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Research article

Preparation of magnetite nanoparticles by high-energy planetary ball mill and its application for ciprofloxacin degradation through heterogeneous Fenton process

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ABSTRACT

In this study, the heterogeneous Fenton oxidation of ciprofloxacin (CIP) in an aqueous solution was examined over the nano-sized magnetite (Fe_3O_4) as a catalyst supplied through high-energy planetary ball milling process. To characterize the magnetite samples after and before ball milling operation, the X-ray diffraction (XRD), High-resolution scanning electron microscopy (HR-SEM), energy-dispersive X-ray spectroscopy (EDX), Brunauer-Emmett-Teller (BET) and Fourier transform infrared spectroscopy (FTIR) analysis were applied. The catalytic properties of the magnetite were considerably improved because of the enhancement in its physical properties, resulted from milling process. The findings also indicated that 6 h ball-milled magnetite demonstrated better properties for elimination of CIP of about 89% following 120 min reaction at optimal conditions of H_2O_2 12 mM, Fe_3O_4 1.75 g L^{-1}, CIP 10 mg L^{-1} and pH 3.0. The effects of various operational parameters, including the initial pH of the solution, H_2O_2 initial concentration, catalyst dosage, milling time and CIP initial concentration was investigated. Application of organic and inorganic scavengers considerably decreased the CIP removal efficiency. Correspondingly, with respect to the leached iron values at pH 3, it was concluded that CIP elimination was mainly occurred through heterogeneous Fenton procedure. This process included the adsorption and oxidation phases in which the hydroxyl radicals (*OH) played a significant role. GC-MS analysis was used for recording of the generated intermediates of the CIP removal in the course of heterogeneous Fenton process.

1. Introduction

During the recent decades, many researchers have focused on developing efficient methods of eliminating the pharmaceutical compounds from wastewaters because of their omnipresent dispersion in the environment, influence and toxic risk potential on the living organisms and the ecosystem, as a whole (Hassani et al., 2017a; Xiong et al., 2017). The antibiotic-resistant bacteria have already been developed as a result of antibiotics discharged into the environment from numerous sources including the human being and livestock. The transportation of such bacteria into the water-bodies, can spoil the quality of water and cause serious problems (Chang et al., 2010), thus leading to severe threat to living ecosystem (Lima et al., 2017). Ciprofloxacin (CIP), a derivative of the fluoroquinolone antibiotics, has extensive application for human

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and livestock treatment (Hassani et al., 2016). Nevertheless, the residues of CIP antibiotic, even in low concentrations, could entail critical problems, threatening the people health and aquatic ecosystems (Diao et al., 2017; Hassani et al., 2015). Hence, the efficient treatment of sewages containing CIP is of great importance concerning the human health because of their lower biodegradability and bacterial resistance (Xu et al., 2016). Application of green treatment technologies such as Advanced Oxidation Processes (AOPs) can greatly help for degradation of many organic pollutants (Acisli et al., 2017b; Khataee et al., 2014; Modirshahla et al., 2012). Fenton process, as a green treatment technology, produces highly reactive $^{\bullet}OH$ radicals via the catalytic decomposition of H_2O_2 by Fe^{2+}. This process is extensively employed for degradation of organic pollutants owing to its low cost, simplicity of the procedure and efficiency for oxidation of refractory compounds (Acisli et al., 2017b; Hassani et al., 2018). In order to achieve desirable results, the operational conditions of the Fenton reactions are of principal importance. In addition to the central roles played by the concentration of H_2O_2 and Fe^{2+} in the oxidation reactions, the precipitation of $Fe(OH)_3$ is controlled by the pH of the solution (Guo et al., 2017; Li et al., 2016; Xu et al., 2017). However, the separation of catalyst from the treated wastewater is often challenging. Taking into account all these concerns, the improvement in $^{\bullet}OH$ production and minimizing the ferric sludge amount would be possible through the application of heterogeneous Fenton process (Acisli et al., 2017b; Lima et al., 2017). From the literature, numerous studies have been conducted for developing effective heterogeneous Fenton catalysts using magnetite (Acisli et al., 2017b), iron sludge-graphene (Fe-G) composite (Guo et al., 2017), novel hybrid Cu-Mn-O catalyst (Zhang et al., 2017), FeS_2/SiO_2 (Diao et al., 2017) and chitosan-Fe catalyst (CS-Fe) (Gao et al., 2016) for catalytic generation of $^{\bullet}OH$ in Fenton process.

Magnetite (Fe_3O_4) is broadly employed in Fenton reaction due to structural Fe^{2+} cations that contributes significantly in hydroxyl radicals' generation by reacting with hydrogen peroxide. Moreover, Fe_3O_4 is highly soluble in aqueous medium, financially affordable, non-toxic and readily recyclable. Accordingly, Fe_3O_4 is a valuable candidate to be used as heterogeneous catalyst in Fenton reaction (Hou et al., 2016). Magnetite nanoparticles were used in this study as the catalyst and CIP was selected as target recalcitrant contaminant. It is believed that the nanostructured and well-dispersed catalyst particles offer both more number of active sites and less resistance to mass transfer (Acisli et al., 2017b). A variety of chemical and hydrothermal methods have recently been utilized to generate nanostructured magnetite (Acisli et al., 2017b; Jung et al., 2008). The methods, however, usually employ toxic and costly chemicals as reactants, complex devices, or high-energy cost (Jung et al., 2008). Recently, a simple and cost-effective substitute, namely mechanical ball milling through high-energy planetary ball mill has been used for the production of nanoparticles rather than the established synthesis procedures (Ambika et al., 2016; Dindarsafa et al., 2017; Naghdi et al., 2017). Numerous advantages such as a facilitated procedure, duplicability, cost-effectiveness of the operation, and production of large quantities of nanoparticles have led to the selection of mechanical ball milling (Dindarsafa et al., 2017; Khataee et al., 2017a). From an economical point of view, this method is highly suitable for sizable industrial manufactures. Therefore, in this study, we used the high-energy planetary ball milling process to produce nano-sized magnetite catalyst. The influence of operational factors including the catalyst dosage, the initial CIP concentration, initial solution pH, H_2O_2 initial concentration, the presence of various radical scavengers and the milling time were investigated. Ultimately, the CIP removal intermediates were determined using as gas chromatography coupled mass spectrometry (GC-MS). The main objective of this study was to determine the efficiency of heterogeneous Fenton process catalyzed by the magnetite nanoparticles obtained by high-energy planetary ball mill for ciprofloxacin removal from polluted water and identify the best removal condition.

2. Experimental procedure

2.1. Materials

In the present study, Sigma-Aldrich Co. (St. Louis, MO, USA) supplied ciprofloxacin (98%). The characteristics and chemical structure of ciprofloxacin are shown in Table 1. Merck Co. (Germany) provided the rest of the substances and reagents. In all the experiments, distilled water was used. With jaw and cone crushers, the collected magnetite samples (Özkoyuncu Mining Co., Turkey) were ground and sieved (0.5–2 cm). In addition, in order to reduce the samples to 0.425 μm, rod milling and ball milling were used. In the final step, to obtain magnetite particles in nanosized, at different intervals (2, 4, and 6 h), a high-energy planetary ball mill (LB 200, Turkey) was employed at 900 rpm.

2.2. Characterization of the catalyst

X-ray diffraction (XRD) patterns were recorded on a Panalytical Empyrean diffractometer with Cu-Kα radiation (40 kV, 30 mA, 1.54051 Å) over a 2θ range from 15° to 80° at room temperature. High-resolution scanning electron microscope (HR-SEM) and the associated energy dispersive X-ray spectroscopy (EDX) were obtained by using Zeiss Sigma 300 equipped with EDAX analyzer (Zeiss, Germany). Fourier transform infrared (FTIR) spectra were recorded on a Tensor 27, Bruker (Germany), in a wavenumber range of 4000–400 cm^{-1} by using the KBr pellet technique. The textural properties of the samples were determined using N_2 adsorption–desorption isotherms at 77 K on a Gemini 2385 nitrogen adsorption apparatus (Micromeritics Instruments, USA); using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods.

2.3. Heterogeneous Fenton process

Heterogeneous Fenton oxidation experiments of CIP were performed in glass round-bottom flasks (100 mL) in a thermostatic shaker (Julabo SW22, Germany) with controlled temperature, time, and stirring speed. In each run, 100 mL containing certain concentrations of CIP solution and magnetite was used, and the reaction was initiated with the addition of H_2O_2. The effect of magnetite dosage (1.0–2.5 g L^{-1}), concentration of H_2O_2 (2.4–30 mM), pH (3–11), initial concentration of CIP (5–20 mg L^{-1}), and ball milling time of magnetite (2, 4 and 6 h) on CIP removal were studied to determine the optimum conditions for the oxidation of CIP. NaOH or HCl (0.1 M) was used to adjust the primary pH of solution; pH was measured with a pH meter (Mettler Toledo, China), which was standardized using buffers prior to each measurement. At the end of each reaction run, the treated solution was centrifuged for 5 min at 6000 min^{-1} (Hettich EBA 20, Germany). To determine CIP removal efficiency, the residual concentration of CIP was measured using Varian Cary 100 UV–vis spectrophotometer (Australia) at the maximum wavelength of 276 nm. In order to estimate the removal efficiency, we used the formula: $[(A_0\text{-}A_t)/A_0] \times 100\%$, where A_0 and A_t show the CIP absorbance before and after removal process. To estimate the Fenton process mechanism, the various organic and inorganic ions, acting as scavengers, were added to the reaction solution. The molar ratio of scavengers to CIP of 1:1 was tested. The concentration of the dissolved iron in the solution depending on the initial solution pH was measured using an Inductively Coupled