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Removal of ofloxacin antibiotic using heterogeneous Fenton process over modified alginate beads

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ABSTRACT

The aim of this work is to study the heterogeneous oxidative degradation of ofloxacin antibiotic using a composite material prepared from sodium alginate and cyclohexane dinitrilo tetraacetic acid (CDTA). The characterization tests indicated the successful incorporation of metal chelator and iron. It was also demonstrated that the synthesized beads are mesoporous. The influence of several experimental parameters (*i.e.*: H_2O_2 dose, working temperature, beads loading and initial drug concentration) on the process performances was evaluated. The reaction temperature significantly affects the drug conversion efficiency. It was also observed that the synthesized material was efficient toward the target antibiotic degradation in the presence of small quantities of hydrogen peroxide. Under optimum conditions (0.05 g of granules, initial drug concentration = 10 mg/L, 25 μL of 10 mmol/L H_2O_2), conducted in a batch reaction, 94% degradation of ofloxacin was reached. The results also indicate that the composite material showed a reasonable stability; a relatively low decrease of activity after four successive runs (only 9%) and a negligible iron leaching (0.8%) have been observed. The synthesized composite material offered interesting advantages in terms of simplicity, good stability, ease of recovery from the liquid medium after use and its efficiency in the presence of low quantities of oxidant. It constitutes a good candidate in the water treatment area.

Introduction

Pharmaceutical products, especially antibiotics, are considered among the most insidious pollution sources as they are extremely harmful to the aquatic environment (Kummerer, 2009; Larsson et al., 2007; Andreozzi et al., 2003). Effluents containing such products are not efficiently treated by conventional water decontamination methods mainly because of their low concentrations. New technologies for the treatment of such molecules, compatible with the classical treatment process are actively sought. Advanced oxidation processes (AOPs) constitute a serious treatment method for effluents containing refractory, toxic and non-biodegradable materials (Gogate and Pandit, 2004; Bouafia and Alloune, 2007). The classical Fenton process constitutes a major advance in wastewater treatment (Neyens and Baeyens, 2003). Nevertheless, it suffers from major drawbacks such as the precipitation of iron hydroxide, $Fe(OH)_3$, in large quantities which represents itself a new pollution (Bautista et al., 2010). In its classical configuration, the Fenton reaction uses iron(II) as catalyst. The latter is directly added to the aqueous solution. Another possibility is the heterogeneous Fenton reactions where the catalyst is immobilized on solid supports. The process is known as catalytic wet peroxide oxidation

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(CWPO) (Gomes et al., 2010). Immobilization of metallic ions, mainly iron and copper, over different supports, such as polymers (Castro et al., 2009, 2010), activated carbons (Zazo et al., 2006; Taran et al., 2010; Santos et al., 2009), zeolites (Kondru et al., 2009; Aravindhan et al., 2006), pillared clays (Carriazo et al., 2003; Galeanoa et al., 2011; Jagtap and Ramaswamy, 2006), resins (Liou et al., 2005) and silica (Xiang et al., 2009) has been described in the literature for application in CWPO processes. Heterogeneous catalysis eliminates the need of treating the resultant sludge formed by the dissolved iron in the effluent and its precipitation (Bautista et al., 2010). Another advantage of the use of metal supported solid catalysts is the ease of separation from the reaction solution by simple filtration giving the possibility of recycling the catalytic support.

Sodium alginate is a widely abundant biocompatible, non-toxic, non-immunogenic and biodegradable polysaccharide used, associated with iron species, in CWPO processes (Dong et al., 2011; Banerjee et al., 2007; Bezbaruah et al., 2009).

In the initial experiments, iron(II) linked directly to alginate was used as catalyst. In order to improve the adhesion of metal ions to alginate polymer, the incorporation of a complexing agent is an interesting way. As a complexing model cyclohexane dinitrilo tetraacetic acid (CDTA), was used as it is a well-known metal chelator such as Fe, Mn, and Cu ions (Norkus et al., 2006; Ammann, 2002). Therefore, the aim of this work is to evaluate the possibility of using CDTA as an iron binder on the surface of alginate and to estimate the improvement of ofloxacin removal against virgin alginate gel.

Ofloxacin is an antibiotic belonging to the fluoroquinolone drugs with an antibacterial activity. This target molecule was selected as a model pollutant because of its widespread use as a human and veterinary antibacterial agent. To the best of our knowledge, no studies are available in the literature dealing with CWPO degradation of this drug.

This study deals with the applicability of alginate–CDTA as a heterogeneous Fenton support in the degradation of ofloxacin antibiotic. Alginate–CDTA–iron composite material was prepared and characterized using Fourier transform infrared spectra (FT-IR) and atomic force microscopy (AFM) analysis. The influence of various parameters related either to the solid synthesis (percentage of impregnated metal and drying duration of the solid) or to the experimental procedure (solid amount, initial drug concentration and temperature) was investigated. The possibility of iron leaching from the solid was also evaluated. Finally to judge the use of the synthesized solid in water treatment, the granules were recovered and reused several times.

1. Materials and methods

1.1. Chemicals

All used reagents were of analytical grade and used as received. Ofloxacin antibiotic (9-Fluoro-2,3-dihydro-3-methyl-10-(4-methyl-1-piperanzinyl)-7-Oxo-7 H pyrido [1,2,3-de]-1,4-benzoxazine-6-carboxylic acid), commercialized as fine pure powder, was kindly supplied by a local pharmaceutical industry with purity higher than 99%. Ammonium iron(II) sulfate (99%, Acro Organics, Belgium), silver and copper sulfate (Prolabo, France) were used as ferrous, Ag^{+} and Cu^{2+} ion source used as testing metallic ions. H_2SO_4 used for pH adjustment was obtained from Prolabo (France) and calcium chloride was used as crosslinker for alginate and was purchased from Applichem (Germany). The alginate material used is a commercial product of sodium alginate, purchased from Sigma Aldrich (Spain) and CDTA (trans-1,2 diaminocyclohexane N,N,N′,N′ tetraacetate) used for the preparation of the composite material was obtained from Fluka. An aqueous H_2O_2 solution (30%) used as oxidant and the potassium permanganate powder used for its titration were purchased from Prolabo (France). Finally, powder of sodium bicarbonate $NaHCO_3$, with purity higher than 99.7%, was supplied by Sigma Aldrich (Spain).

1.2. Methods

1.2.1. Impregnation procedure on virgin and CDTA-modified alginate

In order to prepare iron impregnated alginate (Alg/Fe), 2.5 g of sodium alginate powder was dispersed in 100 mL distilled water to form a 2.5% (W/V) alginate solution. This solution was mixed using a mechanical stirrer at room temperature until complete dissolution was achieved and a viscous solution was obtained. Then calcium alginate beads were obtained by dropping this aqueous solution into 2.5% (W/V) $CaCl_2$ solution using a burette. The beads were kept in contact with $CaCl_2$ solution for one night to improve their stability. Granules are then separated from the cross-linking solution and washed several times with distilled water and then stirred for one night in 50 mL of 0.1 mol/L ammonium iron(II) sulfate to allow iron to be linked to granules. Finally, they were washed with hydrochloric acid (0.01 mol/L) and distilled water and then dried in oven at 60°C for 24 hr.

In order to prepare CDTA-modified alginate gels (Alg/CDTA/Fe), 2.5 g of sodium alginate powder was dispersed in 100 mL distilled water and thoroughly mixed using a mechanical stirrer until complete dissolution. A mass of 0.5 g of CDTA was then added to the viscous alginate until complete homogenization and the beads were then formed as described previously.

1.2.2. Degradation experiments

Synthetic ofloxacin solutions of 20 mg/L were prepared by dissolving the ofloxacin powder in distilled water. The initial pH was adjusted to 3 with 0.1 mol/L H_2SO_4. This value was chosen as it is the optimum value observed for homogeneous Fenton oxidation (Shemer et al., 2006). All the experiments were carried out in batch system using 100 mL glass beakers in continuous stirring during 120 min. A volume of 50 mL of ofloxacin solution and a determined weight of solid were used. Experiments were carried out at ambient temperature, but other temperature values (45, 65 and 85°C) were also tested. A temperature regulating device was used to maintain the temperature at the desired value. Hydrogen peroxide was used as an oxidant in various concentrations and was periodically titrated with $KMnO_4$ to determine its exact concentration. The reaction progress was monitored from the beginning by extracting aliquots, at selected time intervals. Three-milliliter aliquot samples were filtered using a