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Degradation studies of ciprofloxacin on a pillared iron catalyst

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Abstract

Photo-assisted Fenton mineralization of ciprofloxacin (CFX), a broad-spectrum antibiotic used in human and veterinary medicine was studied using a modified laponite clay-based Fe nanocomposite (Fe-Lap-RD) as a heterogeneous catalyst in the presence of hydrogen peroxide and UV light. The catalytic performance has been monitored in terms of CFX (0.15 mM) and total organic carbon (TOC) conversions, whereas the catalyst stability was evaluated according to the metal leached from the solid structure into the aqueous solution. The Fe-Lap-RD was characterized by X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) techniques. Further, the effects of reaction parameters such as H_2O_2 concentration, Fe-Lap-RD catalyst loading and initial solution pH on the mineralization of CFX were investigated. It was found that at the optimal reaction conditions (60 mM H_2O_2, 1.0 g L^{-1} Fe-Lap-RD, initial solution pH 3.0), complete CFX degradation and over 57% total organic carbon (TOC) removal of CFX can be achieved after 30 min reaction. In addition degradation and mineralization kinetics of CFX was also studied to obtain apparent reaction rate constants. The photo-Fenton degradation of CFX follows the pseudo-first-order kinetics. Fe-Lap-RD exhibits good catalytic activity in the photodegradation and mineralization of CFX, with negligible leaching of Fe ions from the catalyst structure.

Keywords: Fe pillared clays; Photo-Fenton; Ciprofloxacin; Heterogeneous catalyst; Mineralization

1. Introduction

Fluoroquinolones (FQs) currently represent one of the most important classes of antibiotics, on the basis of annual global sales and therapeutic versatility [1,2]. FQs are a class of synthetically produced antibiotics, active against a broad spectrum of pathogenic gram-negative and gram-positive bacteria. Consequently, they are used as the antibiotics of first choice for general bacterial infectious diseases, and its efficacies are highly appreciated. Ciprofloxacin, a common FQ, is a primary degradation product of enrofloxacin, which is used worldwide in aquaculture and agricultural applications [1,3]. Because of their continued use in both human and veterinary medicine, the environmental impact of such antibacterial agents represents a serious concern for the public health due to their potential for migration into the environment and the possible development of resistance in pathogens [4–6].

Ciprofloxacin is readily transported into the environment via discharges of wastewater and direct runoff. It has been repeatedly detected at concentrations ranging from μg L^{-1} in untreated hospital sewage [7–9], to ng L^{-1} levels in secondary wastewater effluents [10–17], and surface waters [9].

At present, most of the wastewater treatment plants are not designed to completely remove most pharmaceuticals, and consequently these compounds are released into receiving water bodies. Advanced oxidation processes (AOPs) are known as an effective method to remove non-biodegradable organic pollutants from ground-, surface- and wastewater [17,18]. Their effectiveness results from the fact that the in situ generated hydroxyl radicals are highly reactive species, able to oxidize organic molecules. The radicals are produced by combinations of ozone, hydrogen peroxide, UV radiation, ferrous ions and titanium dioxide. Numerous authors investigated the degradation of organic pollutants such as pesticides, dyes, pharmaceuticals, aromatic compounds, nitrophenols or surfactants by

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photo-Fenton oxidation [18–23]. Traditionally, the photo-assisted Fenton reaction is conducted homogeneously by irradiating a solution containing Fe^{3+} or Fe^{2+} ions and H_2O_2. The decomposition of H_2O_2 in an acidic media is catalyzed by the oxidation of Fe^{2+} to Fe^{3+}, which is subsequently photo-reduced back to Fe^{2+}. The hydroxyl radicals formed are responsible for effecting the degradation of organic compounds in the wastewater.

The major disadvantage of such a system is, reactions are to be studied at acidic $pH < 3$ and it is difficult to remove the sludge containing Fe ions after the treatment. The latter step is expensive and not economical. Extensive information exists on the attempts to find a solid support for the iron ions to eliminate its major disadvantage of homogeneous photo-Fenton process. In a number of studies the development of the heterogeneous photo-assisted Fenton catalyst such as Nafion-based catalysts [24–26] have been reported, but these materials proved to have a low catalytic activity and to be too expensive for an industrial application.

Pillared clays constitute one of the most widely studied materials among the new groups of microporous materials developed by molecular engineering. These solids, also known as cross-linked clays or pillared interlayered clays (PILCs), are obtained by exchanging the interlayer cations of layered clays with bulky inorganic polyoxocations, followed by calcinations. The intercalated polycations increase the basal spacing of the clays and, upon heating, they are converted to metal oxides clusters by dehydratation and dehydroxylation. These metal oxide clusters (named pillars), are inserted between the clay layers, yielding temperature-stable oxide pillars that permanently keep the layers apart, preventing its collapse. As a result, an interlayer space of molecular dimensions, a two-dimensional porous network, is generated [27,28]. The final pillared interlayered clays present a permanent porous network, showing a dramatic improvement in catalytic and adsorption applications [29–32].

Recently, numerous studies reported the synthesis of different smectite clay based Fe nanocomposites by pillaring methods and used them as hetero-catalysts for the photo-Fenton decoloration and mineralization of some azo-dyes pigments [29–31,33] and phenyl-urea herbicides [28,34]. In a diluted aqueous dispersion, laponite RD, model synthetic hectorite-type smectite clay, exists as discrete plates of diameter 20–30 nm. Therefore, this clay is an ideal inorganic medium to form nanometer-scale composite structures with iron oxide particulates [30], named Fe-Lap-RD. The X-ray diffraction (XRD) results revealed that the Fe-Lap-RD mainly consists of Fe_2O_3 (maghemite) crystallites and $Fe_2SiO_{10}(OH)_2$ (iron silicate hydroxide) crystallites [33].

A heterogeneous catalyst for photo-Fenton reaction with a high efficiency as well as an acceptable cost has not been fully established. Hence, there is no doubt that developing sucha catalyst has not only academic significance but also industrial applications. This type of catalyst displays a reasonable good photo-catalytic activity and negligible Fe leaching at an initial solution pH of 6.6, which is very close to neutral pH [35]. These findings enhance the feasibility of the photo-Fenton process for the treatment of wastewater, without the need to pre-adjust the solution's pH or to neutralize it at the end.

The objectives of this study are (i) to prepare laponite clay based Fe-nanocomposites by pillaring technique; (ii) to test the catalytic activity of new material as heterogeneous catalysts for the photo-Fenton degradation and mineralization of ciprofloxacin in aqueous solutions; (iii) to describe the effect of the initial pH, hydrogen peroxide concentration and Fe-Lap-RD catalyst loading on the mineralization of ciprofloxacin.

2. Materials and methods

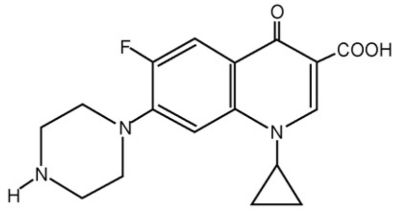
2.1. Materials

Ciprofloxacin (Fig. 1) was supplied by BioChemika, Fluka (Steinheim, Germany). *Ortho*-phosphoric acid (98%), hydrogen peroxide (30%), iron sulphate heptahydrate, sodium hydroxide, hydrochloric acid, manganese dioxide were provided by Merck (Darmstadt, Germany). All other chemicals and solvents were of the highest grade commercially available and were used as obtained. All aqueous solutions were prepared with ultrapure water from a Millipore Waters Milli-Q purification water unit (Millipore, Watford, UK).

The synthetic layered clay laponite (laponite RD) was supplied by Kremer Pigments, Germany and it was used as the starting clay material to prepare the Fe-Lap-RD nanocatalyst. Table 1 presents the chemical composition of the commercial clay supplied by the company as described above. Iron(III) nitrate nano-hydrate, received from Aldrich, was used as iron source. Sodium carbonate deca-hydrate was obtained from Fluka.

2.2. Preparation of Fe-Lap-RD nanocomposite

The Fe-Lap-RD nanocatalyst was synthesized through a reaction between a solution of iron salt and a dispersion of laponite RD clay [28,34]. For that purpose an aqueous dispersion of laponite RD was prepared by adding 2 g of clay to 100 mL water under vigorous stirring condition. Secondly, sodium carbonate was added slowly as powder into a vigorously stirred 0.2 M solution of iron nitrate such that a molar ration of 1:1 for Na^+/Fe^{3+} was established. Subsequently, the obtained solution was added into the dispersion of laponite



Ciprofloxacin
$C_{17}H_{18}FN_3O_3$
MW: 331.4

Fig. 1. The structure of ciprofloxacin [1-cyclopropyl-6-fluoro-4-oxo-7-piperazin-1-yl-qui noline-3-carboxylic acid].