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Natural soil mediated photo Fenton-like processes in treatment of pharmaceuticals: Batch and continuous approach

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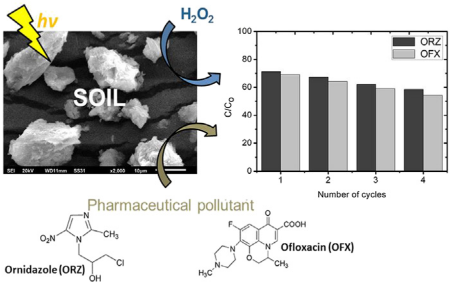
HIGHLIGHTS

- Potential viability of naturally available soil as catalyst in photo-Fenton-like processes.
- Improved degradation efficiency with batch and continuous mode experiments for the removal of ofloxacin and ornidazole.
- Leaching experiments suggested the simultaneous occurrence of homogeneous and heterogeneous reactions.
- Soil beads were effectively reused for four times with ≈13% reduction in degradation efficiency for both the pharmaceuticals.
- Enhanced activity in solar light when compared to UV-A and UV-B.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper manifests the potential viability of soil as a cost-free catalyst in photo-Fenton-like processes for treating pharmaceuticals at large scale. Naturally available soil without any cost intensive modification was utilized as a catalyst to degrade pharmaceuticals, specifically ornidazole (ORZ) and ofloxacin (OFX). Soil was characterized and found enriched with various iron oxides like hematite, magnetite, goethite, pyrite and wustite, which contributes toward enhanced dissolution of Fe^{3+} than Fe^{2+} in the aqueous solution resulting in augmented rate of photo-Fenton reaction. The leached iron concentration in solution was detected during the course of experiments. The degradation of ORZ and OFX was assessed in solar induced batch experiments using H_2O_2 as oxidant and 95% ORZ and 92% OFX removal was achieved. Elevated efficiencies were achieved due to Fe^{2+}/Fe^{3+} cycling, producing more hydroxyl radical leading to the existence of homogeneous and heterogeneous reactions simultaneously. The removal efficiency of solar photo-Fenton like process was also compared to photo-Fenton process with different irradiation sources (UV-A and UV-B) and were statistically analysed. Continuous-scale studies were conducted employing soil either in the form of soil beads or as a thin layer spread on the surface of baffled reactor. Soil beads were found to have satisfactory reusability and stability. 84 and 79% degradation of ORZ and OFX was achieved using soil as thin layer while with soil beads 71 and 68%

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degradation, respectively. HPLC and TOC study confirmed the efficient removal of both the compounds. Toxicity assessment demonstrates the inexistence of toxic intermediates during the reaction.

1. Introduction

Pharmaceutical industries have become widespread due to the rapidly expanding needs of their various products for the medication of human beings and animals (Chelliapan et al., 2006). Because of the high usage and consumption rates for humans and veterinary medicine, antibiotics, from all the pharmaceutical compounds are considered most significant (Elmolla and Chaudhuri, 2010; Benitez et al., 2011). Worldwide, presence of antibiotics has been detected in the aquatic environment (Jeong et al., 2010). ORZ is one of the widely used antibacterial/antiprotozoal drug for human and veterinary treatment (Zhao et al., 2012). OFX is used for treating bacterial infections and respiratory diseases (Oliphant and Green, 2002; Noel, 2009). Due to the mode of excretion, presence of these drugs has been detected in wastewater, ground water, surface water, in soil and sediments of river bed (Nikolaou et al., 2007; Dinh et al., 2011). Existence of even trace amount of antibiotics in the wastewater leads to chronic toxicity and development of antibiotic resistant bacteria (Walter and Vennes, 1985). Conventional techniques involving biological treatment used at sewage treatment plants (STPs) are ineffective in removing pharmaceuticals due to the low biodegradability and stable chemical structure of pharmaceuticals, so it requires more effective treatment technology (Klavarioti et al., 2009; De la Cruz et al., 2012; Epold et al., 2012; De la Cruz et al., 2013; Bhatia and Dhir, 2016). Advanced Oxidation Processes (AOPs) offers rapid and emphatic alternative treatments for enormous toxic and refractory contaminants in wastewaters. Among various AOPs, Fenton reagent ($Fe^{2+} + H_2O_2$) has gained attention because of its better mass transfer, mild operating conditions and lower costs (Pignatello et al., 1999). Hydrogen peroxide is a reactive oxidant preferable to chlorine or ozone based oxidants however, addition of ferrous salt as Fe ions leads to generation of sludge containing iron that require expensive treatment. Moreover, intermediate oxidation products and phosphate anions may deactivate the process by forming complex with Fe ions (Deng et al., 2008). Currently, attention is gained over using iron oxides as Fe ion source in Fenton-like processes and it is generally believed that the natural metal oxides, especially those of iron, may take part in decomposition of hydrogen peroxide and oxidation of contaminants limiting the problems associated with classical Fenton system (Centi et al., 2000; Lee et al., 2009; Dulova et al., 2011; González-Bahamón et al., 2011; Lin et al., 2015; Mirzaei et al., 2017). In photo-Fenton-like processes, efficiency increases via photo reduction of Fe^{3+} to Fe^{2+} as well as through photochemical reactions of Fe^{3+}-complexes, since the reduction of ferric ions by hydrogen peroxide is slow and ineffective in non-irradiated systems (Tokumura et al., 2011). Comprehensive studies of Fenton-like systems have primarily focused on catalysing H_2O_2 decomposition in the presence of various iron oxides like pyrite (Liu et al., 2015), hematite (Chan et al., 2015), magnetite (Marco et al., 2014), goethite (Zamiri et al., 2014), lepidocrocite (Rufen et al., 2015) and ferromagnetic nanoparticles (Xu and Wand, 2012). These systems may include both homogeneous and heterogeneous reactions as described by a modified Haber- Weiss mechanism (Kitajima et al., 1978). In order to obtain desired degradation of pollutants, iron oxides are often prepared artificially, which further makes the process cost intensive. Hence, there is need to explore naturally available, low cost minerals as an alternative iron source to enhance the feasibility of photo-Fenton-like system and its practical application at large scale under solar irradiation in a cost effective manner. Soil, a natural resource, is present in abundant amount on the earth's crust. Among various types, red soil represents the third largest soil group of India covering an area of about 3.5×10^5 ha (10.6% of the total geographical area of the country). Red colour of the soil is attributed to its high content of iron oxides however; it is poor in phosphate, nitrogen and organic matter (Bhattacharyya et al., 2007). Due to the presence of high contents of iron oxides, the use of environmentally friendly and economical applications of soil is of considerable interest in photo-Fenton like processes. Literature reveals very less information over utilization of soil as a catalyst in photo-Fenton-like processes to degrade pollutants. The present work is first reported study of this kind utilizing naturally available soil without any modification as a catalyst in photo-Fenton-like process for treating ORZ and OFX in a batch and continuous system. In batch system, the effect of parameters like soil dosage, hydrogen peroxide concentration, pH, irradiation sources (UV-A, UV-B and solar) and iron leaching on the degradation of ORZ and OFX were investigated. In continuous system, feasibility of soil was investigated in photo-Fenton-like degradation of OFX and ORZ in a baffled reactor. For continuous experiment, soil was used in immobilized mode in two ways viz. spreading soil as a thin layer on the bottom surface of the reactor as well as in the form of small beads and the degradation efficacy was assessed for both the pharmaceuticals.

2. Methodology

2.1. Chemicals and materials

Ornidazole (≥99%), Ofloxacin (≥99%), HPLC grade Methanol (≥99.9%), Acetonitrile (≥99.9%) were purchased from Sigma-Aldrich. The chemical structures along with their properties are presented in supplementary data (S1). 30% (w/v) Hydrogen peroxide, Phosphoric acid (88%), Sodium hydroxide (>99%), Hydrochloric acid (37%), Hydroxyl ammonium chloride (≥98.0%), Ferric chloride (>99%), (Ammonium acetate (≥98.0%), Acetic acid (≥96.0%), 1,10- phenolphthalein monohydrate (≥99.5%), Sulphuric acid (≥98.0%) were purchased from Merck and used as such. Soil was obtained from Warangal region in Tamil Nadu, India and washed thrice with ultra-pure water. Ultrapure water was obtained using a Milli-QTM system (Millipore) and used throughout the study.

2.2. Characterization of soil sample

The crystalline structure of soil was characterized by X-ray diffraction (XRD) using PW3050/60 XPERT-PRO diffractometer (Philips X-Ray diffractometer) with Cu Kα radiation operating at 40 mA, 45 kV and $\lambda = 0.154$ nm. Diffraction peaks were identified by applying Match 3.3.0 build 88 (Crystal Impact, Germany) processing software. For inspecting morphology of soil, Scanning electron microscopy (SEM, JEOL-JSM-6510LV) operating at an accelerating voltage of 20 kV was used. Elemental analysis was achieved by Electron diffraction spectroscopy (EDS). Assessment of specific