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P-type semiconducting NiO nanoparticles synthesis and its photocatalytic activity

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ABSTRACT

Nickel oxide (NiO) nano-size powder is synthesized using nickel (II) acetate tetrahydrate, sodium lauryl sulfate (SLS) and ammonia as precursors. Applied surfactant is anionic surfactant. The sample was characterized by FT-IR, X-ray diffraction (XRD), scanning electron microscopy (SEM). The results obtained confirm the presence of nickel oxide nano-powders produced during chemical precipitation. Evaluation of the catalytic activity of developed nano-NiO particles were carried out using ultraviolet visible spectra. The uv-vis spectra obtained after ultraviolet irradiation in the presence of nickel oxide can indicate the degradation of tetracycline (TC) and dye Acid red -18 (ponceau 4R). The prepared NiO exhibits that 75% of Acid red -18 has been eliminated after 10 min. The results indicate that optimum concentration of NiO catalyst and the best pH for the degradation of AR were 0.5 g L^{-1} and pH 7, respectively. The best TC degradation results were obtained with 2 g L^{-1}of the photocatalyst at pH 11.

*Keywords*: Ammonia precipitation, NiO, Tetracycline, Ponceau 4R, Catalytic activity.

1. Introduction

Nickel oxide (NiO), a p-type oxide semiconductor is an important transition metal oxide which exhibits a wide band gap of 3.6–4.0 eV [1]. NiO has attracted a considerable attention as a promising candidate for use in optoelectronic industry. This is basically due to its inherent potential properties which make it a useful material in electrochromic devices, ultraviolet photodetectors and gas sensors [2–4]. Nanometer sized nickel oxide materials has received great attention in research and various application purposes. The nanomaterial system also serves as an alternative material for energy applications, such as p-type semiconductor material for solar cells, electrochemical capacitors, photocatalyst, smart windows and organic light emitting diodes [5,6]. Nanostructured NiO materials with different morphologies have been prepared via various methods, such as sol–gel, hydrothermal, hard template, electrodeposition and microwave-assisted synthesis [7-14]. Zhang *et al.* recently developed NiO slices or nanocrystals using hydrothermal method [15].

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Lu *et al.* fabricated NiO nanosheets using Nickel hydroxide precursor [16]. Textile processing is one of the most important industries in the world employing various organic chemicals (dyes) depending on the nature of raw material and products that makes the environment challenge for textile industry not only as liquid waste but also in its chemical composition [17]. These chemicals are different types of enzymes, detergents, dyes, sodas, salts and acid [18,19]. The presence of these compounds in industrial wastewater and the discharge of textile wastewater, force us to look for alternative process to achieve it effective elimination of the contaminated water. Also, the introduction of antibiotics residual into environment through various sources can lead to serious environmental problems including ecological and human health damages [20]. In general, advanced oxidation processes (AOPs) are the most efficient technology for degradation of various refractory pollutants in aqueous solutions and, during the last few decades, have been widely applied for removal of many organic pollutants [21-23]. The heterogeneous photocatalytic oxidation process has been applied to decompose dirty, hazardous, bad smelling or toxic materials produced in daily life and the global

environment. Nezamzadeh-Ejhieh *et al.* reported on the preparation of supported PbS–CdS onto clinoptilolite and its photocatalytic activity for degradation of a mixture of tetracycline (TC) and cephalexin (CPX) in aqueous solution [24]. NiO is a semiconductor catalyst. There are some studies related to the use of semiconductor in the photo degradation of photo stable dyes [25,26]. Photocatalytic reaction at the surface of semiconductor particles to organic synthesis is recognized as one of the most important and attractive target in field of chemistry. In this study, we proposed simple and direct method for the synthesis of highly reproducible NiO nanostructures. The other aim of the study was to investigate the degradation of tetracycline antibiotic and azo dye acid red-18 (AR) by nanosized nickel oxide under ultraviolet irradiation.
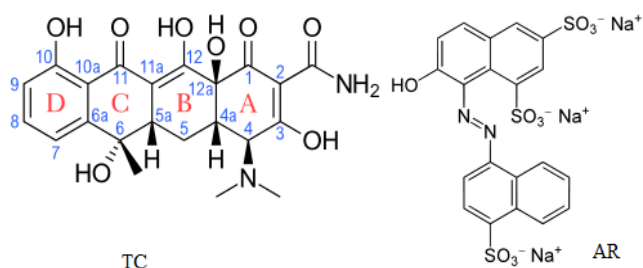
Scheme 1. Structure of AR and TC.

2. Experimental

2.1. Materials

All the compounds used were prepared from Merck company and used without further purification. The azo dye, Acid red -18, was obtained from the Kimiagostar Company (Iran). Distilled and deionized water was used in all experimental work.

2.2. Characterization

Infrared spectra were recorded on a Jasco FTIR spectrometer equipped with a liquid-nitrogen-cooled HgCdTe (MCT) detector and a KBr beam splitter. The phase X-ray diffraction (Holland Philips Xpert) was applied to determine the structural phase. The surface morphology of the product analyzed by using a field emission scanning electron microscope (Holland Philips XL30). Spectrophotometric measurements were conducted using an UV-VIS Shimadzu 2101 spectrophotometer.

2.3. Synthesis of nickel oxide nanoparticles.

First, we prepared two separate solutions; one 150 mL solution of 1M of Nickel(II) acetate tetrahydrate, then was added dropwise ammonia 25% into the solution until the pH of the system reaches to 7.5. Blue solution

is resulted. The other contains a solution of 3.0 g sodium luryl sulfate in 200mL of deionized water. Next, the former solution was added dropwise into the later. The mixed solution was stirred by magnetic stirring apparatus (1000 rpm) at room temperature. The resultant green precipitation was filtered, and then washed with deionized water and ethanol for 3–8 times and was dried at 60°C for 24 hours, then calcined at 400°C, for 3 hours . The surfactant was removed after the mentioned processes.

2.4. Catalytic activity determination

TC stock solution (20 ppm) was prepared weekly using distilled deionized water and stored in dark at 4 ºC. All experiments were performed in laboratory scale and batch system and at constant temperature (25ºC) with 100 mL of TC solution (20 ppm). After adjusting the initial pH, solution was mixed with the required amount of NiO and magnetically stirred for 30 min in the dark to ensure complete equilibration of adsorption/desorption of TC onto the NiO surface.

The decolorization experiments were carried out in the 100 ml of 20 ppm dye. The concentration of AR was determined by measuring absorption intensity at its maximum absorbance wavelength at 505 nm with a UV–Vis spectrophotometer.

The removal efficiency of TC and dye was expressed using following equation:

$$\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (1)$$

3. Results and Discussion

3.1. Structural investigations

The FT-IR spectra of nickel acetate tetrahydrate, and NiO nanopowder are shown in Fig. 1. Generally speaking, owing to their inter-atomic vibrations, metal oxides (e.g., nickel oxide) have absorption bands lower than 800 cm^{-1} [27]. The broad peak at 3661-3482 cm^{-1} are due to OH stretching vibrations of adsorbed water.
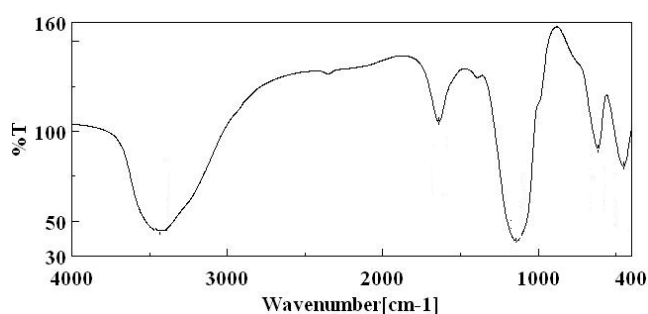

Fig. 1. The FT-IR spectra of NiO nanopowder.

A similar phenomenon is observed for the H O H bending vibration mode of water molecules located at 1630 cm−1. The strong band at 453 cm^{-1}corresponds to the banding vibration of NiO. Therefore, FT-IR spectra is in agreement with literature [28].

Fig. 2 shows the powder XRD patterns of NiO sample. All the observed sharp peaks can be ascribed to a cubic NiO phase. The peak position with 2θ values of 37.147°, 43.209°, 62.747°, 75.250° and 79.300° are indexed as (111), (200), (220), (311) and (222) planes, which are in good agreement with those of powder NiO obtained from the International Center of Diffraction Data card (JCPDS-47-1049).

The average grain size (D) from X-ray line broadening has been calculated using the Debey–Scherrer equation [28]. The mean particle size of the as synthesized NiO samples estimated from Scherrer's equation was 20 nm. Fig. 3 shows the SEM image of the product synthesized.

3.2. Catalytic activity determination.

3.2.1. Removal of tetracycline

Fig. 4 shows the removal of tetracycline. Catalytic activity of the prepared nano NiO was evaluated by the adsorption of tetracycline.

3.2.1.1. Influence of NiO concentrations on TC degradation

To investigate the effect of NiO concentration on photocatalytic efficiency, a set of experiments were done at pH 11 with different NiO concentration at range of 0.25–2 g/L. The removal efficiencies after 90-min irradiation were 7and 78 % at concentration 0.25 and 2, respectively.
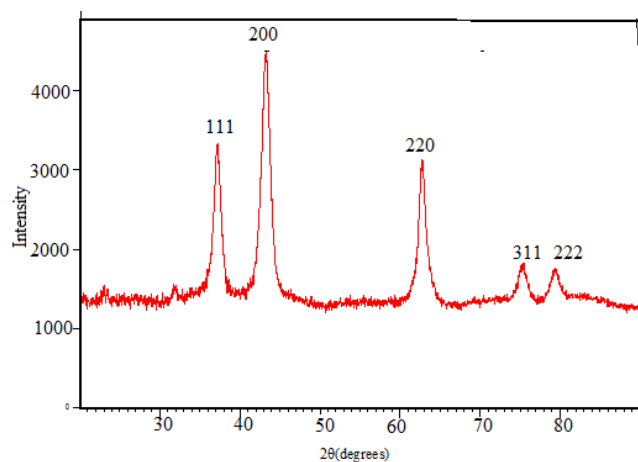
The results showed, the optimum concentration of NiO catalyst was 2 g/L(Fig. 5).

3.2.1.2. Influence of initial TC concentration

We investigated the influence of initial TC concentration on the removal efficiency of drug. Irradiation of TC solution was done with the initial drug concentrations of 25,50,75 and 100 ppm for 90 min. The photodegradation conversion of drug increases with the initial concentration 25 ppm .

3.2.1.3. Influence of initial pH on TC degradation

To investigate the effect of initial pH of the solution on the photocatalytic degradation of TC, the pH of the solution was adjusted at the range of 5-11 .The results indicate that the best pH for the degradation of TC is the basic pH value (pH = 11)
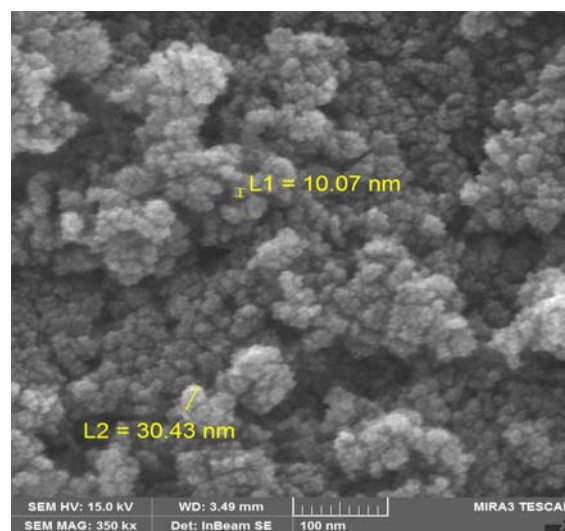

Fig. 3. SEM image of the synthesized NiO nanoparticles.

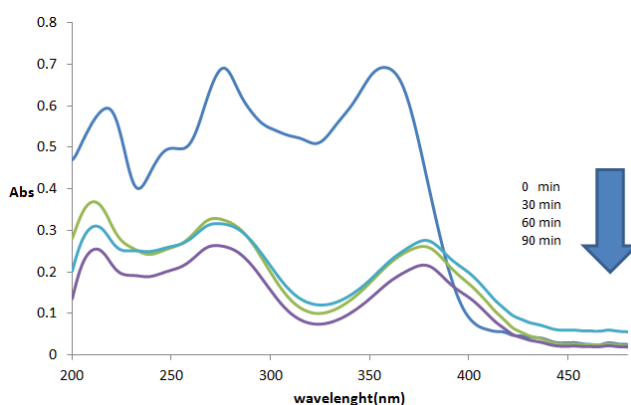**Fig. 2.** XRD pattern of the synthesized nickel oxide nanosheets.

Fig. 4. Changes of UV–Vis spectra of 20 mg/L aqueous solution of tetracycline during photocatalytic process of NiO with irradiation time 0, 30, 60, and 90 min, respectively.
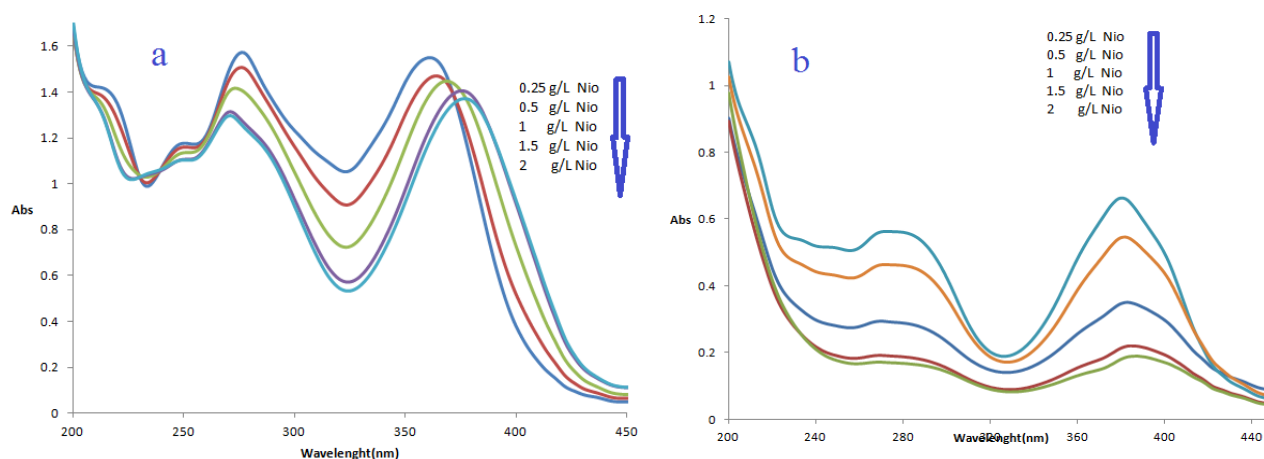
Fig. 5. Changes of UV–Vis spectra of 20 ppm aqueous solution of tetracycline during photocatalytic process of NiO with irradiation time 30 (a) and 90(b) min.

3.2.2. Removal of ponceau 4R

The results of AR degradation and removal under the optimum conditions are shown in Fig. 6.

3.2.2.1. Influence of NiO concentrations on AR degradation

To investigate the effect of NiO concentration on photocatalytic efficiency, a set of experiments were done at pH 7 with different NiO concentrations at range of 0.1–1 g/L. The results showed, the optimum concentration of NiO catalyst was 0.5 g/L. Thus, at concentration of 0.1 to 0.5 g/L, removal efficiency increased and maximum removal was observed at a concentration of 0.5 g/L (completely removal). However, with increasing concentrations to higher than 0.5 g/L, there was a downward trend, and at the

concentration of 1g/L, removal efficiency decreased to 65%.The cause of this decrease can be attributed to increased turbidity caused by the increasing of nano-NiO. Higher turbidity decreased the penetration of UV light into the solution and thus this contact with contaminant becomes less.

3.2.1.2. Influence of initial AR concentration

The effect of initial concentration of AR on photodegradation efficiency is studied. The photodegradation conversion of AR decreases with an increase in the initial concentration of AR because, when the concentration of dye is increased, it causes the dye molecules to adsorb light and the photons never reach the photo-catalyst surface, thus the photodegradation efficiency decreases.
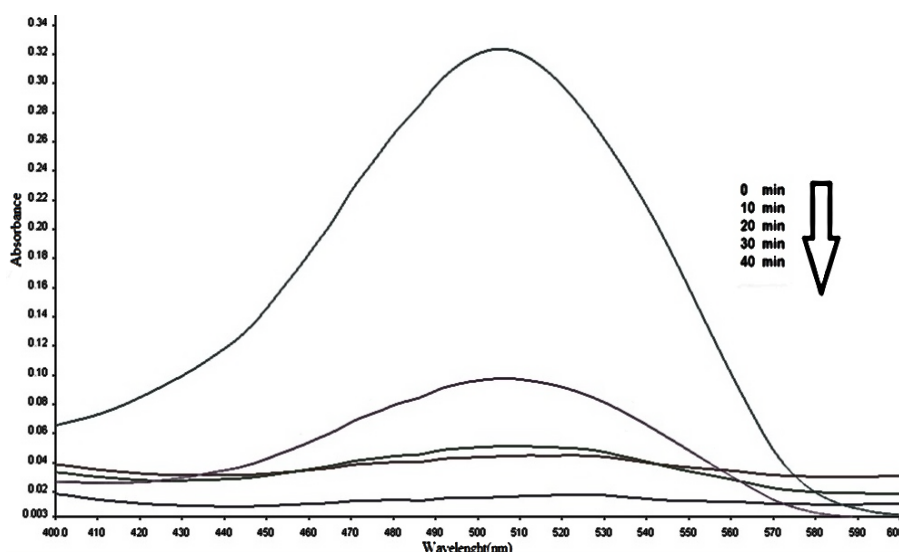

Fig. 6. Variation of the UV absorption spectra of 20 ppm aqueous solution of AR in the presence of NiO with irradiation time 0, 10, 20, 30 and 40 min, respectively.

3.2.2.3. Influence of initial pH on AR degradation

The photocatalytic degradation of dye molecule was effected by catalyst, pH and light intensity. In order to evaluate the influence of initial pH on the removal efficiency, experiments were conducted pH in the range of 4–12. The results indicate that the best pH for the degradation of AR is the neutral pH value (pH = 7). The degradation efficiency of AR increased significantly when the initial pH was increased from 4.0 to 7.0. However, the degradation efficiency of AR slowed down on further increase of the initial pH from 7.0 to 10. The reason for lower percentage degradation of dye molecules in the range of acidic pH may be that more H+ ions are available for the adsorption to mask the surface of the catalyst thus preventing the photoexcitation of semiconductor particles, thereby reducing the generation of free radicals.

Monitoring of the dye adsorption was studied by determination of the decrease in the absorbance by a UV-Vis spectrophotometer (Fig. 6). Recall that the percentage of adsorption shows the catalytic efficiency of the NiO as a function of time at 505 nm. As indicated, the prepared NiO exhibits that 75% of AR has been eliminated after 10 min.

4. Conclusions

Nano NiO powder is prepared via a simple and rapid procedure. In fact, the precipitation preparation of NiO nanoparticles is composed of two stages: the formation of meta-stable nickel precursor precipitate and the subsequent transformation of this precipitate to nano-NiO by thermal treatment. Therefore, various parameters like pH, temperature and solution concentration have to be controlled because they play significant roles in the preparation of nanoscaled NiO. NiO used as photocatalyst gives very good result and successfully improves the degradation rate of dyes. The degradation rate increased with increase in catalyst concentration because of availability of more catalyst surface area for absorption of photons and interaction of molecules of reaction with catalyst result is that number of holes and hydroxyl radicals and super oxide radicals were increased. The decrease in the degradation efficiency at concentrations above 0.5 g/L of the catalyst may be due to the reduction in the photoactive volume, thereby resulting in lower light penetration [30-32]. The photocatalytic degradation was found to be inversely affected by an increase in the concentration of AR. This could be due to the fact that with an increase in the initial concentration of AR, the number of AR molecules adsorbed on the surface of NiO increases but the number of ·OH radicals formed

on the surface of NiO is constant. Hence, photodegradation of the dye decreases. The experimental results demonstrated excellent separation of AR by NiO. Also, the presence of TC in surface water and even in ground water has been reported. A possible photocatalytic degradation pathway of TC was proposed. The degradation of TC included electron transfer, hydroxylation, open-ring reactions and cleavage of the central carbon. The UV–Vis spectra obtained before irradiation of TC show two major absorption bands at 275 and 360 nm. The absorption of TC in 360 nm was originated from aromatic rings B–D, including the developed chromophores [30]. This absorption band slowly reduced with the irradiation time, which indicated that the fragmentation of phenolic groups attached to aromatic ring B [33,34]. The decay of absorbance at 270 nm band was ascribed to the production of acylamino and hydroxyl groups [35]. It was evident that TC was degraded more quickly in basic solution than in acidic one. Similar trends were reported for its photolysis and ozone oxidation [36].

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