

## **Adsorption properties of nickel oxide nanoparticles for removal of Congo Red from aqueous solution**

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### **ABSTRACT**

The effective removal of dyes from aqueous wastewaters is among the most important issues for many industrialized countries. Removal of Congo Red (CR) dye from aqueous solutions was studied using nickel oxide nanoparticles. The operating variables studied were initial pH of solution, adsorbents dosage, temperature and contact time. The morphological information of nickel oxide nanoparticles were characterized using scanning electron microscopy (SEM) and X-ray diffractometer (XRD). The adsorbent exhibits high efficiency for CR adsorption and equilibrium can be achieved in 25 min. In order to investigate the efficiency of CR adsorption on nickel oxide nanoparticles, pseudo-first-order, pseudo-second-order kinetic models were studied. It was observed that the pseudo-second-order kinetic model fits better than other kinetic model with good correlation coefficient. Equilibrium data were fitted to the Langmuir model.

**Keywords:** Congo red; Removal; Nickel oxide nanoparticles; Equilibrium; Adsorption

### **INTRODUCTION**

The discharge of highly colored effluents into natural water bodies is not only aesthetically unpleasant, but it also impedes light penetration, thus upset biological processes within a stream. In addition, many dyes are toxic to some organisms causing direct destruction of aquatic communities. Some dyes can cause allergic dermatitis, skin irritation, cancer and mutation in man. Among the various classes, azo dyes and basic dyes are found to be the brightest classes used by the textile industry as their tinctorial value is high.

CR is a benzediene based dye. It is known to cause allergic reactions and to be metabolized to benzedine. Its decomposition results in carcinogenic

products. It acts as a skin, eye and gastrointestinal irritant. It impresses blood factors such as clotting and induces drowsiness and respiratory problems [1, 2].

Wastewater containing these dyes is difficult to treat using conventional methods, since the dyes are stable to light, oxidizing agents, and aerobic digestion [3]. Adsorption techniques have also been used [4]. Some procedures can be used for treating waters containing dyes, for instance, coagulation and flotation [5], ozonization [6], membrane separation [7] and adsorption [8] extensively employed due to its efficiency and economy [9].

Nickel oxide (NiO) is considered as a good adsorbent due to its chemical and magnetic properties. Nickel oxide powders

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with same sizes and good dispersion are used in different fields such as producing films, magnetic materials, ceramic, heterogeneous catalytic materials, alkaline batteries, electrochrom, etc [10]. Nickel oxide as an effective catalyst has been used for oxidation of a wide range of organic compounds [11, 12].

In this paper, the possibility of using Nickel oxide (NiO) nanoparticles to remove Congo Red was investigated using batch adsorption studies. The effects of various factors such as contact time, pH, temperature and adsorbent dosage on the removal efficiency of CR onto NiO nanoparticles were also studied. The kinetic and equilibrium data were analyzed so that we can understand the adsorption mechanism and different models were applied to fit the experimental data.

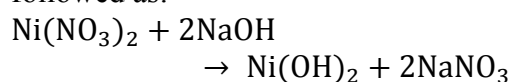
## EXPERIMENTAL

### Material

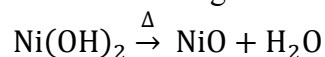
Congo Red (CR),  $C_{32}H_{22}N_6Na_2O_6S_2$ , a bright red crystalline powder with a molecular weight of  $696.66 \text{ g.mol}^{-1}$  and  $\lambda_{\text{max}} = 500 \text{ nm}$  was purchased from Sigma-Aldrich (Munich, Germany) and used without further purification. Nickel (II) nitrate hexahydrate ( $Ni(NO_3)_2 \cdot 6H_2O$ ) and sodium hydroxide (NaOH) were obtained from Merck Company. All solutions were prepared with deviations of less than  $\pm 0.1\%$  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 dropwise with constant stirring until the solution pH reached to 12. The chemical reaction between nickel nitrate and sodium hydroxide solution was followed as:



The resulting gel was washed several times with distilled water. Finally gel was dried by heating at  $100^\circ\text{C}$  for 10 hours. Nickel hydroxide decomposed into nickel oxide on heating as follows:



In this work, nanoparticles of NiO sample was prepared by heating the nickel hydroxide at  $300^\circ\text{C}$  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.

### Removal experiments

Adsorption experiments were carried out by batch method at room temperature. 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 at  $2 \text{ mg L}^{-1}$ , while the dose of NiO nanoparticles was  $0.5 \text{ g/L}$ . 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 500 nm (CR). The adsorption capacity of dye on adsorbent was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (1)$$

where  $C_0$  and  $C_e$  are the dye concentrations in  $\text{mg/L}$  initially and at a given time  $t$ , respectively,  $V$  is the volume of dye solution 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 identical. The peaks were observed at scattering angle ( $2\theta$ ) 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

The removal of CR increases with time

and attains saturation in 25min. Fig. 2 represents the amount removal of CR versus the contact time and temperature for the initial concentration 2 mg/L. The CR dye showed a fast rate of sorption during the first 25 min of the sorbate–sorbent contact and the rate of amount removal becomes almost insignificant due to a quick exhaustion of the adsorption sites. The rate of amount dyes removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the dyes. It is revealed from the Fig. 2 that removal of the CR is enhanced by increasing the temperature of solution. It may be due to more interaction between adsorbate and adsorbent [13].

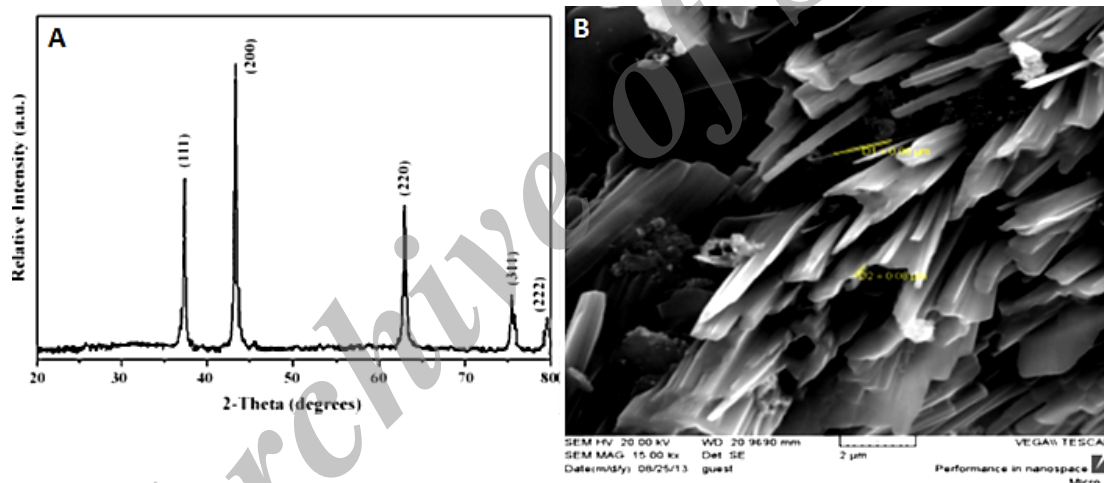


Fig. 1. The X-ray diffraction pattern (A) and SEM micrograph (b) of NiO nanoparticles.

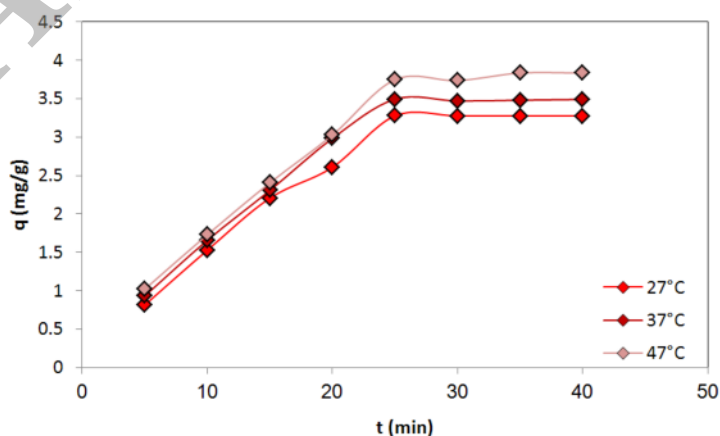


Fig. 2 Effect of contact time and temperature on the amount of dye removal by NiO nanoparticles, (initial concentration 2 mg/L; adsorbent dosage 0.5 g/L; pH 5.0).

### Effect of initial pH

Fig. 3 shows that pH plays an important role in the adsorption process. As the pH increases up to values higher than 5-10, the adsorption of CR will be less favorable. It is due to the electrostatic repulsion between the adsorptive anion and the surface of the NiO nanoparticles that gradually becomes more negatively charged [14]. The acidic medium is desirable for the adsorption process of CR.

removal of the CR from aqueous solution was carried out using NiO nanoparticles powder with their amount varying from 0.1 to 0.9 g/L. The maximum amount of dye removal for Congo red adsorption attained for adsorbent dose of 0.5 g/L as shown in Fig. 4. The amount of dye removal increases by increasing the adsorbent dose, Because all available sites are not covered and active sites are available for further binding of dye molecules to adsorbent surface.

### Effect of adsorbent dose

The study of adsorbent dose for the

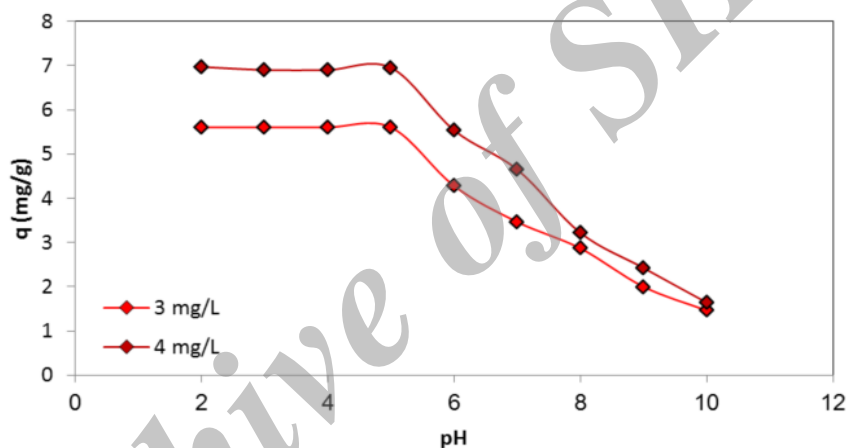


Fig. 3. Effect of pH on the amount of dye removal by NiO nanoparticles (contact time 25 min; adsorbent dosage 0.5 g/L; temperature 40°C).

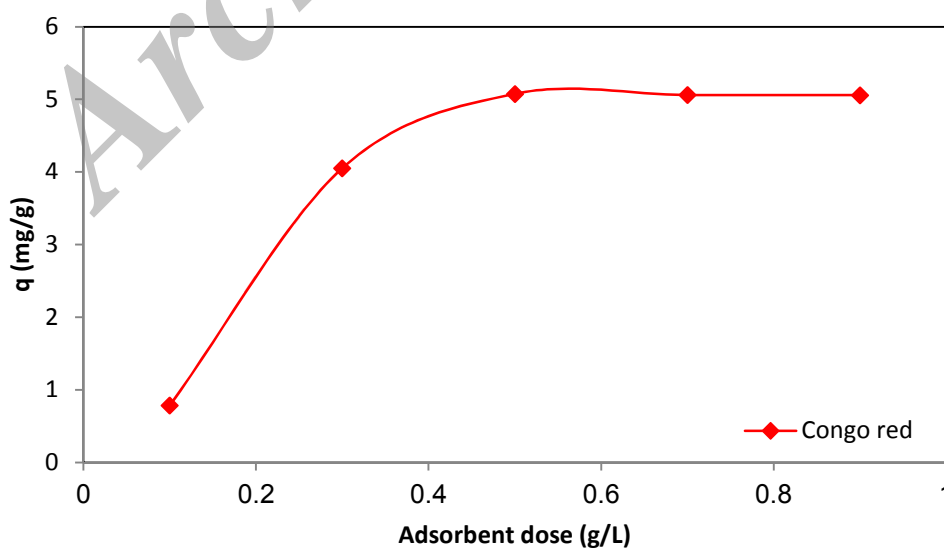


Fig. 4. Effect of adsorbent dose on the amount of dye removal by NiO nanoparticles (contact time 25 min; initial concentration 2mg/L; pH 5.0; temperature 40°C).

### Adsorption equilibrium study

Adsorption isotherms are prerequisites to understand the nature of the interaction between adsorbate and the adsorbent used for the removal of organic pollutants. The parameters were obtained from the different models and provided important information on the surface properties of the adsorbent and its affinity to the adsorbate. Several isotherm equations have been developed and employed for such analysis and the two important isotherms, the Langmuir, Freundlich isotherms are applied in this study.

**Langmuir isotherm:** The Langmuir isotherm is based on the assumption that the adsorption process takes place at specific homogeneous sites within the adsorbent surface and that once a dye molecule occupies a site, no further adsorption can take place at that site, which concluded that the adsorption process is monolayer in nature. The Langmuir equation, which is valid for monolayer adsorption onto a completely homogenous surface with a finite number of identical sites with negligible interaction between adsorbed molecules, is represented in the linear form as follows [15]:

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

where  $K_L$  is the Langmuir adsorption constant ( $Lmg^{-1}$ ) and  $q_m$  is the theoretical maximum adsorption capacity ( $mg g^{-1}$ ). The value of  $q_m$  and  $K_L$  constant obtained

by the Langmuir plots ( $C_e/q_e$  vs.  $C_e$ ) that these values and the correlation coefficient of this model is presented in Table 1. The isotherms of CR on adsorbent was found to be linear over the whole concentration range studies and the correlation coefficients were extremely high as shown in Table 1 and Fig 5.

**Freundlich isotherm:** The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of sorption heat over the surface was presented in the linear form as follows [16]:

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

where  $K_F$  ( $(mg g^{-1}) / (mgL^{-1})^{1/n}$ ) is the Freundlich constant related to the bonding energy and can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent. The  $1/n_F$  factor is heterogeneity factor and  $n_F$  is a measure of the deviation from linearity of adsorption, which its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of  $n=1$ , the adsorption is linear;  $n < 1$ , the adsorption process is chemical; if  $n > 1$ , the adsorption is a favorable physical process [16]. From the plot of  $\ln q_e$  versus  $\ln C_e$ , the values of  $K_F$  and  $1/n_F$  can be achieved from the intercept and slope respectively (Table 1). As seen, Freundlich is an unsuitable model for whole isotherm interpretation.

**Table 1.** Isotherm constants and correlation coefficients

Isotherm model	Congo Red
Langmuir	
$q_m$ (mg/g)	10.101
$K_L$ (L/mg)	6.038
$R^2$	0.9950
Freundlich	
$n$	1.9964
$K_F$ (mg/g)/(mg/L) <sup>1/n</sup>	10.385
$R^2$	0.9868

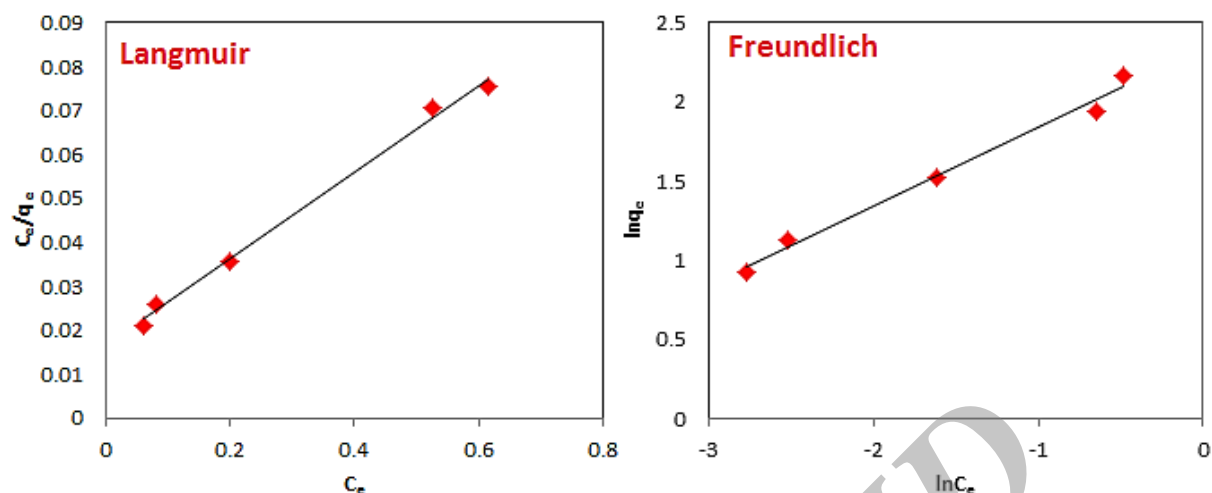


Fig. 5. Langmuir and Freundlich plots for the adsorption of CR on NiO nanoparticles.

### Kinetic study

The rate and mechanism of adsorption processes can be elucidated on the basis of kinetic study. Dye adsorption on solid surface may be explained by two distinct mechanisms; (i) an initial rapid binding of dye molecules on the adsorbent surface followed by (ii) relatively slow intra-particle diffusion. The adsorption kinetic data were described by the Lagergren pseudo-first-order model that is the earliest known equation describing the adsorption rate based on the adsorption capacity. The linear form of Lagergren equation as follows [17]:

$$\log (q_e - q_t) = \log (q_e) - \left( \frac{k_1}{2.303} \right) t \quad (4)$$

By plotting the values of  $\log (q_e - q_t)$  versus  $t$ , a linear relationship is achieved and then  $k_1$  and  $q_e$  can be determined from the slope and intercept, respectively (Table 2). If the intercept dose not equal  $q_e$  then the reaction is not likely to the first-order reaction even this plot has high correlation

coefficient. The variation in the rate of adsorption should be proportional to the first power of concentration for strict surface adsorption.

The adsorption kinetic may be described by the pseudo-second-order model [18], which is simplified as can be rearranged and linearized to obtain:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where  $k_2$  (g /mg min) is the second-order rate constant of adsorption. By plotting of  $t/q_t$  against  $t$  the values of  $q_e$  and  $k_2$  yield from the slope and intercept respectively . Fig. 6 shows a plot of linearization form of pseudo-second order model. As seen in Table 2, the  $R^2$  value of the second-order model for adsorption of CR is higher than that for first-order model. This results show pseudo second-order equation can fit well over the range of contact times and describe well the rate of CR sorption onto 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)	$R^2$
Congo Red	0.027	3.791	0.9889	0.0166	4.6641	0.9947

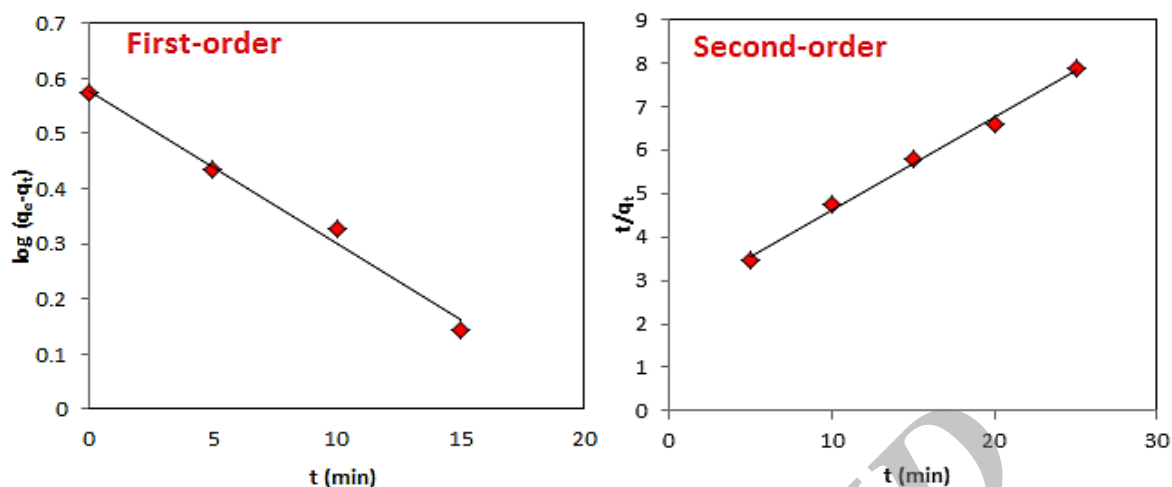


Fig. 6. Pseudo first and second-order kinetics for the adsorption of CR on NiO nanoparticles.

## CONCLUSION

The present study shows that the NiO nanoparticles were successfully used as an adsorbent for the quantitative removal of CR from aqueous solutions. UV-Vis spectroscopy was used to determine the amount of CR removed by NiO nanoparticles. The effects of temperature, contact time, adsorbents dosage and pH on the rate of removal were examined. The maximum amount of CR removal from the aqueous solutions for NiO nanoparticles was in the contact time = 25 min. The experimental adsorption equilibrium data of CR on NiO nanoparticles were compared with the Langmuir and Freundlich isotherm models and adsorption capacities were determined. These results showed that Langmuir isotherm model was better than Freundlich and its kinetics can be successfully fitted to pseudo-second-order kinetic model.

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