

Nickel-Chitosan Hybrid as a Precursor for Nickel Oxide Nanoporous Particles for Organic Dyes Photodegradation

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Abstract

Hydrothermal synthesis of nickel-chitosan hybrid has been accomplished using $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, chitosan and water as starting material, template and solvent respectively, followed by calcination at 800 and 900°C to provide nanoporous NiO_{800} and NiO_{900} . The solid products were characterized by X-ray diffraction (XRD), nitrogen adsorption-desorption, scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) techniques. NiO_{800} proved to be active for adsorption of Congo red with pseudo-second order kinetic model and adsorption isotherms, respectively fitted by Freundlich equation. NiO_{900} was also found to successfully catalyze the photodegradation of organic dye pollutants such as Congo red and methylene blue. The kinetic of photocatalytic behavior of NiO_{900} have proven to obey the first order and Langmuir–Hinshelwood model.

Keywords: Nanoparticles; Nickel Oxide; Photodegradation; Adsorption; Organic dyes.

Introduction

The removal of toxic pollutants from industrial waste water reduce their environmental impact and health effects [1]. Whereas organic dyes are an important class of materials widely used in textile and many other industries, their hazardous effects in waste water have been a major concern. Several methods for removal of the dye contaminants from wastewater including adsorption [2], coagulation/flocculation [3], advanced oxidation processes [4], ozonation [5], membrane filtration [6] and biological treatments [7] have been developed and use. Amongst which, adsorption has been recognized as the most popular treatment process in aqueous solution with the advantages of high efficiency, simple operation, easy recovery and reuse of adsorbent. Several adsorbent

materials including clays [8], cellulose-based wastes [9], fly ash [10] and microorganisms [11] are examples in this regard. Since adsorption is a non-destructive method that simply transfers the dye from one phase/substance to another, often it is inadequate and/or inappropriate for removing large amounts of organic dyes from waste water streams. In contrast, advanced oxidation processes (AOP) have the capability of converting dye molecules into non-toxic compounds [12]. Among AOPs, heterogeneous photocatalytic oxidation has received considerable attention for destructive oxidation of dyes and textile effluents, since many aromatic compounds have proven to be degraded effectively to CO_2 , H_2O and small molecules [13, 14]. Catalysts such as inorganic-organic hybrids [15], TiO_2 [1], ZnO [16], ZnS [17],

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CdS [18], and Fe₂O₃ [19] have been reported for photodegradation. However, there are challenges for development and controlling parameters for new heterogeneous photocatalysis systems and deeper investigation on catalyst operation together with performance evaluation and other relevant aspects.

Although nanostructure NiO has many application in a wide range of area such as catalysis [20] electro chromic films [21], fuel cell electrodes [22], gas sensors [23], but there has been limited studies on heterogeneous catalysts and photocatalytic processes [24]. There are different methods reported for the synthesis of NiO nanoparticles such as hydrothermal or solvothermal synthesis [25-26], pulsed laser ablation [27], microemulsion [28], precipitation-calcination [29], sonochemical [30-31] and sol-gel methods [32]. Particularly significant is hydrothermal synthesis as a well-known method for the preparation of microporous crystals, complex oxides and inorganic-organic hybrid materials [33].

In this study, nickel-chitosan hybrid has been prepared hydrothermally using Ni(CH₃COO)₂·4H₂O, chitosan and water as starting material, template and solvent respectively, followed by calcination at appropriate temperature in order to prepare nanoporous NiO. Congo red and methylene blue as cationic and anionic dyes served as model dyeing pollutant to evaluate the adsorption and photocatalytic degradation activity of the prepared catalysts.

Materials and Methods

Materials and Instruments details

All solvents and chemicals such as nickel acetate, chitosan, potassium hydroxide, ethanol 98%, acetic acid, Congo red and methylene blue were purchased from Merck Chemical Company and used without further purification.

Powder X-ray diffraction (XRD) data were recorded on XRD 3003 PTS Seifert with Cu K α radiation ($\lambda=1.54\text{\AA}$). FTIR spectra were measured on KBr disks with a Bruker-Tensor 27 2002 spectrometer. Scanning electron micrograph (SEM) images were taken by XL-30 Phillips (1992). TGA thermal curve was studied by Perkin-Elmer Pyrif 1. Nitrogen adsorption was recorded at 77K by means of a Quanta Chrome Nova version 2.2 Analyzer and degradation progress was monitored by UV-Vis spectroscopy using a Unicam 8700 series spectrometer.

Preparation of Catalysts

Nickel acetate solution (100 mL, 0.2 mol/L) was slowly added to the chitosan solution (1.6 gr, 100

mmol in 80 mL acetic acid 3% V/V). The mixture was heated in a 100 mL autoclave at 130 °C for 24 h. The resultant gel was washed with ethanol and dried. Calcination of the sample at 800 and 900 °C for 6 h afforded NiO₈₀₀ and NiO₉₀₀, respectively.

Photocatalytic evaluation

Congo red and methylene blue were used as dye pollutant sample in this study. NiO₉₀₀ (0.5 g) was added into the dye solution (50 ppm, 100 mL) while stirring. For methylene blue solution, pH was adjusted at 11 with NaOH (0.4 N). A 55W UV lamp was used as light source. The distance between the UV lamp and pyrex vessel containing catalyst and dye solution was fixed at 8 cm. Air was bubbled into the solution throughout the entire experiment to provide a constant source of dissolved oxygen. Prior to irradiation, the set up was kept in the dark for about 15 min in order to reach an adsorption/desorption equilibrium among the photocatalyst particles, dye and atmospheric oxygen molecules. The UV lamp was then turned on. During irradiation, the degraded dye was sampled in regular intervals and then centrifuged. The photocatalytic degradation was monitored by measuring the sample absorbance with a UV spectrophotometer. The degradation of dye was calculated using the following formula:

Degradation = $(A_0 - A) / A_0$, where A_0 and A are the absorbance of the primal and remaining dye, respectively.

Adsorption studies

Adsorption equilibrium experiments were carried out by adding the desired amount of NiO₈₀₀ as adsorbent to 100 mL of Congo red solution with known concentration at pH = 7 at ambient temperature. The mixture was vigorously stirred over 110 min as equilibrium time. The suspension was then centrifuged and the final concentration of dye solution was measured using an UV-Vis spectrophotometer at $\lambda_{\text{max}} = 497$ nm. The equilibrium adsorbed Congo red concentration was calculated using the equation $q_e = V(C_0 - C_e) / W$ in which C_0 , C_e , V and W stand for the Congo red initial and equilibrium concentrations (mg/L), solution volume (L) and used adsorbent mass (g), respectively.

Results and Discussion

Catalysts characterization

The FTIR spectra of chitosan, Ni(II)/chitosan hybrid, calcined NiO₈₀₀ and NiO₉₀₀ are shown in Fig1.a-d, respectively. The broad peak centered at

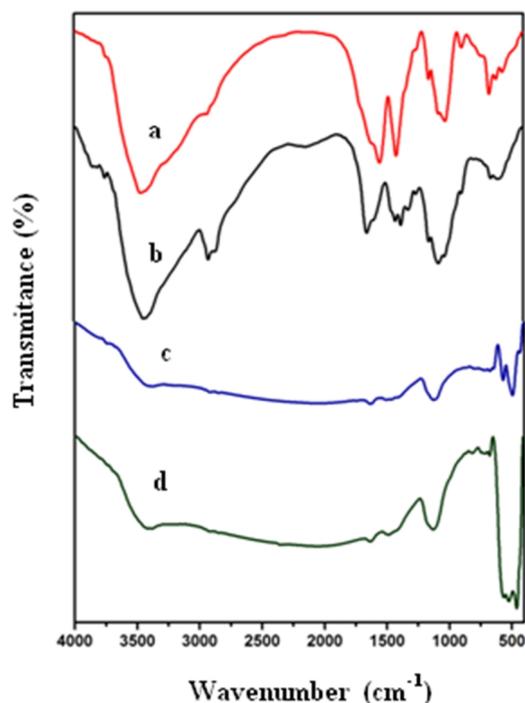


Figure 1. FTIR Spectra of (a) chitosan (b) as prepared Ni(II)/chitosan hybrid, (c) NiO nano spheres obtained after calcinations at 800 °C, for 6 h, (d) NiO nano spheres obtained after calcination at 900 °C, for 6 h.

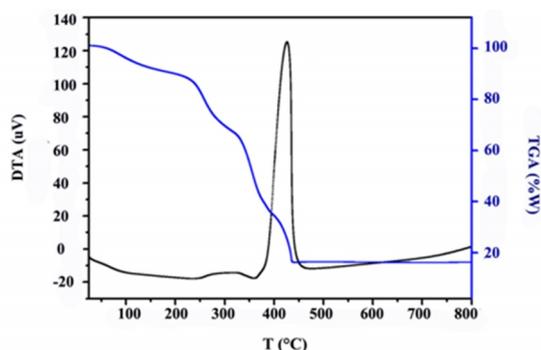


Figure 2. TGA and DTA curves of Ni-Chitosan hybrid.

3450 cm^{-1} in all four spectra is due to the stretching vibrations of OH present in chitosan and adsorbed water. The vibration bands at the region 2948, 2869, 1623 and 1153 cm^{-1} reveal the chitosan CH_2 , NH_2 and C-O-C groups, respectively. The intensity of these peaks decrease after calcination to 800 °C due to the decomposition of chitosan (Fig.1.c, d). Whereas an increase in temperature to 800 °C decreases the vibration mode due to the chitosan decomposition, an increase and decrease in a peak intensity at 1200 cm^{-1} is observed for the C-N or C-OH vibrations of

adsorbed species on NiO surface prior to and beyond 900 °C, respectively (Fig.1.d). Two new peaks were also found at 490 and 445 cm^{-1} (Fig. 1d) due to the Ni-O stretching vibrations [34-36].

In order to reveal the changes occur during heat treatment of the prepared hybrid powder, the sample TGA and DTA were carried out within 30° to 900 °C in atmosphere. As seen in TGA curve (Fig. 2a), the major weight loss occur below 410 °C. It also reveal 5% weight loss in the temperature range of 50-120 °C due to the evaporation of adsorbed water. Observing an exothermic peak at 410 °C in DTA (Fig. 2b) might be due to the chitosan (template) decomposition and formation of NiO with 71% weight loss.

The SEM images of nanoparticles NiO_{800} and NiO_{900} with particle sizes of 25 and 35 nm are shown in Fig. 3a,b respectively.

The XRD patterns of the calcined Ni (II)/chitosan at 800° and 900 °C are shown in Fig. 4(a,b) respectively. As indicated, the XRD patterns of calcined NiO at 800° and 900 °C are similar. Whereas amorphous NiO phases were obtained after heating up to 200 °C, increasing the temperature to 800° and 900 °C afforded crystalline phases. The calcined samples at 800 ° and 900 °C exhibited the diffraction angle and characteristic peak intensities consistent with those of the standard JCPDS card no. (04-0835). The main diffraction peaks were observed at 2θ 37.13°, 43.35°, 63.11°, 75.80° and 79.22°.

All diffraction peaks can be indexed to the pure NiO crystalline phase (space group: $\text{Fm}\bar{3}\text{m}$) and no peaks due to impurity were observed in the XRD pattern.

The textural characteristic of NiO nanospheres was investigated by the gas sorption measurement at 77 K. The nitrogen adsorption-desorption isotherms of the NiO_{800} and NiO_{900} are depicted in Fig.5 and the inset shows the Barrett-Joyner-Halenda (BJH) pore size distributions obtained from the adsorption branch. The specific surface area of NiO_{800} and NiO_{900} are 6.8 and 3.7 m^2g^{-1} , respectively. Both NiO samples can be categorized as IUPAC type IV isotherms with H_3 type hysteresis. The pore sizes of NiO_{800} and NiO_{900} are 3.45 nm and 3.36 nm, respectively. It is noticed that the pore size distribution curves of NiO_{800} and NiO_{900} show bimodal porosity. As such, it provides an efficient transport pathway for reactants of the NiO_{800} and NiO_{900} interiors, a beneficial catalytic property.

Photo-catalytic evaluations

The adsorption of cationic methylene blue and anionic Congo red dyes on the catalyst surface is important in photodegradation. Similarly, electric

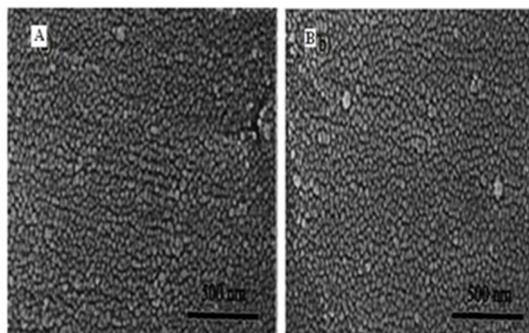


Figure 3. SEM images of NiO nanoparticles calcinated at (a) 800°C (b) 900°C for 6h.

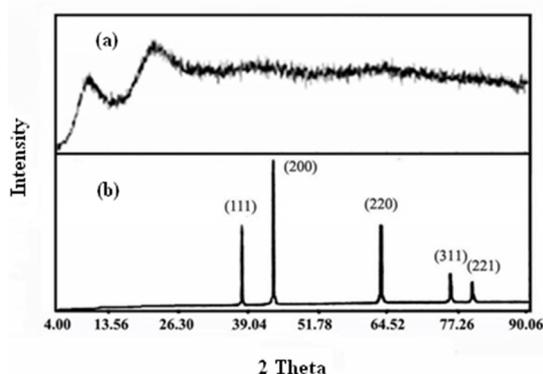


Figure 4. XRD patterns of (a) as-prepared Ni(II)/Chitosan hybrid (b) after calcination at 800 and 900°C.

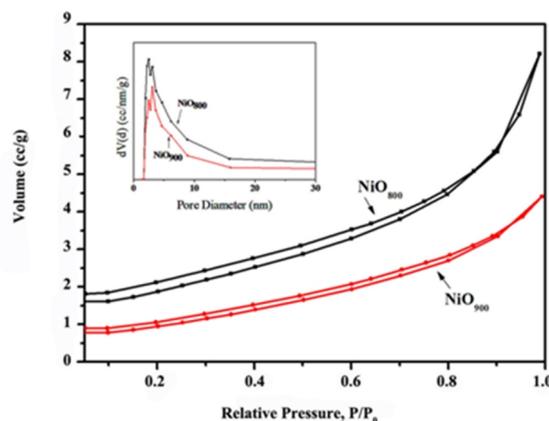


Figure 5. N₂ adsorption and desorption isotherms of NiO₈₀₀ and NiO₉₀₀. Inset is the corresponding pore size distribution of NiO₈₀₀ and NiO₉₀₀.

charge properties of both catalyst and substrate play an important role on adsorption process. Moreover, the nano NiO shows amphoteric behavior in aqueous media. The point of zero charge (pzc) of nano NiO, was found to be 10.5 [37]. Notably, nano NiO surface was found to be negatively charged and in protonated

form at pH higher than pH_{pzc} and lower pH values, respectively. For the adsorption of dye on NiO surface, photodegradation processes of methylene blue and Congo red were conducted at alkaline and natural pH using UV-Vis absorptions at wavelength of 664 and 497 nm, respectively.

The absorbance decrease after adding NiO nano particles and upon reaching equilibrium in dark for 15 min prior to irradiation onto the NiO surface due to the calculated 10 and 5% adsorption of Congo red and methylene blue, respectively. As observed in Fig. 6, under UV irradiation the intensity of the 497 nm and 664 nm absorption bands in the visible region due to the chromophores decreased rapidly and almost disappeared after 20 min and 90 min respectively.

The heterogeneous photocatalysis kinetic models have proven to obey the Langmuir–Hinshelwood (L–H) kinetic expression 1.

$$r = dC/dt = kKC / (1 + KC) \quad (1)$$

where r , C , t , k and K are reactant oxidation rate (mg/l min), reactant concentration (mg/l), illumination time (s), reaction rate constant (mg/l min) and reactant adsorption coefficient (l/mg), respectively. If one works with low initial concentrations, the equation is simplified to an apparent first-order equation 2.

$$\ln(C_0/C) = kt \quad (2)$$

Where C_0 and C are the dye concentrations at zero and t times, respectively. A plot of $\ln C_0/C$ versus time then represents a straight line, the slope of which upon linear regression equals the apparent first-order rate constant k . As illustrated in Fig.6, obtaining linear plots of $\ln (C_0/C)$ versus irradiation time for Congo red and methylene blue suggest that the photodegradation reactions follow the first order kinetics. The slopes of $\ln (C_0/C)$ versus time plots in optimized conditions then give 0.102 min^{-1} and 0.0269 min^{-1} as the corresponding rate constants, respectively.

Adsorption studies

Adsorption equilibrium experiments were carried out by vigorous stirring of NiO₈₀₀ in desired amount as adsorbent and 100 ml of Congo red solution in known concentration at natural pH and ambient temperature within 110 min as equilibrium time. The suspension was then centrifuged and the final dye concentration was measured using an UV-Vis spectrophotometer at $\lambda_{max} = 497 \text{ nm}$. Congo red uptake at equilibrium adsorbed was calculated by means of $q_e = V(C_0 - C_e) / W$ equation in which C_0 and C_e (mg/L) stands for the

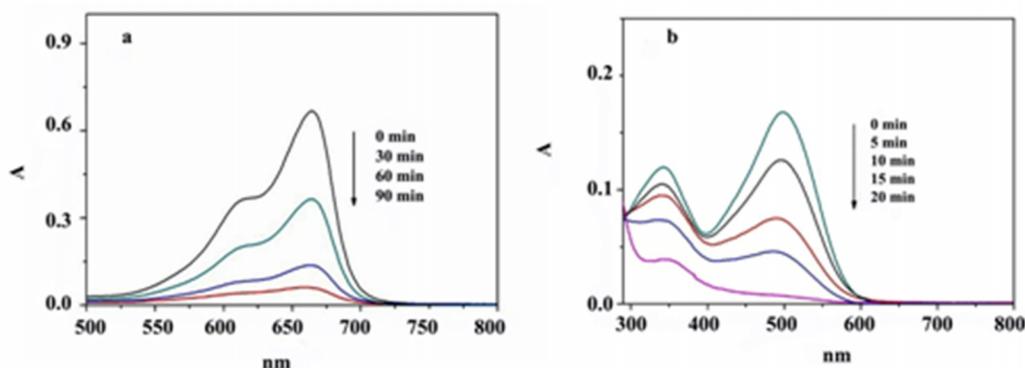


Figure 6. UV-Vis spectra changes of, Methylene blue(5ppm) (a) Congo red (5 ppm) (b) in aqueous NiO₉₀₀ dispersion under illumination at different times.

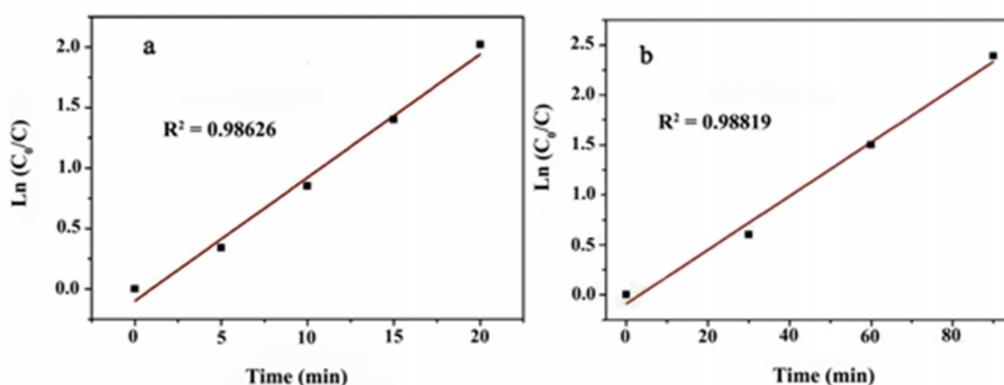


Figure 7. Plot of $\ln(C_0/C)$ versus T for (a) Congo red and (b) Methylene blue.

Congo red concentrations at initial and equilibrium times respectively, V (L) as the solution volume and W (g) as the used adsorbent mass.

Equilibrium isotherm modeling

To simulate the interaction between Congo red and NiO₈₀₀, the equilibrium experimental data were analyzed using two commonly Freundlich and Langmuir isotherm models as are listed below:

Freundlich isotherm:

The adsorption equilibrium of the dye in solution and on the adsorbent surface using a multi-site adsorption isotherm for heterogeneous surfaces especially those involving organic compounds is described by equation 3 [38].

$$q_e = K_F C_e^{1/n} \tag{3}$$

It rearranges to linear equation 4 by taking the logarithm.

$$\log q_e = \log K_F + 1/n \log C_e \tag{4}$$

Where q_e (mg/g) and C_e (mg/L) represent the Congo red concentration adsorbed on NiO₈₀₀ and in solution at equilibrium, respectively and K_F and $1/n$ stand for the Freundlich adsorption isotherm constants that can be calculated from intercept and slope of the linear plot between $\log C_e$ and $\log q_e$.

Langmuir isotherm:

The Langmuir theory describes the monolayer coverage of adsorbent on a homogeneous adsorbent surface. The adsorption isotherm is based on the assumption that sorption takes place at specific homogeneous sites with constant adsorption energy. The adsorbed dyes were correlated by two parameters (equation 5).

$$q_e = q_m K_L C_e / (1 + K_L C_e) \tag{5}$$

Rearranging equation 5 gives equation 6.

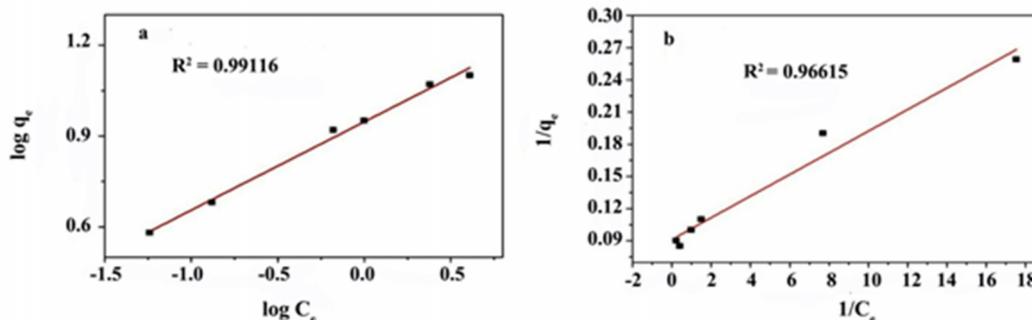


Figure 8. Adsorption isotherms for adsorption of Congo red on NiO₈₀₀ (a) Freundlich and (b) Langmuir.

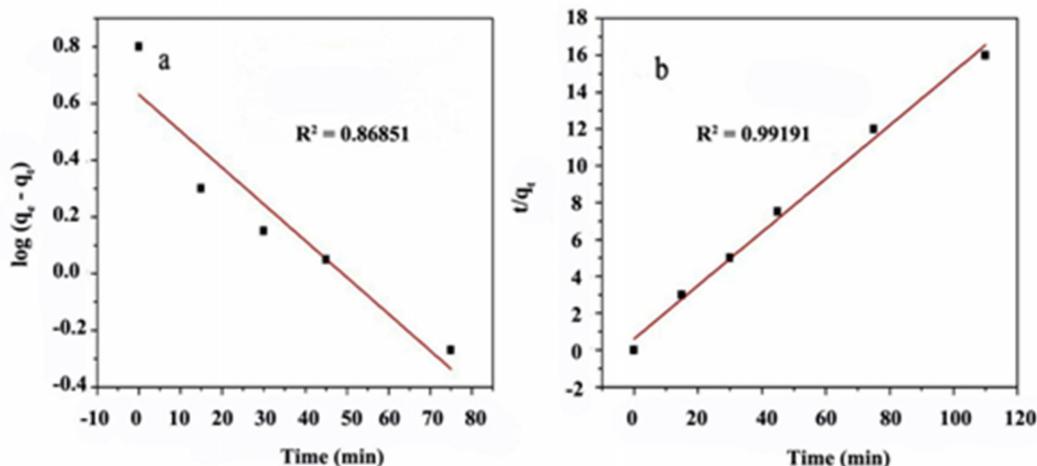


Figure 9. Adsorption kinetic for adsorption of Congo red on NiO₈₀₀ (a) Pseudo-first order and (b) Pseudo-second order.

$$1/q_e = 1/q_m + 1/K_L q_m 1/C_e \tag{6}$$

Where C_e (mg/L), q_e (mg/g) and q_m (mg/g) are the concentration and the amount of Congo red at equilibrium, adsorbed and the theoretical maximum adsorption capacity at equilibrium corresponding to monolayer coverage on NiO₈₀₀, respectively. K_L (L/mg) is the Langmuir isotherm constant related to the energy of adsorption, respectively which can be determined from the linear plot of $1/C_e$ versus $1/q_e$. The adsorption isotherms of Congo red on NiO₈₀₀ are shown in Fig.7.

The adsorption of Congo red on NiO₈₀₀ exhibits better fit to Freundlich equation by giving greater R^2 value (Table 1). This adsorptive behavior indicates that there are various active sites on NiO₈₀₀. As such, it can be concluded that adsorption takes place on a heterogeneous surface.

Adsorption kinetic study

In order to investigate the adsorption process of Congo red on the NiO₈₀₀, pseudo-first order and pseudo second-order kinetics were experimented. Pseudo-first order equation 7 is widely used for the adsorption of an adsorbant from an aqueous solution [39].

$$dq_t/dt = k_1(q_e - q_t) \tag{7}$$

Where q_e and q_t (mg/g) are adsorbed dye at equilibrium and time t , respectively. By integration, it rearranges to equation 8.

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \tag{8}$$

The pseudo-first order rate constant k_1 (min⁻¹) was calculated as the slope of plot $\log(q_e - q_t)$ against t . The pseudo second-order kinetic model (equation

Table 1. Isotherm data value of the fitted Freundlich and Langmuir model.

Langmuir	
q_m (mg/g)	10.9565
K_L (l/mg)	0.904
R^2	0.96615
Freundlich	
K_F (mg/g (mg/l) ^{-1/n})	8.852
n	3.427
R^2	0.9911

9) its integrated form (equation 10) were represented by Ho and McKay [40].

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (9)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (10)$$

The q_e and k_2 can be obtained by linear plot of t/q_t versus t .

The pseudo-first order and second order kinetics of Congo red adsorption on NiO₈₀₀ are shown in Fig. 8. The calculated kinetic parameters show that the mechanism follows Pseudo-second order model with extremely high linearity ($R^2 = 0.99191$).

The best-fit to the pseudo-second order kinetics indicates that the adsorption mechanism depends on both adsorbed dye and adsorbent [41].

To the best of our knowledge, many catalysts have been used for adsorption and photodegradation of organic pollutants, but there are few reports using NiO nanoparticles as photodegradation catalyst. Among various methods for preparation of NiO nanoparticles, the hydrothermal method has more advantages such as simple process, easier to obtain high purity products and low cost. Hence, it is quite promising and easy to use for industrial applications.

In summary, The hydrothermal synthesis of Ni-chitosan hybrid and its use as precursor for the synthesis of NiO₈₀₀ and NiO₉₀₀ was described. It was found that NiO₈₀₀ is active for adsorption of Congo red and the kinetics as well as adsorption isotherms were fitted by pseudo-second order and Freundlich equation, respectively. Complete mineralization reactions of methylene blue and Congo red dyes can be effectively photo-catalyzed by NiO₉₀₀ nanoparticles under UV radiations. The photodegradation kinetic of both dyes with NiO₉₀₀ were proven to follow the first order.

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