



## Research article

## Degradation of Diclofenac by sonosynthesis of pyrite nanoparticles

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## ABSTRACT

The aim of this work is to evaluate the ability of synthesized pyrite nanoparticles (NPs) on the degradation of Diclofenac (DCF) as a model pharmaceutical pollutant. Pyrite NPs were synthesized by sonication with 20 kHz apparatus under optimum conditions. The effects of pyrite loading (0.02–0.20 g/L), DCF concentration (10–50 mg/L) and initial pH (2–10) on the degradation were investigated. The results revealed that the NPs have a great activity in the degradation of DCF with 25 mg/L concentration. A first-order kinetic model was found to match the experimental data. Complete degradation (100%) of DCF was achieved by pyrite within 3 min and 20 min in acidic and natural pH, respectively. To gain an understanding of the degradation mechanism and the role of pyrite, a UV–Vis spectrophotometer was employed to follow the DCF concentration. In addition, the Chemical Oxygen Demand (COD) and the amounts of ammonium and chloride ions verified complete degradation of DCF in both pH values. The results demonstrated that  $\text{Fe}^{2+}$  ions were generated by the pyrite surface and the hydroxyl radical ( $\text{OH}^\bullet$ ) was formed by  $\text{Fe}^{2+}$  ions through the Fenton reaction. Based on using radical scavengers in the degradation process,  $\text{OH}^\bullet$  was mainly responsible for the fast degradation of DCF. COD measurements confirmed that DCF finally degraded to further oxidized forms ( $\text{NH}_4^+$ ,  $\text{Cl}^-$ ).

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## 1. Introduction

One important group of compounds and personal care products which are regarded as a rising environmental problem, is pharmaceutical pollutants. The increase of pharmaceuticals in the surface water is due to the excretion of unused drugs from human or domestic animals (Šćepanović et al., 2012; Anquandah et al., 2013). The pharmaceuticals persistence to processes of human metabolism is so high. As a result, they can be excreted through feces or urine (Bae et al., 2013). Moreover, the pharmaceutical pollutants can reach waterways via the discharge of wastewaters that are not properly treated (Do et al., 2011). From the other point of view, it was verified that when pharmaceuticals arrive at sewage wastewater treatment plants (SWTP), they are not totally removed. Consequently, improvement of water treatment technologies is necessary to face this new sort of contamination (Dantas et al., 2010).

Diclofenac (DCF) is known as the most noticeable of pharmaceuticals in the water environment. A number of analytical ways have been illustrated in the literature for the DFC quantitative determination (Bae et al., 2013). Sungjun Bae et al., demonstrated that DCF cannot be completely removed during SWTP (only about 20–30% of elimination efficiency) and thus its concentration increases in the surface waters through sewage treatment plants STP-ejections (Bae et al., 2013).

In another attempt, the development of oxidation methods has been proposed for reduction of water pollutants (Dalmázio et al., 2008). Among numerous chemical treatment routes that have been introduced recently, the advanced oxidation process (AOPs) seems to be a hopeful and effective way for the degradation of pharmaceuticals in a water environment. In these processes hydroxyl radical ( $\text{OH}^\bullet$ ) is a more influential oxidant in comparison with other ones. Among AOPs, Fenton oxidation route has several superiorities such as simplicity of operation, cost effectiveness, and efficient degradation of organic resistance contaminants (Manu, 2012).

The degradation of DCF in aqueous solutions has been reported by several authors: pyrite/Fenton (Bae et al., 2013), Fenton (Manu, 2012),  $\text{O}_3$ ,  $\text{UV}/\text{H}_2\text{O}_2$ , solar UV-Fenton,  $\text{O}_3/\text{UV}/\text{sonolysis}$  (Vogna et al., 2004; Ziyilan and Ince, 2013),  $\text{UV}/\text{TiO}_2$  (Rizzo et al., 2009;

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Czech and Rubinowska, 2013), TiO<sub>2</sub> (Calza et al., 2006), UV/TiO<sub>2</sub>/O<sub>3</sub> (Vogna et al., 2004), simulated sunlight (Zhang et al., 2011), photo-Fenton (Pérez-Estrada et al., 2005), TiO<sub>2</sub>/ZnO/Fe-ZnO/US (Madhavan et al., 2010), sonolysis/TiO<sub>2</sub>/SnO<sub>2</sub>/SiO<sub>2</sub> (Hartmann et al., 2008), zero-valent iron/sonocatalytic (Ziylan et al., 2013), molecularly imprinted polymer (MIP)/UV (Mohammad, et al., 2011), hybrid photolysis-DCMD/UV (Mozia et al., 2013), sonolysis (Naddeo et al., 2010), sonolysis + O<sub>3</sub> (Naddeo et al., 2012), TiO<sub>2</sub>, ZnO and Ag-doped TiO<sub>2</sub> (Dewoolkar Karan and Jayaram Radha), UV-A/TiO<sub>2</sub> (Achilleos et al., 2010), homogeneous or heterogeneous with H<sub>2</sub>O<sub>2</sub>/UV (Trapido et al., 2012), and homogeneous/heterogeneous sonolysis (Güyer and Ince, 2011). However, the classic Fenton oxidation of DCF has been described more extensively in the scientific literature.

The classic Fenton reaction as catalyzed by means of soluble Fe<sup>2+</sup>, however, has some vital limitations such as the rapid precipitation of Fe(OH)<sub>3</sub> and competition in consumption of hydroxyl radicals with pollutants. For these reasons, the reaction needs to be done at low pH so that considerable amounts of sludge would not be produced (Hofmann et al., 2007).

Pyrite is one of the most available iron sulfur inorganic compounds in nature. There are many applications for pyrite as a heterogeneous catalyst in degradation of pollutants by the Fenton reaction (Mozia et al., 2013).

Up to now, the pyrite Fenton method was utilized by many researchers for the oxidative degradation of organic contaminants. For example; DCF was degraded by J. Hofmann et al. They used various catalysts such as mixed metal oxides as heterogeneous catalysts. By means of the best catalyst, they degraded DCF in 40 min (Hofmann et al., 2007). Pyrite performance was investigated by some researchers. Based on studies of Weerasooriya and Dharmasena, the S<sup>2-</sup> site of pyrite generates electrons that can degrade trichloroethylene (TCE) (Weerasooriya and Dharmasena, 2001). Y. Zhang et al. used a Fenton reaction catalyzed by natural low-cost heterogeneous pyrite to degrade nitrobenzene. The results showed that 80% of the nitrobenzene was degraded by the pyrite Fenton system and the degradation proceeds continuously for 5 h (Zhang et al., 2014). Other researchers eliminated CFCs (Hinsby et al., 2007), anthraquinone dye reactive blue 4 (RB4) (Becelic-Tomin et al., 2014) and other pollutants by a pyrite Fenton system in different conditions and its efficiency sometimes compared with classic Fenton system (Cohn et al., 2006; Sebol et al., 2007; Che and Lee, 2011; Brito Benetoli et al., 2012).

Pyrite was selected for two reasons: (i) pyrite is abundant in natural environments (ii) it demonstrates dual surface properties of hydrophilicity and hydrophobicity, in media with different pH values; as a result pyrite can influence various compounds with different surface characteristics (Zhang et al., 2014).

Until now, numerous works have focused on the removal of the medicinal pollutant (DCF) using catalysts and photocatalysts. However, other added components such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or light have been employed in all published works. For example, the best study that has been carried out recently is DCF removal by natural pyrite micro particles in the presence of added H<sub>2</sub>O<sub>2</sub>. In that effort, pyrite and H<sub>2</sub>O<sub>2</sub> act as a Fenton reagent. In this research, the DCF has been removed completely after 2 min and mineralized totally after 5 min. However, the presence of H<sub>2</sub>O<sub>2</sub> in water as a strong oxidant is harmful. The novelty of this present paper is that we used synthesized pyrite NPs as catalyst and did not add H<sub>2</sub>O<sub>2</sub>. It was concluded that synthesized pyrite NPs demonstrated high efficiency for DCF degradation because of the unique characteristics of nano pyrite particles, namely elevated purity and uniform phase. The results revealed that the required time for complete degradation of DCF using this catalyst is 3 min. In addition, the mineralization was completed after 4 min and proved using a COD test. Besides, DCF degradation was compared in acidic

and inherent pH.

In the present work, various parameters such as pH, DCF concentration and catalyst dosage were optimized simultaneously using Minitab software. Finally, the kinetic assessment of current experiments suggested that the kinetics of degradation was first order.

## 2. Experimental

### 2.1. Materials

Diclofenac sodium salt (C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>NNaO<sub>2</sub>) was donated by Mashhad Medical Science University, Pharmaceutical Faculty. Iron (II) sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O, 99%) and sodium thiosulfate pentahydrate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O, 98%), sodium acetate (NaC<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, 98%) and glacial acetic acid were supplied from Merck Company. Ethanol (99%, Merck), sodium azide (NaN<sub>3</sub>, 99%, BDH), potassium iodide (KI, 99.5%, Merck), ammonium oxalate ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 99%, BDH) and chloroform (CHCl<sub>3</sub>, 99.9%, Sigma) were used as scavengers. Ethanol and distilled water were used for the washing of the synthesized pyrite. Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, %90, BDH), iron ammonium sulfate (FAS) (Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, %99, BDH) and dense sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (Merck) were used as standards for chemical oxygen demand (COD) analysis.

### 2.2. Pyrite synthesis

In outset, FeSO<sub>4</sub>·7H<sub>2</sub>O and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O were mixed with each other in a classical cell with molar ratio of 1:6. Then, ethanol was added as dispersant to the cell contents. The cell was sealed and degassed using Argon gas for 15 min. For conducting the experiment at the desired temperature (70 °C), the cell was equipped with circulator. After that, ultrasound with acoustic amplitude of 70% was applied to the heterogeneous mixture for 10 min. The cell was reduced to room temperature and finally the produced black precipitate was washed with ethanol and distilled water and dried at 80 °C for 4 h in a vacuum oven.

### 2.3. Analysis

X-ray diffraction patterns were determined with a Bruker-axs, D8 Advance model using monochromatized Cu K $\alpha$  radiation ( $k = 1.5406 \text{ \AA}$ ) at a scanning rate of 0.05°/s, and a wide range angle ( $2\theta = 20\text{--}60$ ). The morphology and particle size were investigated by TEM (model: Philips CM120 120 kV). Measurements of the pH were made with 827 pH lab,  $\Omega$  metrohm, Swiss made. In order to monitor the DCF concentration, UV–Vis spectrophotometer (Unico 2800 UV/VIS) was used. The total Fe (Fe<sup>2+</sup> + Fe<sup>3+</sup>) was measured by atomic absorption/ flame emission spectrophotometry (AA-670) and Fe<sup>2+</sup> ion was determined with phenanthroline agent by UV–Vis spectrophotometer. Also chloride (Cl<sup>-</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>) ions were evaluated by potentiometric method (AZ8306 model) and spectrophotometer, DR 5000, HACH German model, respectively.

### 2.4. Degradation of DCF

Firstly, a stock solution of DCF with concentration of 50 mg/L was prepared. This solution was utilized for making solutions with lower concentrations in order to calibrate the concentration of DCF at pH = 3 and at the normal pH of DCF (about 6.5). The normal pH of DCF solution was decreased to pH = 4, when pyrite was added. At pH = 4, DCF structure is almost in its anionic form and was not precipitated. Therefore no adjustment in inherent pH by buffer was necessary. The pH of another solution (50 mg/L) was adjusted to 3

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