spontaneous and feasible. The present study indicated that CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> could be employed as an effectively adsorbent for the adsorption of Orange 3R from industrial and other effluents.

# 1. Introduction

Main organic pollutant compounds such as dyes and pigments are extensively utilized in various textile industries and directly without degradation discharge into the rivers and aquatic ecosystems. The presence of dyes in aqueous bodies, even at low concentrations, leads to serious carcinogenic influence on aqueous systems and human health [1]. The colored dye effluents are considered highly toxic and resistant to break down with time, very stable to light, reducing the clarity of the water, generating problems in aquatic life [2]. Different methods such as adsorption, coagulation -flocculation, ozonation, reverse osmosis, biological treatment and chemical oxidation have been used for the removal of dyes and other colored contaminants. In the last few years, attention has been focused on adsorption due to its high efficiency, the low prices and easy access [3]. Natural biopolymer such as chitosan (CTS) and clay minerals such as motmorillonite (MMT) are considered useful adsorbents due to their high adsorption capabilities for the removal of dyestuffs. Chitosan (CTS) is the N- deacetylated derivative of chitin as adsorbent in wastewater treatment has gained interest due to its biodegradability, low cost and non-toxic nature [4]. Motmorillonite (MMT) is composed of hydrous layered aluminum silicate along with exchangeable cations and active hydroxyl groups and play an important role in the environment by acting as a natural scavenger of pollutants by taking up cations and anions either through ion exchange or adsorption or both. [5]. However, montmorillonite because of its negatively charged surface shows low interaction with anionic dyes. So, modification of montmorillonite with biopolymers such as chitosan can effectively improve its affinity for anionic dyes. On the other hand, magnetic separation technology has gained remarkable interest. By employing magnetic force, magnetic matters can be separated easily from water without considering of its size. Magnetite (Fe<sub>3</sub>O<sub>4</sub>) has been extensively used as magnetic material due to their high magnetic properties and chemical stableness. The preparation of magnetic CTS/MMT was executed as a notable biocomposite due to enhancing the stability, reducing the cost and improving the separation ability of adsorbent from the dye solution with the aid of an external magnet after absorption [6]. Wang and Wang studied adsorption of Congo Red dye using CTS/MMT nanocomposites. The obtained results that the adsorption capacity of CTS/MMT nanocomposites was higher compared to CTS and MMT [7]. Gecol et al. evaluated the removal of tungsten from water using CTS/MMT nanocomposite [8]. Chang and Jaung investigated removal of tannic acid, humic acid and dyes (methylene blue-reactive dye R222) from water using of CTS and activated clay [9]. Singh et al. prepared chitosan thiomer by microwave irradiation method and used it to remove both arsenic forms. The results indicated that synthesized chitosan thiomer had good efficiency for removal of both ionic forms existing in groundwater. The removal efficiency was obtained 85.4% for As(III) and 87% for As(V) [10]. Fan et al. studied the removal of Cu (II) from aqueous system using the magnetic chitosan bead. The results showed that the adsorbent possesses considerable adsorption capacity (167.22 mg g-1) [11]. In this study, Reactive Orange 3R, an anionic azo dye, was collected as a common pollutant due to its difficult biodegradable. Hence, present study aimed to synthesize modified biocomposite in order to obtain new adsorbent applicable for removal of Reactive Orange 3R dye from aqueous solution. The effects of different parameters such as contact time, initial dye concentration, temperature and pH along with thermodynamic and kinetic have been investigated.

#### 2. Materials and methods

#### 2.1. Materials

Chitosan (middle viscous) with a deacetylation degree of 85% and medium molecular of weight 220000 g/mol was supplied by Sigma Aldrich and without further purification. Sodium used montmorillonite (Na-Mt, 90%) was prepared by Sigma-Aldrich, Germany. Reactive Orange 3R dye (C<sub>20</sub>H<sub>17</sub>N<sub>3</sub>Na<sub>2</sub>O<sub>11</sub>S<sub>3</sub>, C.I. 177757, M<sub>W</sub>=617.54 gmol<sup>-</sup> <sup>1</sup>,  $\lambda_{max}$ =496 nm) was obtained from Alvan Sabet Co. and was used without further purification. The molecular structure of Reactive Orange 3R dye is shown in Figure 1. All other reagents were analytical reagent and all solutions were prepared with distilled water.



2.2. Preparation of the  $CTS-MMT-Fe_3O_4$  nanocomposite adsorbent

The CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> nanocomposite was prepared according to modified method of Wang [12]. For preparation chitosan solution, 4g CTS was dissolved in 196 ml of 2% V/V acetic acid. Then, the pH of chitosan solution was adjusted to 5 by adding NaOH 0.1 M for preventing of any change in MMT Structure. An amount of 2.5 g MMT was dispersed in 100 ml of distilled water and then was sonicated in ultrasonic bath for 1h. So after, 5 ml of a Fe<sup>3+</sup>/Fe<sup>2+</sup> solution (Fe<sup>3+</sup>: 0.875 mol L-1, Fe<sup>2+</sup>: 0.438 mol L-1) was added to the CTS-MMT solution during stirring at 60°C and a homogeneous CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> suspension was obtained after 45 min. The mixture was vigorously stirred at 3500 rpm for 1hour in order to separating the CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> composite from the solution. Afterwards the suspension was filtered through a Whatman No.1 filter paper and the solid was washed thoroughly with distilled water twice and dried at 70°C for 24 hours. The obtained product was ground and then passed through a 200 mesh sieve.

# 2.3. Characterization of chitosan–montmorillonite- $Fe_3O_4$ adsorbent

IR spectra of CTS and CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> were characterized by FT-IR Spectrophotometer (model Spectrum 100; Perkin Elmer) using KBr pellets. XRD analyses was performed by wide-angle X-ray diffraction (D8Advance, Bruker, Germany) with Cu anode, running at 40 kV and 30 mA at 20 °C, scanning from  $4^{\circ}$  to  $18^{\circ}$  at  $3^{\circ}$ /min. The surface morphology of CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> nanocomposite was revealed using scanning electron microscopy (SEM; Hitachi SU9000, Japan).

## 2.4. Adsorption experiments

Dye adsorption experiments were conducted by addition of 20 mg of CTS-MMT-Fe3O4 adsorbent into 50 ml of dye solution with desired concentration. The effects of various parameters such as contact time (1-4.5 hr), adsorbent dosage (0.1-0.9 g/l), pH (3-11), initial dye concentration (20-100 mg/l) and temperature (303, 313, 323 and 333 K) were studied. The pH of the solution was adjusted to the desired value by adding small amount of HCl or NaOH (0.1M). The adsorption experiments were executed at UV-Vis spectrophotometer (Shimadzo, Model UV-1800) at a wavelength of 496 nm. The amount of adsorbed dye was calculated using the following equation:

$$q_e = \frac{(C_\circ - C_e)V}{W}$$
(1)

The percent removal of dye was evaluated as follows:

Figure 1. Molecular structure of Reactive Orange 3R

% Removal of dye = 
$$\frac{(C_{\circ} - C_{e})}{C_{\circ}} \times 100$$
 (2)

Where  $C_{\circ}$  and  $C_{e}$  are the initial and equilibrium dye concentrations (mg L<sup>-1</sup>), V is the volume of dye solutions (L), and W is the weight of adsorbent (g). To ensure reproducible measurement results, each experiment was carried out in triplicate under the same controlled conditions.

# 3. Results and Discussion

#### 3.1. Characterization of CTS-MMT- Fe<sub>3</sub>O<sub>4</sub> adsorbent

The FTIR spectrum of the infrared spectrum of CTS (Figure 2a) shows peaks at 3446 cm<sup>-1</sup> is assigned to because of the overlapping of O–H and N–H stretching bands, 2976 and 2887 cm<sup>-1</sup> for

aliphatic C–H stretching, 1747 cm<sup>-1</sup> for N–H bending, 1373 cm<sup>-1</sup> for C–H bending, 1075 cm<sup>-1</sup> for C–O stretching. The spectrum of the CTS–MMT-Fe<sub>3</sub>O<sub>4</sub> indicates the combination of characteristic absorptions owing to the CTS and MMT-Fe<sub>3</sub>O<sub>4</sub> groups (Figure 2b). The peak at 1747 cm<sup>-1</sup> belongs to the –NH<sub>2</sub> group in the chitosan was changed to 1607 cm<sup>-1</sup> in the CTS–MMT-Fe<sub>3</sub>O<sub>4</sub> spectrum, due to formation of the protonated amine groups (–NH<sub>3</sub><sup>+</sup>) of chitosan. This –NH<sub>3</sub><sup>+</sup> group interacts with the negatively charged sites of MMT. This result was consistent with the observation of the XRD studies, indicating the intercalation of chitosan in the MMT structure [13].





SEM is a widely used method to evaluate the morphology and surface characteristic of the adsorbent. SEM analysis of CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> as depicted in Figure 3. The SEM image showed that the particles of CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> composite have different size and uneven

form. Also, it can be observed that the surface morphology of CTS-MMT-Fe $_3O_4$  is not homogenous and it is composed of particles with small flakes and rough surfaces.



Figure 3. The SEM images of CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> biocomposite

The XRD patterns of MMT and CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> are shown in Figure 4. The different peak of MMT observed at 2 $\theta$  of 7.45°. After mixing MMT with chitosan, the different peak of MMT disappeared and a new peak was shown at 2 $\theta$  = 5.85°. The shift of

diffraction peak of MMT was shifted to a lower angle, demonstrating the formation of an intercalation of chitosan in the MMT structure [14].



Figure 4. XRD pattern of MMT (a) CTS–MMT-Fe<sub>3</sub>O<sub>4</sub> (b)

#### 3.2. Effect of CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> dosage

For choosing the optimum CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> dosage, the removal of Orange 3R was evaluated under different initial dosage from 0.1 to 0.9 g (Figure 5). Results explained that the removal efficiency of dye increased

with increasing in CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> dosage and afterward it decreased. This clearly demonstrates during early stage of adsorption process, uptake rate may be ascribed to the increase in the number of unoccupied sites

available for adsorption and the time required to achieving equilibrium decreases, resulting in an increased concentration gradient between adsorbent and solution. Thereafter, the concentration gradient is reduced because of the adsorption of the dye molecules on the unoccupied sites, resulting in decreased adsorption within the later stages [15]. The optimum dosage for adsorption of Orange 3R obtained 0.7 g, where CTS–MMT composite had 86% adsorption efficiency.



Figure 5. Effect of adsorbent dosage on the adsorption of Orange 3R onto CTS-MMT-Fe<sub>3</sub>O<sub>4</sub>

#### 3.3. Effect of pH

The pH of dye solution is an important parameter to influence particularly on removal efficiency due to pH affects the reaction rate between adsorbate and adsorbent in aqueous solutions. The obtained results of the experiments at different pH values, applied to determine the optimum pH range for dye solution on CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> are illustrated in Figure 6. The optimum pH for adsorption of Orange 3R obtained at pH 5, where CTS– MMT composite had 78% adsorption efficiency. This might be ascribed to the fact that in acidic medium, due to the high abundance of positive charge in the medium, amino groups of chitosan were protonated and electrostatic interaction between protonated amino groups of chitosan and negatively charged dye anions was occurred so that adsorption of dye increases. In alkaline medium, because of existence the excessive hydroxyl ions in solution and electrostatic repulsion between dye anions and hydroxyl ions, removal efficiency was decreased. These outcomes are in a good agreement with the results of researchers were reported adsorption of reactive red 189 (RR 189) on crosslinked chitosan beads [13] and adsorption of reactive blue 19 (RB19) on crosslinked chitosan/oil palm [16].



Figure 6. Effect of solution pH on the adsorption of Orange 3R onto CTS-MMT-Fe<sub>3</sub>O<sub>4</sub>

#### 3.4. Effect of initial of concentration

The influence of initial concentration on the adsorption of Orange 3R by CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> was evaluated over a range of 20-100 mg/L, initial dosage 0.7 g/L at the initial pH 5 (Figure 7). It can be observed that as the initial concentration of dye increased, removal efficiency gradually decreased. Generally, as initial concentration of dye increased, the number of dye molecules increased, resulting in adsorption sites on the surface area of the composite is saturated. In other words, at minimum initial concentrations compared with the

available surface area, the proportion of the initial molecules of dye, is low, hence, the adsorption efficiency is independent of the initial concentration of dye. But, at the high concentrations, the available sites for adsorption are fewer than the molecules of the dye. Thus, the removal efficiency is dependent on the initial dye concentrations [17].



Figure 7. Effect of initial dye concentration on the adsorption of Orange 3R onto CTS-MMT-Fe<sub>3</sub>O<sub>4</sub>

#### 3.5. Effect of contact time

The effect of contact time on adsorption of Orange 3R was evaluated under the following experimental conditions: initial concentration 50 mgL<sup>-1</sup>, and CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> dosage 0.7g/50cc. As evident from Figure 8, removal of dye increased and reached a high value within 3 hours. This meant that a large number of adsorption active sites on the adsorbent surface were available at this process. Thereafter, did not significantly change with time due to the equilibrium of the repulsive forces between the dye molecules on the solid and in the

bulk phases. Therefore, it can be said that the adsorption is increased instantly at initial steps due to rapid attachment of dye to the surface of the adsorbent, and then keeps increasing gradually until the equilibrium is reached and then remains constant. Therefore, the time 3 hours was considered for the other batch experiments [18]. In other research, similar results were found for RB dye removal efficiency around 80% at 240 min and pH 3.5 into chitosan hollow fibers biosorbents [19].



Figure 8. Effect of contact time on the adsorption of Orange 3R onto CTS-MMT-Fe<sub>3</sub>O<sub>4</sub>

#### 3.6. Effect of temperature

The impact of temperature on adsorption capacity of CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> was studied by varying the reaction temperature from 303 K to 333 K using 0.7 g of adsorbent CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> at pH 5. Figure 9 shows that the adsorption capacity of Orange 3R on CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> increased as the temperature raises, indicating that high temperature was favorable for the dye removal. It may be ascribed to the fact that the increase of solution temperature decreases the time for the sample reaches to

equilibrium. Besides, increasing of the temperature, leads to increasing mobility of adsorbate molecules and consequently kinetic energy increases and with decreasing viscosity of solution, dye molecules occupy adsorbent active sites. The results clearly express that the dye adsorption reaction is an endothermic process [18]. Other researchers have illustrated similar dependence to temperature [20].



Figure 9. Effect of temperature on the adsorption of Orange 3R onto CTS-MMT-Fe<sub>3</sub>O<sub>4</sub>

#### 3.7. Adsorption Isotherm

#### 3.7.1. Langmuir isotherm

Adsorption isotherms were applied to explain the mechanism of adsorption. The adsorption of Orange 3R was determined using two isotherm models namely the Langmuir and the Freundlich models. The Langmuir-adsorption model describes single molecular layer adsorption, where the adsorption occurs at distinct localized adsorption sites and presumes that the sorbent surface has identical affinity for adsorbate molecules. The chemisorption process is described by the Langmuir adsorption equation, or Langmuir isotherm, which can be derived from a simple model of the equilibrium between adsorption and desorption. The linear form of Langmuir-adsorption model is expressed by using equation 3:

$$\frac{1}{q_{e}} = \frac{1}{q_{m}} + \frac{1}{K_{L}q_{m}C_{e}}$$
(3)

Where  $C_e$  is equilibrium concentration of dye (mg/l),  $q_e$  is amount of dye adsorbed at equilibrium (mg/g),  $q_m$  is the maximum adsorption capacity of the adsorbent (mg/g) and the  $K_L$  (l/mg) is Langmuir constant indicating the degree of the adsorption affinity of the adsorbate. The higher  $K_L$  is related to the intensive affinity of the ions towards the adsorbent. The linear plot of  $1/q_e$  versus  $1/C_e$  as depicted in Figure 10. The constants  $q_m$  and  $K_L$  were obtained from slope and intercept of the plot and the values were represented in Table 1. The maximum monolayer adsorption capacity of CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> was found to be 25.14 mg/g.

Table 1. Parameters of Langmuir and Freundlich isotherms for Orange 3R adsorption on CTS-MMT

	Langmuir isotherm				Freundlich isotherm		
	qm (mg/g)	K <sub>L</sub> (L/mg)	RL	R <sup>2</sup>	$K_{f} \left( mg^{1-1/n} L^{1/n} g^{-1}  ight)$	1/n	<b>R</b> <sup>2</sup>
Orange 3R	25.14	2.70	0.05	0.9988	14.34	0.352	0.9564

The experimental data had good compliance with Langmuir isotherm model with the correlation coefficient  $(R^2)$  of 0.99, demonstrating monolayer adsorption of the adsorbate and the homogeneous nature of the adsorbent surface. The shape of the Langmuir isotherm was studied by the dimensionless constant separation factor  $(R_L)$  to assess high affinity adsorption.  $R_L$  was obtained as follows:

$$R_{\rm L} = \frac{1}{1 + K_{\rm L} C_{\circ}} \tag{4}$$

 $R_L$  determines the type of isotherm to be irreversible ( $R_L=$  0), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) (or) unfavorable ( $R_L > 1$ ). In the present investigation, the  $R_L$  values were less than one for Orange 3R, which showing that the adsorption process was favorable [21].



Figure 10. Langmuir adsorption isotherm for Orange 3R adsorption on CTS-MMT-Fe<sub>3</sub>O<sub>4</sub>

#### 3.7.2. Freundlich isotherm

The Freundlich isotherm model describes heterogeneous of the sites on solid surface and the multilayer capacity and is represented as following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$
(5)

Where  $C_e$  is the equilibrium concentration of the solute (mg/L) and  $q_e$  is the equilibrium adsorption capacity (mg/g). The Freundlich isotherm constants  $K_F$  (L/g) and (1/n) can be calculated from the linear plot of logq<sub>e</sub> versus logC<sub>e</sub> (Figure 11). The slope (1/n) estimates the surface heterogeneity and intensity of adsorption. When 1/n is near to zero, it is more heterogeneous while a slope near to unity implying the chemisorption process, and the value of 1/n below unity validates the normal Langmuir isotherm where 1/n higher than unity, indicating cooperative adsorption. It can be observed that CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> was best described by Freundlich

model ( $R^2$ =0.95), however, the experimental data were better fitted to the Langmuir model with high  $R^2$  value ( $R^2$ =0.99) than Freundlich model for adsorption on the CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> [22]. Hence, the Langmuir model exhibited that adsorption of Orange 3R belongs to the monolayer adsorption. Kinetic studies confirmed that Langmuir is better as compared to Freundlich isotherm in prevision of dye adsorption processes [15].

#### 3.8. Kinetic studies

The kinetic of adsorption is proper method for studying of the adsorption rate. The adsorption rate displays how fast the reaction befalls between the adsorbate and adsorbent. Due to further understand the rate of adsorption of Orange 3R on the adsorbent, two different models namely the Lagergren's pseudo first order kinetic model and the Ho's pseudo second order kinetic model were applied to the adsorption data to assess the adsorption rate.



Figure 11. Freundlich adsorption isotherm for Orange 3R adsorption on CTS-MMT-Fe<sub>3</sub>O<sub>4</sub>

3.8.1. Pseudo first-order equation (Lagergren's model) Kinetic modeling of adsorption process predicts adsorption rate and provides valuable information about application of adsorbent. Adsorption kinetics are commonly modeled using pseudo-first and pseudosecond order rate laws. The pseudo first order has been used extensively to describe adsorption dynamics. The model supposes that the adsorption is a pseudo chemical reaction process and the limiting factor for adsorption is the persistence of mass transfer inside granules. According to the Largergren pseudo first order kinetic model, proposed in 1898, the occupation rate of adsorption in the active sites is commensurable to the number of the unoccupied sites [23]. The pseudo first order expression can be demonstrated by using the equation 6:

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}\mathrm{t}} = \mathrm{k}_{1}(\mathrm{q}_{\mathrm{e}} - \mathrm{q}_{\mathrm{t}}) \tag{6}$$

Where:  $q_e$  and  $q_t$  (mg/g) are the amounts of Orange 3R dye adsorption capacity at equilibrium and at time t (h), respectively,  $k_1$  is the pseudo first-order rate (h<sup>-1</sup>). After integration and utilizing boundary conditions t = 0 and  $q_t$  = 0, the integrating form as follows:

$$\log(q_e - q_t) = \log(q_e) - k_1 t \tag{7}$$

The linear plot of log  $(q_e -q_t)$  versus t gave straight line plot as depicted in Figure 12. The slope and intercept of the plot of log  $(q_e -q_t)$  versus t were applied to specifying the pseudo-first-order rate constant  $k_1$  and the equilibrium adsorption capacity  $q_e$  respectively, as represented in Table 2 [1].



Figure 12. The pseudo-first-order kinetic of Orange 3R adsorption on CTS-MMT-Fe<sub>3</sub>O<sub>4</sub>

Table 2. The values of parameters and correlation coefficients of kinetic models for Orange 3R adsorption on CTS-MMT-Fe<sub>3</sub>O<sub>4</sub>

	]	Pseudo first-oro	der	Pseudo second-order			
	k1(1/sec)	q <sub>e</sub> (mg/g)	R <sup>2</sup>	k <sub>2</sub> (g/mg sec)	qe(mg/g)	$\mathbb{R}^2$	
Orange 3R	0.024	56.4	0.9338	0.003	74.6	0.9913	

3.8.2. The pseudo second-order equation (Ho's model) The pseudo second order kinetic model is based on the assumption that the adsorption process pursues a second-order mechanism. Hence, the occupation rate of the site adsorption is associated with the square of the number of the unoccupied sites and reveals the relation of the adsorption capacity of the adsorbent on time. The pseudo second order model can be expressed based on Equation (8) as follows:

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}\mathrm{t}} = k_2(q_{\mathrm{e}} - q_{\mathrm{t}})^2 \tag{8}$$

Integration of Eq. (8) results in Eq. (9) when the initial condition is  $q_t = 0$  at t = 0:

$$\frac{\mathrm{t}}{\mathrm{q}_{\mathrm{t}}} = \frac{1}{\mathrm{K}_{2}\mathrm{q}_{\mathrm{e}}^{2}} + \frac{\mathrm{t}}{\mathrm{q}_{\mathrm{e}}} \tag{9}$$

Where  $q_t$  and  $q_e$  are the amounts of adsobate at equilibrium and at time t (h), respectively, and  $K_2$ (g/mg sec) is the equilibrium constant of secondsecond-order adsorption. The linear plot of the t/q<sub>t</sub> versus t is used to defining values of  $q_e$  and  $K_2$  from the slope and intercept, respectively as depicted in Figure 13. The value of  $R^2$  for the pseudo first–order was 0.9338 whereas it for the second order ranged between 0.99 and 1. The higher the correlation coefficient demonstrating that nanocomposite was better described by the pseudo second-order compared to by the pseudo-first-order and the process of adsorption follows pseudo second order kinetics [21].



Figure 13. The pseudo-second-order kinetic of Orange 3R adsorption on CTS-MMT-Fe<sub>3</sub>O<sub>4</sub>

#### 3.9. Thermodynamic Studies

The plot of  $lnK_L$  against 1/T yielded a straight line so that the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the slope and intercept, respectively.

$$\ln K_{\rm L} = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$
(10)

The Gibbs free energy  $(\Delta G^{\circ})$  of adsorption was calculated by using Equation 11:

$$\Delta G^{\circ} = -RT \ln K_{\rm L} \tag{11}$$

Where  $K_L$  is the adsorption distribution coefficient, T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>). The value of  $K_L$  is calculated by the ratio of qe to Ce at different temperatures. Standard free energy change ( $\Delta G^\circ$ ) at

303, 318, 333 and 358 K were calculated to be -2.59, -2.81, -2.94 and -3.16 kJ mol<sup>-1</sup>. As the temperature increased from 303 to 333, the  $\Delta G^{\circ}$  values also enhanced, demonstrating that further driving force is formed at higher temperature and therefore lead to more adsorption capacity for Orange 3R. Besides, the negative  $\Delta G^{\circ}$  value indicates that the adsorption process is spontaneous and feasible and thermodynamically favorable process of adsorption of Orange 3R onto CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> nanocomposite. The positive value of  $\Delta H^{\circ}$  (12.6 kJ mol<sup>-1</sup>) offers that adsorption process is endothermic in nature, and positive of  $\Delta S^{\circ}$  (0.346 mol.K<sup>-1</sup>) indicated the randomness state solid-solution interface during dye adsorption process is increasing [24].

# 4. Conclusion

The findings suggest the CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> adsorbent as a suitable adsorbent for the treatment of dyeing industry wastewater. The experimental data was well described with Langmuir isotherm model. It was shown that the adsorption of Orange 3R onto CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> best fitted by pseudo second-order model. The rate of adsorption of Orange 3R on CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> increases with the increase in temperature, thus suggesting the reaction to be spontaneous and endothermic in nature. The present study indicated that CTS-MMT-Fe<sub>3</sub>O<sub>4</sub> could be applied as an effectively adsorbent for the adsorption of Orange 3R from industrial and other effluents.

# Acknowledgements

The author extends gratitude to Islamic Azad University, Safadasht Branch, for support of this research project.

# References

- S. Arabi, M.R. Sohrabi, M. Khosravi, Adsorption kinetics and thermodynamics of vat dye onto nano zero-valent iron, *India. J. Chem. Technol.*, 20 (2013) 173-179.
- [2] E. Eren, B. Afsin, Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated bentonite surfaces, *Dyes and Pigments*, 76 (2008) 220-225.
- [3] S. Zhu, M. Xia, Y. Chu, M.A. Khan, W. Lei, F. Wang, T. Muhmood, A. Wang, Adsorption and desorption of Pb(II) on 1-lysine modified montmorillonite and the simulation of interlayer structure, *Appl. Clay Sci.*, 169 (2019) 40-47.
- [4] C.C.D. Santos, R. Mouta, M.C.C. Junior, S.A.A. Santana, C.W.B. Bezerra, Chitosan-edible oil based materials as upgraded adsorbents for textile dyes, *Carbohydr. Polym.*, 180 (2017) 182-191.
- [5] S. Kang, Y. Zhao, W. Wang, T. Zhang, T. Chen, H. Yi, F. Rao, S. Song, Removal of methylene blue from water with montmorillonite nanosheets/Chitosan hydrogels as adsorbent, *Appl. Surf. Sci.*, 448 (2018) 203-211.
- [6] A.A. Adeyemo, I.O. Adeoye, O.S. Bello, Adsorption of dyes using different types of clay: a review, *Appl Water Sci.*, 7 (2017) 543-568.
- [7] L. Wang, A. Wang, Adsorption characteristics of congo red onto the chitosan/ montmorillonite nanocomposite, J. Hazard. Mater., 147 (2007) 979-985.
- [8] H. Gecol, E. Ergican, P. Miakatsindila, Biosorbent for tungsten species removal from water: effects of cooccurring inorganic species, *J. Colloid Interf. Sci.*, 292(2) (2005) 344-353.
- [9] M.Y. Chang, R.S. Juang, Adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay, J. Colloid Interf. Sci., 278 (2004) 18-25.
- [10] P. Singh, K. Chauhan, V. Priya, R.K. Singhal, A greener approach for impressive removal of As(III)/As(V) from an ultra-low concentration using a highly efficient

chitosan thiomer as a new adsorbent, RSCAdv., 6(69) (2016) 64946-64961.

- [11] C. Fan, K. Li, Y. Wang, X. Qian, J. Jia, The stability of magnetic chitosan beads in the adsorption of Cu<sup>2+</sup>, RSCAdv., 6(4) (2016) 2678-2686.
- [12] S.F. Wang, L. Shen, Y.J. Tong, L. Chen, I.Y. Phang, P.Q. Lim, T.X. Liu, Biopolymer chitosan/montmorillonite nanocomposites: preparation and characterization, Polym. Degrad. Stab., 90(1) (2005) 123-131.
- [13] M.S. Chiou, H.Y. Li, Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads, Chemosphere, 50(8) (2003) 1095-1105.
- [14] P. Lertsutthiwong, K. Noomun, S. Khunthon, S. Limpanart, Influence of chitosan characteristics on the properties of biopolymeric chitosan–montmorillonite, Prog. Nat. Sci., 22 (2012) 502-508.
- [15] C. Liu, A.M. Omer, X. Ouyang, Adsorptive removal of cationic methylene blue dye using carboxymethyl cellulose/k-carrageenan/activated montmorillonite composite beads: Isotherm and kinetic studies, Int J Biol Macromol., 106 (2018) 823-833.
- [16] M. Hasan, A.L. Ahmad, Hameed B.H. Adsorption of reactive dye onto cross-linked chitosan/oil palm ash composite beads, Chemical Engineering Journal, 136(2) (2008)164-172.
- [17] Z. Cheng, X. Liu, M. Han, W. Ma, Adsorption kinetic character of copper ions onto a modified chitosan transparent thin membrane from aqueous solution, J. *Hazard. Mater.*, 182 (2010) 408-415.
- [18] S. Arabi, M.R. Sohrabi, Removal of methylene blue, a basic dye, from aqueous solutions using nano-zerovalent iron, Water Science & Technology, 70(1) (2014) 24-31.
- [19] A. Mirmohseni, M.S. Seyed Dorraji, A. Figoli, F. Tasselli, Chitosan hollow fibers as effective biosorbent toward dye: preparation and modeling, Bioresour. Technol., 121 (2012) 212- 220.
- [20] B.H. Hameed, A.A. Ahmad, N. Aziz, Adsorption of reactive dye on palm-oil industry waste: equilibrium, kinetic and thermodynamic studies, Desalination, 247 (2009) 551-560.
- [21] H. Fan, J.S. Yang, T.G. Gao, H.L. Yong, Removal of low-molecular basic dye (azure blue) from aqueous solutions by a native biomass of a newly isolated adsorption sp.: Kinetics equilibrium and biosorption simulation, *J. Taiwan Ins. Chem. Eng.*, 43 (2012) 382-392.
- [22] B. Xu, H. Zheng, Y. Wang, Y. An, K. Luo, C. Zhao, W. Xiang, Poly (2-acrylamido-2-methylpropane sulfonic acid) grafted magnetic chitosan microspheres: Preparation, characterization and dye adsorption, Biomac, 112 (2018) 648-655.
- [23] J.K. Xie, Q.Y. Yue, B.Y. Gao, Q. Li, Adsorption kinetics and thermodynamics of anionic dyes onto sewage sludge derived activated carbon, Int. J. Environment and Pollution, 45(1-3) (2011) 123-144.
- [24] V.K. Gupta, R. Jain, M.N. Siddiqui, T.A. Saleh, S. Agarwal, S. Malati, D. Pathak, Equilibrium and thermodynamic studies on the adsorption of the dye Rhodamine-B onto mustard cake and activated carbon, *J. Chem. Eng. Data*, 55 (2010) 5225-5229.