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Study of the adsorption of methyl orange from aqueous solution using nickel oxide nanoparticles: Equilibrium and Kinetics Studies

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ABSTRACT

Methyl orange is one dye resulted from the textile industry. The aim of this study is to test the adsorption capacity of nickel oxide nanoparticles for removing the methyl orange from aqueous solution. The parameters studied were the effect of temperature, contact time and initial pH of solution. Results indicate that the removal efficiency of nickel oxide nanoparticles increases with increasing concentration of methyl orange and temperature. Adsorption isotherms were investigated to complete understanding the adsorption processes. The adsorption behavior was analyzed by Langmuir, Freundlich and Tempkin isotherms. The values of correlation coefficients (R^2) showed that the Langmuir isotherm model has a better fitting than Freundlich and Tempkin isotherms. Sorption kinetic data were fitted to the pseudo second-order model.

Keywords: Dye adsorption; kinetics; Adsorption isotherms; Nickel oxide nanoparticles

INTRODUCTION

Progress in industrialization for particular textile industries have led to the discharge of unprecedented amount of wastewater containing synthetic dyes, which pollutes the rivers and consequently causes harm to human and other living organisms [1]. Methyl orange (MO) dye is a commonly used mono azo dye in laboratory assays, textiles and other commercial products and has to be removed from water due to its toxicity [2,3]. Therefore, it is a major environmental challenge to remove the dyes from industrial effluents [7].

Comparatively, adsorption is a more effective process for the removal of dyes due to its simplicity and high efficiency [8]. Many kinds of adsorbents, such as activated carbon [9], peat [10], chitin [11], silica [12], and fly ash, were used, but the adsorption capacity of these were not so effective [13,14].

Nickel oxide (NiO) is considered as a good adsorbent due to its chemical and magnetic properties. Nickel oxide powders with same sizes and good dispersion are use in different fields such as producing

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films, magnetic materials, ceramic, heterogeneous catalytic materials, alkaline batteries, electrochrom, etc [15]. Nickel oxide as an effective catalyst has been used for oxidation of a wide range of organic compounds [16, 17].

This study is focused to utilize the NiO nanoparticles to remove of MO from aqueous solution. It was investigated using batch adsorption studies. The combined effect of temperature, contact time and initial pH of solution on methyl orange removal from aqueous medium by NiO nanoparticles has been investigated. Adsorption isotherm and kinetic studies were also investigated in order to understand the adsorption mechanism and efficiencies of NiO nanoparticles.

EXPERIMENTAL

Material

Methyl Orange (MO), a bright orange crystalline powder with a molecular weight of 327.34 g/mol was purchased from LABCHEM and used without further purification. Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) and sodium hydroxide (NaOH) were obtained from Merck Company. All solutions were prepared with deviations of less than ±0.1% from the desired concentrations.

Synthesis of NiO nanoparticles

The $Ni(OH)_2$ was prepared by reacting aqueous solutions of 0.1M nickel nitrate and 0.5M sodium hydroxide. The NaOH solution was added drop wise with constant stirring until the solution pH reached to 12. The chemical reaction between nickel nitrate and sodium hydroxide solution was followed as:

$$\mathrm{Ni(NO_3)_2 + 2NaOH \rightarrow Ni(OH)_2 + 2NaNO_3}$$

The resulting gel was washed several times with distilled water. Finally gel was dried by heating at 100°C for 10 hours. Nickel hydroxide decomposed into nickel oxide on heating as follows:

$$\mathrm{Ni(OH)_2 \overset{\Delta}{\rightarrow} NiO + H_2O}$$

In this work nanoparticles of NiO sample was prepared by heating the nickel hydroxide at 300°C for 3 hours A scanning electron microscope (SEM)., JEOL JSM-5600 Digital Scanning Electron Microscope and X-ray diffractometer (XRD), Philips X'Pert were used to characterize the adsorbent for its morphological information

Batch Adsorption Studies

Adsorption experiments were carried out by batch method at room temperature (293 K). The time-dependent behavior of dye adsorption was studied by varying the contact time between the adsorbate and adsorbent in the range 5-40 min. The initial concentration of dye was kept as 2 mg L^{-1}, while the dose of NiO nanoparticles was 0.5 g/L. At the end of each adsorption experiment, the solution and solid phase were separated by centrifugation at 4000 rpm for 2 min. The residual dye concentration in the supernatant part was analyzed using a spectrophotometer (Shimadzu, Model UV 1601) at a wavelength of 482 nm (methyl orange). The adsorption capacity of dye on adsorbent was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

where C_0 and C_e are the dye concentrations in mg/L initially and at a given time t, respectively, V is the volume of dye solutions in L, and w is the weight of sorbent in g.

Results and Discussion

Characterization of Nickel oxide (NiO) nanoparticles

Fig. 1A illustrates the typical XRD pattern of NiO nanoparticles. The peaks for the synthesized NiO nanoparticles are

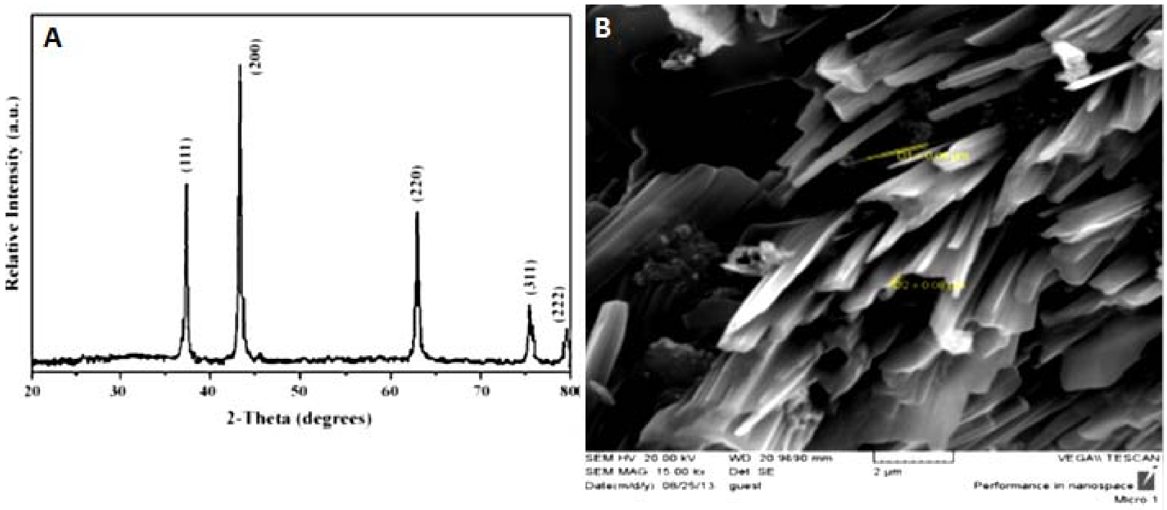

Fig. 1. The X-ray diffraction pattern (A) and SEM micrograph (b) of NiO nanoparticles.

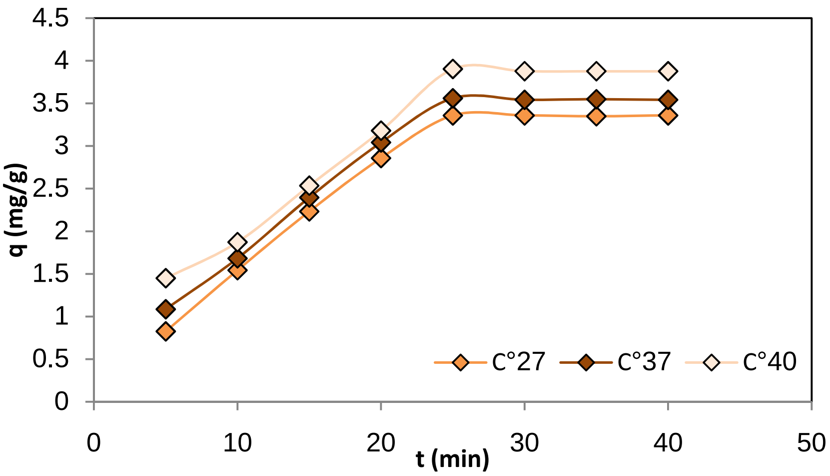

Fig. 2. Effect of contact time and temperature on the amount of dye removal by NiO nanoparticles, (initial concentration 2 mg/L; adsorbent dosage 0.5 g/L; pH 5.0).

identical. The peaks were observed at scattering angle (2θ) of 36.8, 43.6, 62.2, 75.01, 78.98 correspond to the reflections from (111), (200), (220), (311) and (222) crystal planes, respectively. Fig. 1B shows the typical scanning electron micrographs of NiO nanoparticles. Single-phase primary particles, near to spherical shaped nanocrystallites were observed. The average diameter determined by SEM analysis was 80 nm.

Effect of contact time and temperature

Results of effect of contact time on MO removal are shown in Fig. 2. In initial minutes of experiment, dye was quickly removed and then the dye removal was increased constantly with increasing contact time. According to results, 25 min was obtained as equilibrium contact time of MO; after this time, due to saturation of adsorption sites on adsorbent, dye removal efficiency won’t change. It is revealed from the Fig. 2 that removal of the MO is enhanced by increasing the temperature of solution. It may be due to more interaction between adsorbate and adsorbent [18].

Effect of initial pH

Fig. 3 shows that pH plays an important role in the adsorption process. Consequently, as the pH increases up to values higher than 5, the adsorption of MO will be less favourable. It is due to the electrostatic repulsion between the adsorptive anion and the surface of the NiO nanoparticles that gradually becomes more negatively charged [19]. The acidic medium is desirable for the adsorption process of MO.

Effect of adsorbent dose

Fig. 4 shows that the quantity removal of the MO is enhancing with increasing the dose of adsorbent. The increased removal of MO was found to be poor after a dose of 0.5 g/L for NiO nanoparticles. So, it was fixed as optimum dose of adsorbent for further studies.

Isotherm data analysis

The most widely accepted surface adsorption models for single-solute systems are the Langmuir [20], Freundlich [21] and Tempkin [22] models. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

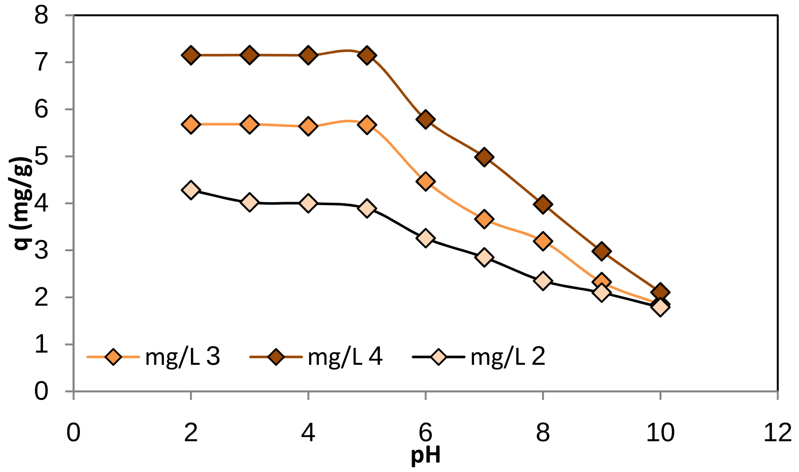

Fig. 3. Effect of pH on the amount of dye removal by NiO nanoparticles (contact time 25 min; adsorbent dosage 0.5 g/L; temperature 40°C).

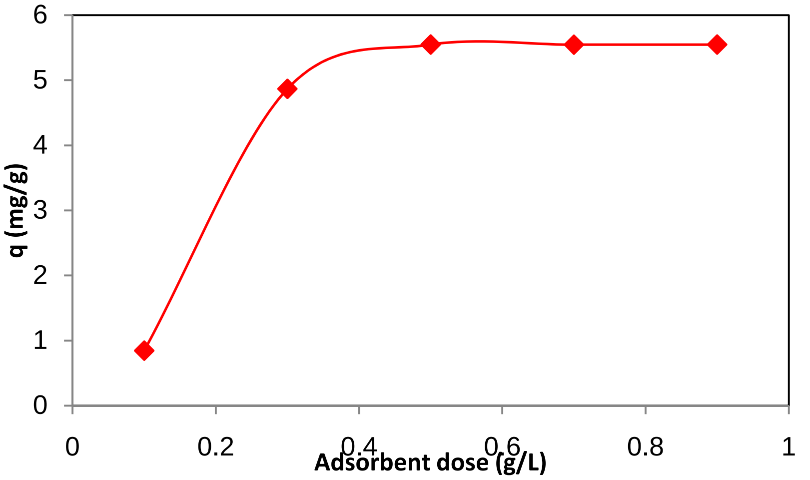

Fig. 4. Effect of adsorbent dose on the amount of dye removal by NiO nanoparticles (contact time 25 min; initial concentration of MO 2mg/L; pH 5.0; temperature 40°C).

Langmuir isotherm

The theoretical Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. The linear form of this isotherm can be written as:

$$\frac{C_e}{q_e} = \frac{1}{K_L\, q_m} + \frac{C_e}{q_m} \qquad (2)$$

where q_m is a theoretical maximum adsorption capacity corresponding to monolayer coverage (mg/g), K_L is adsorption equilibrium constant (L/mg) that is related to the apparent energy of sorption. A plot of C_e/q_e versus C_e should indicate a straight line with slope of $1/q_m$ and intercept of $1/K_Lq_m$ (Fig. 5).

The Freundlich isotherm

The Freundlich isotherm model is the earliest known equation describing the adsorption process. The linear form of this isotherm can be written as:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (3)$$

where K_F is a constant for the system, related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. 1/n is indicating the adsorption intensity of dyes onto the adsorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. The applicability of the Freundlich adsorption isotherm was also analyzed, using the same set of experimental data, by plotting ln qe versus ln Ce (Fig. 5).

The Tempkin isotherm

Tempkin adsorption isotherm model was used to evaluate the adsorption potentials of the NiO nanoparticles for removal of MO. The derivation of the Tempkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Tempkin isotherm has commonly been applied in the following form

$$q_e = \beta \ln \alpha + \beta \ln C_e \qquad (4)$$

where $\beta = (RT)/b$, T is the absolute temperature in Kelvin and R is the universal gas constant, 8.314 J $(\text{mol K})^{-1}$.The constant b is related to the heat of adsorption [22].

The linear isotherms constants and coefficients are presented in Table 1. The correlation coefficients R^2 obtained from model were comparable to that obtained for Langmuir, Freundlich and Tempkin equations, which explain the applicability of Langmuir model to the adsorption of MO onto NiO nanoparticles.

Kinetic modeling

In order to investigate the controlling mechanism of removal processes such as mass transfer and chemical reaction, the pseudo first-order and pseudo second-order equations are applied to model the kinetics of dye removal onto NiO nanoparticles.

Pseudo first-order model

The pseudo-first order rate expression, popularly known as the Lagergren equation, is generally described by the following equation [23]:

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right)t \qquad (5)$$

where, q_e is the amount of the dye adsorbed at equilibrium per unit weight of sorbent (mg/g); q_t is the amount of dye adsorbed at any time (mg/g). Besides, k_1 is the adsorption rate constant of first-order adsorption (1/min). In order to obtain rate constants, the straight-line plots of $\log(q_e-q_t)$ against t (min) were made (Fig. 6).

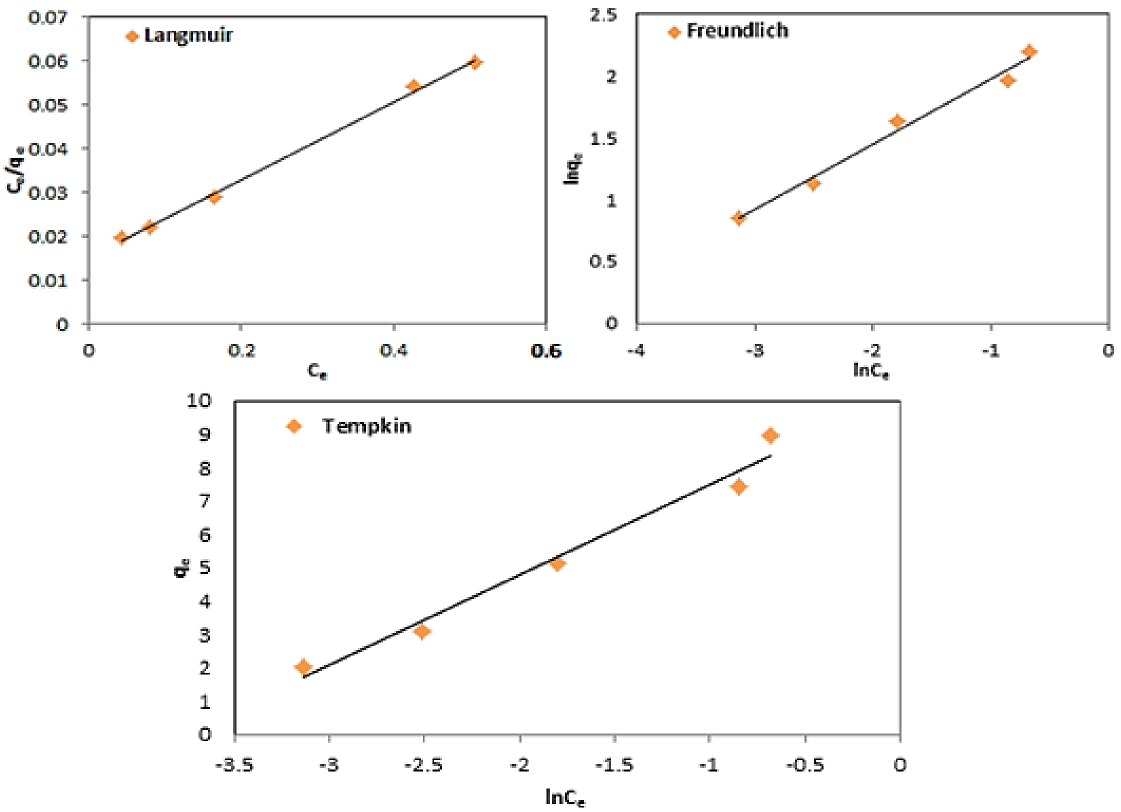

Fig. 5. Langmuir, Freundlich and Tempkin plots for the adsorption of MO on NiO nanoparticles.

Table 1. Isotherm constants and correlation coefficients

Isotherm model	**Methyl orange**
Langmuir	
q_m (mg/g)	11.210
K_L (L/mg)	5.8820
R^2	0.9983
Freundlich	
n	1.8978
K_F (mg/g)/(mg/L)$^{1/n}$	12.263
R^2	0.9847
Tempkin	
β (mg/L)	2.7202
α (L/g)	42.862
b	916.91
R^2	0.9752

Pseudo second-order model

The sorption data was also analyzed in terms of a pseudo second-order mechanism [24] given by

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{t}{q_e} \qquad (6)$$

where k_2 (g /mg min) is the second-order rate constant of adsorption. The slope and intercept of the linear plot of t/q_t against t yielded the values of q_e and k_2. Fig. 6 shows a plot of linearization form of

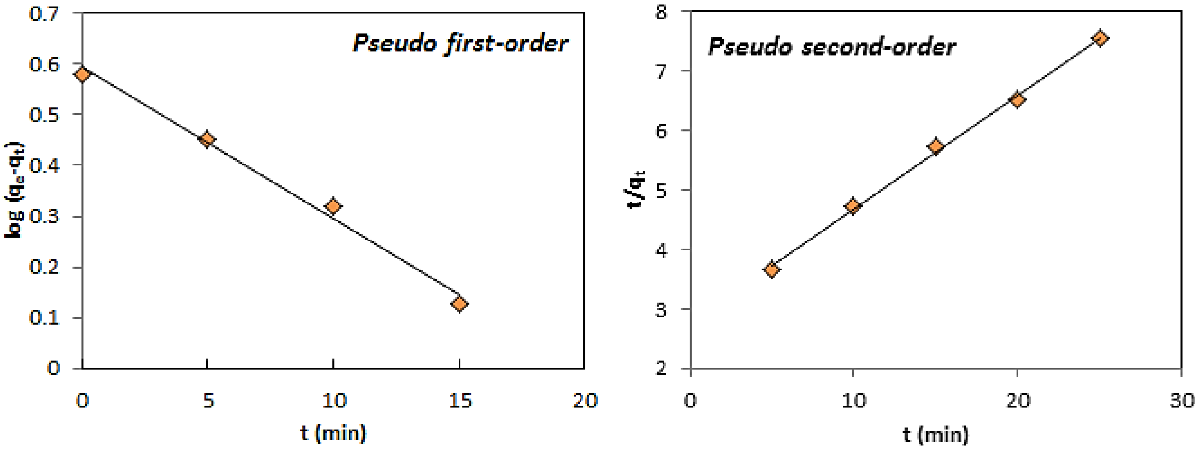

Fig. 6. Pseudo first and second-order kinetics for the adsorption of MO on NiO nanoparticles.

Table 2. Comparison of the pseudo first- and second-order rate constants

Kinetics	**Pseudo first-order**			**Pseudo second-order**		
	K_1 (1/min)	q_e (mg/g)	R^2	K_2 (g/mg min)	q_e (mg/g)	R^2
Methyl orange	0.030	3.927	0.9901	0.0132	5.2246	0.9984

pseudo-second order model. As can be seen from Table 2, the value of R^2 of the second-order model for adsorption of MO is higher than corresponding value for first-order model. This results show pseudo second-order equation could fit well over the range of contact times and describe well the rate of dye sorption onto NiO nanoparticles.

CONCLUSION

NiO nanoparticles can be used as an effective adsorbent for removing methyl orange(MO) from water sources. By increasing the temperature and contact time, the dye adsorption rate increased. Since the value of R^2 for the pseudo second-order kinetic model was higher than that for the pseudo first-order model, it was accepted as the accurate adsorption kinetics. Also the values of R^2 indicated that the adsorption patern for MO on NiO nanoparticles followed the Langmuir isotherm. The Langmuir isotherm showed a better fitting than Freundlich and Tempkin isotherms, thus, it indicated the applicability for both monolayer and homogeneous adsorption and is based on the assumption that methyl orange adsorbed onto the heterogeneous surface of NiO nanoparticles.

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