



# Enhancement of the photocatalytic activity of Ferrous Oxide by doping onto the nano-clinoptilolite particles towards photodegradation of tetracycline



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## HIGHLIGHTS

- FeO supported on nano-clinoptilolite increases degrading TC in aqueous solution.
- Nano sized zeolite significantly affects on the efficiency of process.
- Results of COD confirms the results of degradation by UV–Vis.

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## ABSTRACT

Photodegradation of tetracycline (TC) aqueous solution by FeO doped onto nano-clinoptilolite particles was investigated using a high pressure Hg lamp as radiation source. Nano-particles of clinoptilolite were prepared using ball-milling of micro crystals of zeolite. The pretreated nano-particles ion exchanged in a ferrous solution and the Fe(II)-exchanged form was calcined at 450 °C. All samples were characterized by FT-IR, DRS, SEM and XRD. The degradation extent was determined via UV–Vis absorption spectroscopy and COD. Based on the study of the effect of key operating parameters, the optimal conditions were determined to reach the higher efficiency of the process. The best photocatalytic activity was obtained in presence of the catalyst containing 5.4% FeO.

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## 1. Introduction

Nowadays, the risk and fate of pharmaceuticals in the environment is an important topic regarding the overuse and misuse of antibiotics which significantly pollute surface water, seawater, groundwater and drinking water (Trautweina and Kummererc, 2012). Approximately 50% of the used antibiotics in the world are administrated in livestock and aquaculture for therapy and promotion aims. Nevertheless, most of the administrated antibiotics enter the environmental matrixes via different ways such as: direct run off and excretion of feces or urine as un-metabolized original drugs or active metabolites and degradation products (Shaojun et al., 2008; Yahiat et al., 2011). The occurrence of the cumulated antibiotics in the natural environments causes irreversible adversity by directly threatening ecosystem function and decreasing the rate of pollutants degradation. This also increases the

resistance of bacteria against drugs, spreading the antibiotic resistance genes among bacterial populations. These phenomena threaten the human's health (Shaojun et al., 2008; Yahiat et al., 2011). In general, these pollutants can enter to the environment via different sources such as: pharmaceutical origin (antibiotics, and analgesics) or dedicated to personal care while they belong to other families such as plasticizers, pesticides, and phenols (Gharbani et al., 2010). It is important to emphasize that some of these compounds are disrupting materials for the endocrine system of living beings (Escher et al., 2011). Hence removal or degradation of pharmaceutical pollutants is an important research subject.

Nowadays it is well confirmed that advanced oxidation processes (AOPs) are the best recommended technologies for the removal of different pollutants from water. Heterogeneous photocatalysis, as the most popular AOP method, has been widely used for removal of water pollutants because of its advantages especially capability of carrying out under ambient conditions and also probably complete mineralization of organic carbon into CO<sub>2</sub>, water and inorganic ions. In this process, irradiating of a semiconductor

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produces electron–hole pairs which finally produce the hydroxyl and super oxide radicals by reaction with the surrounded environment (Wols and Hofman-Caris, 2012). The used semiconductor FeO in this work has band gap energy about 2.3 eV, so permits it to absorb photons in the UV region and excite an electron from FeO ground state to the conduction band to produce the electron–hole pairs (Li et al., 2007; Mohapatra and Anand, 2010; Giri et al., 2011). FeO semiconductor is widely available, inexpensive, non-toxic and shows a relatively high chemical stability.

In recent decades, supported semiconductors onto suitable supports such as zeolites, due to their ion–exchange, molecular sieving and adsorption properties, have been widely studied (An et al., 2011; Hussain and Siddiqa, 2011; Sillanpää et al., 2011). From a practical aspect, zeolites are environmentally friendly materials (Aboul-Gheit et al., 2008). Among many natural zeolites, clinoptilolite is the most abundant of them and is widely used (Rajic et al., 2010). Zeolites have high cation-exchange capacities (CEC) (1–3 meq g<sup>-1</sup>), depending on their Si/Al ratios (Haron et al., 2007; Martinez and Perez-Pariente, 2011).

In this work, nano-particles of an Iranian natural zeolite were obtained by ball-milling mechanical method and its Fe(II)-exchanged form was calcined to obtain FeO-nanoclinoptilolite (FeO-NCP) as a heterogeneous catalyst for degradation of tetracycline pharmaceutical capsule in an aqueous solution. The use of pharmaceutical capsule is because of its better similarity to a real waste water sample.

## 2. Experimental

### 2.1. Reagents

Natural clinoptilolite tuffs were obtained from Semnan region in the north-east of Iran. Common tetracycline (C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>8</sub>) pharmaceutical 250 mg capsule was prepared from Iran Daru Company. All other salts were purchased from Merck and used as received. Distilled-water was used throughout the experiments. The pH of solutions was appropriately adjusted with sodium hydroxide or hydrochloric acid solution.

### 2.2. Preparation of the nano-zeolite and catalysts

The used natural zeolite in this work was mechanically pre-treated, by crushing in an agate mortar and sieving in analytical sieves to separate the particles with sizes less than 100 µm. Nano-particles of clinoptilolite were prepared using a planetary ball mill in a dry milling method. The milling conditions including the dry milling speed, the dry milling time and the ball-to-powder ratio were optimized to reach size reduction and crystallinity retention. The milling duration, speed and balls-to-powder ratio were respectively 6 h, 600 rpm and 4.

In order to remove the water-soluble impurities and also paramagnetic impurities, especially one entered during the ball milling step, the obtained nanoparticles were heated at 70 °C for 8 h in distilled water while the suspension was stirred magnetically for 8 h. This process was repeated 3 times to reach more purification extent. It is essential to mention that before the reflux process, some magnets were added to the aqueous powder suspension and was shaken by a magnet rod for several hours. During definite time intervals the magnets were leaved from the suspension and adsorbed magnetic particles were removed. Finally the suspension was magnetically shaken during night. In this stage, the adsorbed magnetic particles by magnets were negligible and the suspension was applied in reflux process. In order to reach fixed water content, after filtration, washing, and drying of the powder, the purified material was stored in a desiccator over saturated sodium chloride solution for 1 week. The

used catalysts were prepared by the following procedure: For ion exchange experiments, 10 g powder of NCP was added to 100 mL Fe<sup>2+</sup> solutions (as nitrate salt) with concentrations of 0.1, 0.2, 0.3 and 0.4 M. The prepared suspensions were shaken for 24 h. After filtering, the obtained solid was washed with water and dried at ambient temperature for 1 d and finally calcined at 450 °C for 12 h.

### 2.3. Characterization techniques

Nano-particles of clinoptilolite were prepared using a planetary ball mill (PM100; M100; Retsch Corporation). The amount of Ferrous in the catalysts and in the solutions was measured using atomic absorption spectrometer (AAS) (Analyst 300, Perkin Elmer Co., USA, Retsch Corporation). Infrared spectroscopy (FT-IR, model Impact D400) and UV–Vis DRS spectrophotometer (V-670, JASCO, Japan) are another instruments for characterization of samples. The structure of the raw zeolite and FeO-NCP was examined by using a diffractometer Bruker, D8ADVANCE (with X-ray tube anode and Cu Kα wavelength: 1.5406 Å). The surface morphology of samples was studied using a Philips XL30 scanning electron microscope (SEM). The microstructures of the NCP and FeO-NCP samples were recorded using Transmission Electron Microscope S-3500 N with Absorbed Electron Detector S-6542 (Hitachi Science System Ltd.). A UV–Vis spectrophotometer (Model Cary100, double beam, Australia) was used to record the absorbance of samples. COD of the solutions was performed using common COD volumetric method (Ghalya et al., 2007; Joshi et al., 2011). Total organic carbon (TOC) was measured by TOC analyzer (Shimadzu TOC-VCSN).

To determine the pH of point of zero charge, pH<sub>pzc</sub>, experiments were carried out as follows (Faria et al., 2004): The pH of a series of 50 mL 0.01 M NaCl solutions was adjusted to a value between 2 and 12 by adding HCl 0.1 M or NaOH 0.1 M solution in closed Erlenmeyer flasks. Before adjusting the pH, all solutions were degassed by purging N<sub>2</sub> gas to remove dissolved CO<sub>2</sub>. The pH of these solutions was recorded and called the initial pHs (pH<sub>i</sub>). Then, 0.2 g of the FeO-NCP was added and the suspensions were shaken for 48 h at room temperature and the final pHs (pH<sub>f</sub>) were measured. Finally, the plots of pH<sub>f</sub> versus pH<sub>i</sub> and also pH<sub>i</sub> versus pH<sub>f</sub> were constructed. In this case, plot of pH<sub>f</sub> versus pH<sub>i</sub> yield a linear line (can consider as bisector the curve) which intersect other curve. The intersection of these curves consider as pH<sub>pzc</sub> value.

### 2.4. The catalytic activity

To prepare tetracycline (TC) solution, the content of a 250 mg capsule was dissolved in water and it was shaken for 30 min and filtered in 100 mL volumetric flask and diluted with water. The obtained solution was diluted 50, 100, 200, 300 and 400 times and as shown later, the best degradation results were obtained using 100 times diluted solution.

Photodegradation experiments were performed with a photocatalytic reactor system equipped with a 50 mL Pyrex-glass cell. During the photocatalytic degradation experiments, 10 mL of 100 times diluted suspension of TC (which assigned TC solution later) containing 0.2 g L<sup>-1</sup> of FeO-NCP (optimized catalyst) at initial pH = 4.3 was irradiated with a Hg lamp (30 W). The lamp was located in 30 cm length with respect to the cell. In specific time intervals of 30, 60, 90, 120, 150 and 180 min, an aliquot suspension was withdrawn and centrifuged at 5000 rpm to remove solid particles. The degradation extent was calculated according the following formula based on the absorbance of the solution (at λ<sub>max</sub> = 355 nm) before and after irradiation.

$$\begin{aligned} \text{TC degradation \%} &= [(C_0 - C_t)/C_t] \times 100 \\ &= [(A_0 - A_t)/A_t] \times 100 \end{aligned} \quad (1)$$

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