



Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Enhanced photocatalytic activity of nickel oxide supported on clinoptilolite nanoparticles for the photodegradation of aqueous cephalexin



Neda Ajoudanian, Alireza Nezamzadeh-Ejhih*

Department of Chemistry, Shahreza Branch, Islamic Azad University, P.O. Box 311-86145, Shahreza, Isfahan, Iran

ARTICLE INFO

Available online 14 April 2015

Keywords:

NiO semiconductor
 Nano-clinoptilolite
 Photodegradation
 Heterogeneous catalysis

ABSTRACT

NiO was incorporated into nano particles of clinoptilolite via ion exchange and calcination processes and characterized by XRD, FT-IR, DRS, BET, SEM, and TEM. The prepared catalyst was used in the photocatalytic degradation of cephalexin (CEX) using Hg-lamp irradiation and the best experimental parameters were obtained as: 0.2 g L⁻¹ of the catalyst, 50 times diluted of the initial cephalexin solution at pH 4.5 and irradiation time of 300 min. At these optimum conditions about 76% of CEX molecules can be degraded. The degradation extent was monitored by UV–vis spectroscopy and the results were confirmed by HPLC and the chemical oxygen demand (COD). The degradation efficiencies of 73.5% and 89% were respectively obtained by COD and HPLC results after the photodegradation of the proposed system at optimal conditions.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The presence of pharmaceutical ingredients in aqueous environment (pharmaceutical residues, from sewage effluents, hospital waste, animal excrements, and improper disposal of unused drugs) has raised increasing concerns in recent years [1]. It seems probable that most urban wastewater is contaminated with medicinal compounds which affects the water quality and drinking water supplies and may constitute a potential risk for the ecosystems and the human and animal welfare in the long term [2]. Most of the pharmaceuticals are only partially degraded in the environment or in wastewater treatment plants and their exposure to the environment may give rise to the production or maintenance of bacterial resistance [3]. Cephalexin (CEX), with a wide spectrum of antibacterial activity and high water solubility, is one of the most prescribed antibiotics and is produced in great

quantities [4]. The resistant bacteria may be transmitted to humans and cause disease, which is a serious challenge to the efficacy of conventional antibiotics. CEX, a kind of semisynthetic cephalosporin antibiotic, is widely used to treat infections throughout the body due to its broad antibacterial activity. Antibiotic pollution in the environment, including pollution by CEX is considered an emerging issue. However, up to now, the public has not paid enough attention to antibiotic pollution with respect to other pollutants such as dyes [5].

Heterogeneous photodegradation process, as the most famous method of advanced oxidation methods (AOPs), involving metal-oxide semiconductors has been widely used for photocatalytic environmental remediation especially wastewater decontamination, due to high photosensitivity, nontoxic nature, low cost and environment friendly features [6]. In this technique, when a semiconductor such as NiO is irradiated with photons of energy equal to or higher than its band gap, an electron can be excited from the valence band to the conduction band (e⁻) and leaving a hole in the valence band (h⁺). Finally, the produced e⁻-h⁺ pairs in aqueous solution can result

* Corresponding author. Tel.: +98 321 3292515; fax: +98 321 3291018.
 E-mail address: arne zamzadeh@iaush.ac.ir (A. Nezamzadeh-Ejhih).

to production of nonselective hydroxyl radicals ($\cdot\text{OH}$, $E^\circ=2.8\text{ V}$ versus SHE) and superoxide radical anions ($\text{O}_2\cdot^-$). The $\cdot\text{OH}$ radicals are considered to be the dominant oxidizing agent contributing to the destruction of organic pollutants to yield almost complete mineralization of organic substrates to CO_2 , H_2O , and relevant inorganic ions [7].

Nickel oxide (NiO) has been received considerable attention due to their wide range of applications in various fields, such as catalysis, electrochromic films, fuel cell electrodes and gas sensors, smart windows, electrochemical supercapacitors, battery cathodes, magnetic materials and photovoltaic devices. NiO is a p-type semiconductor with the wide band gap covering the range from 3.6 to 4.0 eV. Because of the quantum size and surface effects, NiO nanoparticles exhibit optical, catalytic, electronic and magnetic properties that are significantly different than those of bulk NiO particles [8,9].

It has been reported that supporting of semiconductors onto a suitable support, such as zeolites, significantly increases the photocatalytic efficiency of the supported semiconductors with respect to un-supported one [10–12]. Hence, for increasing the photoactivity of NiO, it was supported on clinoptilolite nano-particles (NCP) and the obtained NiO/NCP was used as an effective photocatalyst in the degradation of cephalixin under Hg lamp irradiation. To achieve the best performance, the effects of some key operating experimental parameters were studied.

2. Experimental

2.1. Materials

Natural clinoptilolite tuffs belong to the Semnan region in the north-east of Iran were purchased from Afrand Tuska Company (Isfahan-Iran). Nickel(II) chloride hexahydrate and other reagents used in the present study were obtained from Merck. Titanium dioxide P25 was from Degussa Corporation (Germany). pH of solutions was appropriately adjusted by hydrochloric acid or sodium hydroxide solution. Distilled water was used throughout the experiments. Cephalixin (CEX) pharmaceutical capsules (500 mg, Iran Daru Co.) were prepared from the local drugstores.

2.2. Preparation of nano-clinoptilolite powder and catalysts

Natural clinoptilolite tuffs were mechanically pre-treated, by crushing in an agate mortar and sieving in analytical sieves, for separating the particles $\leq 100\ \mu\text{m}$. The obtained powder was used to prepare the nanoparticles of zeolite using a planetary ball mill under controlled milling conditions such as rotational speed, ball to powder ratio as well as, grinding time, so the crystallinity retained during the size reduction process (dry milling duration 6 h). In order to remove any water soluble and magnetic impurities, the obtained nano-particles were heated at $70\ ^\circ\text{C}$ in distilled water for 8 h on a magnetic stirrer ($n=3$). In order to reach fixed water content, after filtration, washing and drying, the pretreated powder was

stored in a desiccator over saturated sodium chloride solution for 2 weeks.

To prepare the NiO/nano-clinoptilolite powders (NiO-NCP), first the Ni(II)-exchanged clinoptilolite (Ni-NCP) was obtained by adding 3 g NCP into a polyethylene bottle containing 50 mL of 0.1, 0.2, 0.4 and 0.5 mol L^{-1} Ni^{2+} aqueous solutions (as chloride salt) and the suspensions were shaken for 24 h at room temperature. At the end of the process, the Ni-NCP particles were separated by centrifuging (rpm=5000) for 15 min, re-suspended in water and re-centrifuged and the solid materials air dried during the day. Finally, the obtained Ni-NCP powders were calcined at $450\ ^\circ\text{C}$ for 16 h to obtain the NiO-NCP catalysts. Bulk NiO was also prepared in the similar method by calcination of solid nickel chloride particles at $450\ ^\circ\text{C}$.

2.3. Characterization techniques

XRD patterns of samples were recorded using a Bruker diffractometer (D8 Advance) with Ni-filtered copper radiation ($K\alpha=1.5406\ \text{\AA}$). FT-IR spectra were recorded at room temperature using a Nicolet single beam FT-IR (Impact 400D) spectrophotometer and KBr pellets. DRS spectra of samples were recorded using Shimadzu UV 3600 equipped with an integrating sphere at room temperature in the wavelength range of 200–900 nm using BaSO_4 as the reference material. The surface morphology of the samples was studied using a Philips XL30 scanning electron microscope (SEM). The microstructure of the NiO-NCP catalyst was studied using Transmission Electron Microscope (TEM) S-3500 N with Absorbed Electron Detector S-6542 (Hitachi Science System Ltd). A BET instrument (model Nova 1200) was used for studding of the surface texture properties of samples. The absorption spectra were registered on a double beam spectrophotometer (Varian Carry 100 Scan). The absorbance of samples before and after irradiation process was used to calculate the degradation extent of the pollutant. HPLC analysis of samples was performed by an Agilent Technologies 1200 Series instrument with Quaternary pump, column XDB-C18 ($L=15\ \text{cm}$, $\text{id}=4.6\ \text{mm}$ and particle size= 5 mm) and UV detector. An atomic absorption spectrometer 121 Perkin Elmer Analyst (Air- C_2H_2 , $\lambda=232\ \text{nm}$) was used for determination of nickel content of the catalysts after digesting the catalysts in HF, HClO_4 and HNO_3 acids [13]. The pH of point of zero charge of the catalyst, pH_{pzc} , was determined based on the reported procedure in literature [14,15].

2.4. Photocatalytic degradation experiments

In first step, the surface adsorption extent of the pollutant was measured in dark condition. To do this, an appropriate amount of the photocatalyst was added to a 20 mL CEX aqueous solution (50 fold diluted of original solution as the optimum concentration) to obtain a suspension containing $0.2\ \text{g L}^{-1}$ of the catalyst. The suspension was shaken at dark and sampled off in the regular time intervals and centrifuged to remove any suspended solid particles. The absorbance of the cleaned solutions before and after the adsorption process was used to determine the surface adsorption extent. Based on the

Download English Version:

<https://daneshyari.com/en/article/7119273>

Download Persian Version:

<https://daneshyari.com/article/7119273>

[Daneshyari.com](https://daneshyari.com)