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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 μ L 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.

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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; Aravindhnan 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

45 μm filter and then immediately analyzed by absorbance measurement. Blank experiments were also performed, under the same operating conditions, without hydrogen peroxide addition but with adding granules to discriminate between the contribution of adsorption and oxidation in the drug removal.

1.3. Analytical procedures

The absorbance measurements of samples were carried out at 294 nm using a UV-Vis spectrophotometer (DU-530, BECKMAN COULTER, USA). The removal efficiency of the drug was expressed as (E , %) according to Eq. (1):

$$E = \frac{(A_0 - A_t)}{A_0} \times 100\% \quad (1)$$

where, A_0 and A_t are, respectively, absorbance values at the beginning and through time.

The leached iron was determined in the liquid phase by colorimetric titration using the 1,10-phenantroline method (Jeffery et al., 1989). The absorbance was measured at 510 nm.

Drug degradation was also evaluated using a High Performance Liquid Chromatography (HPLC-DAD system, AGILENT Technologies, Germany) operating at a flow rate of 1 mL/min. A Microsorb C18 column (15 cm \times 4.6 mm) was used as the stationary phase. A mixture of acetonitrile and buffer solution was used as the mobile phase. The buffer solution was prepared with an aqueous solution containing 4 g ammonium acetate and 7 g sodium perchlorate in 1300 mL distilled water. The solution is acidified to pH 2.2 with phosphoric acid and added to 240 mL acetonitrile. The drug was detected at the wavelength of 294 nm.

For characterization purpose, the synthesized solids were subject of FT-IR spectroscopy using a Fourier transform spectrometer (Alpha, Bruker, France). The FT-IR spectra of alginate before and after CDTA and iron incorporation were scanned in the range of 400–4000 cm^{-1} with 4 cm^{-1} resolution.

For morphological characterization AFM system (XE-70, PARK, Korea) was used. The scan rate was 0.5 Hz. Topographic images were taken in three dimensional organizations.

Textural properties of the synthesized composite material including porosity were measured by nitrogen adsorption-desorption isotherms method at 77 K using a BET instrument (ASAP 2020, MICROMERITICS, USA). The Barrett-Joyner-Halenda (BJH) method was used to derive the pore size distribution.

2. Results and discussions

2.1. Characterization of synthesized beads

2.1.1. FT-IR analysis

The infrared spectra of pure and modified alginate are shown in Fig. 1 and the functional groups associated with the most characteristic peaks of these spectra are summarized in Table 1 according to the literature. Fig. 1, line a shows the characteristic peaks of virgin alginate: carboxylate groups (CO_2^-) at 1593 cm^{-1} (I) and 1407 cm^{-1} (II) (asymmetric and symmetric stretching vibration respectively) (Papageorgiou et al., 2010; Valenzuela et al., 2014) and dual peaks at 1080 cm^{-1} (III) and 1024 cm^{-1} (IV)

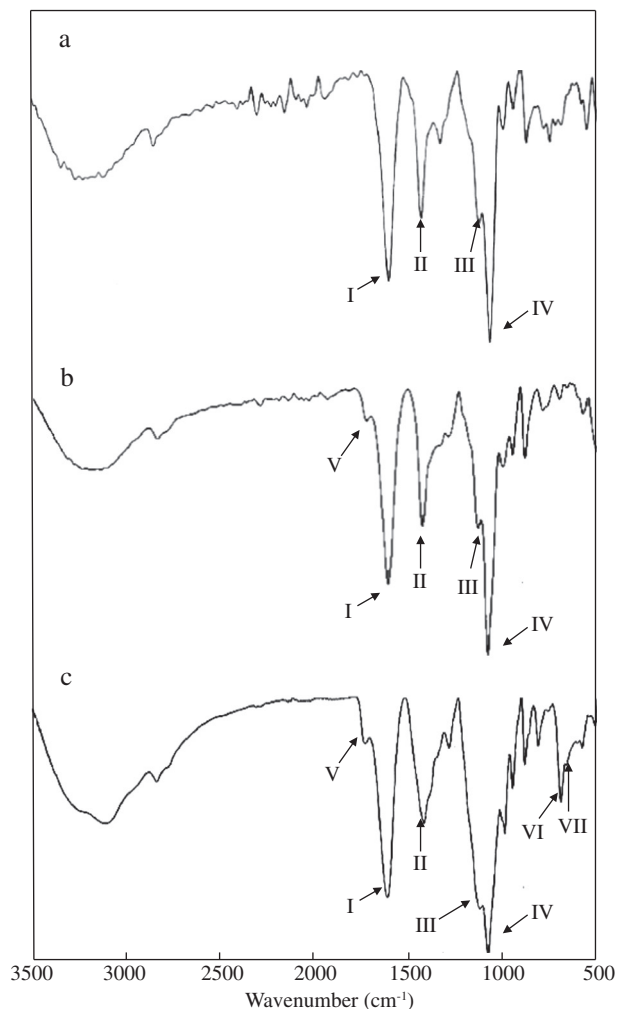


Fig. 1 – Fourier transform infrared spectra (FT-IR spectra) of (line a) virgin alginate, (line b) alginate/cyclohexane dinitrilo tetraacetic acid (CDTA) (Alg/CDTA) and (line c) Alg/CDTA/Fe.

which are related to stretching vibrations of C–O groups of the pyranosyl ring (Papageorgiou et al., 2010; Valenzuela et al., 2014). A new peak which appeared at 1723–1730 cm^{-1} (V) in the spectrum of Alg/CDTA (Fig. 1 line b) and Alg/CDTA/Fe (Fig. 1 line c) respectively could be attributed to the absorption of carbonyl groups ($-\text{C}=\text{O}$) (Repo et al., 2013; Ezzeddine et al., 2015) and thus indicating the incorporation of CDTA in the alginate matrix. In the spectrum of Alg/CDTA/Fe, the peak corresponding to the asymmetric vibration of carboxylate groups shifted to a higher wavenumber (1603 cm^{-1}) and that corresponding to the symmetric vibration shifted to lower value (1395 cm^{-1}). This indicated the interaction between Fe^{2+} and the oxygen of $-\text{COO}^-$ groups (Rosales et al., 2012) since the carboxyl group plays the key role in metal sorption (Papageorgiou et al., 2010). The position of the C–O peak has also been affected when alginate is modified with CDTA and iron. Finally, a new strong peak which appeared at 608 cm^{-1} (VI) in the spectrum of Alg/CDTA/Fe and an adjacent one at 576 cm^{-1} (VII) are consistent with the Fe–O vibration (Haixia et al., 2015; Castelló et al., 2015) and thus proves the successful incorporation of iron.

Table 1 – Assignment of the main vibration modes for virgin and composite alginate beads.

	Peak position (cm ⁻¹)		Assignments
	Alg	Alg/CDTA	
1593	1596	1603	Asymmetric stretching vibration of carboxylate (CO ₂)
1407	1401	1395	Symmetric stretching vibration of carboxylate (CO ₂)
1080 and 1024	1082 and 1024	1072 and 1026	Stretching vibrations of C–O groups
–	1723	1730	Carbonyl groups (–C=O)
–	–	608 and 576	Fe–O vibration

Alg: virgin alginate, Alg/CDTA: composite alginate/cyclohexane dinitrilo tetraacetic acid, Alg/CDTA/Fe: composite alginate/cyclohexane dinitrilo tetraacetic acid/fer.

2.1.2. Morphological study with atomic force microscopy

The surface modification of virgin alginate after incorporation of iron and CDTA was confirmed by morphological studies by atomic force microscopy as shown in Fig. 2.

AFM results clearly indicated that virgin alginate (Fig. 2a) shows smooth surface morphology with individual granules, whereas the composite material formed between alginate, CDTA and iron species forms dense structure (Fig. 2b). The incorporation of the chelating agent and iron ions made the surface coarser. The roughness average (R_a) of the surface of pure alginate was estimated to be 7.43 nm. This value increased to 24.26 nm for the composite material. It is seen that spherical particles existed on the surface of virgin sodium alginate indicating its porous structure which favors the diffusion of ions into the matrix, but aggregates characterized the surface of the composite material supporting the strong adhesion of the incorporated elements onto the polymer.

2.1.3. Quantification of carboxylic groups

The modifications introduced on alginate surface were also characterized with titration by the Boehm method (Kalijadis et al., 2011) which gives a quantitative measurement of surface functions. This method is based on acid–base titration of acidic and basic centers. The procedure was used in this work to quantify the carboxylic groups, per gram of solid, which can be neutralized by NaHCO₃ solution.

We noticed that the number of carboxylic groups increased when incorporating CDTA in alginate and passes from 4.5 mmol/g (Alg) to 7 mmol/g (Alg/CDTA). This is because CDTA contains itself carboxylic groups. The number decreased when iron is added to the matrix (3 mmol/g for Alg/CDTA/Fe). It's probable that iron interacts with deprotonated carboxylate ions (negatively charged) which have a great affinity to cations and hence represent adequate binding sites of metallic cations (Sreeram et al., 2004). A previous work (Papageorgiou et al., 2010) advanced different modes of metal-carboxylate coordination and cited that the nature of interaction is not yet clear. For the solid containing alginate and iron only (Alg/Fe) we notice that carboxylic groups are lower than the CDTA-modified one (Alg/CDTA/Fe). The value is only 2 mmol/g. This is because the concentration of the incorporated iron may not be sufficient to react with all the carboxylate ions present in the composite matrix; some of them remain free.

2.1.4. Porosity of the composite material

Physical properties deduced from N₂ adsorption at 77 K on Alg/CDTA/Fe composite beads are as follows: BET surface area

2.779 m²/g, pore volume 4.626 × 10⁻³ cm³/g, and average pore diameter 106.373 Å. The IUPAC classified the porosity into three principal groups according to the pore diameter (d): macropores ($d > 50$ nm), mesopores ($2 < d < 50$ nm) and micropores ($d < 2$ nm). According to the obtained results, it can be concluded that the composite material falls into the category of mesopores.

Fig. 3 shows the adsorbed volume distribution over the entire pore size range for the solid. The pore size distribution of the composite material revealed a distinct peak, with the majority of pores having a diameter of 10.8 nm. The beads are mesoporous, having large pore diameter.

2.2. Influence of metallic ion nature on ofloxacin oxidation using virgin alginate

In a preliminary work, virgin alginate was used and three metals (iron, copper and silver) were tested in order to compare their catalytic activities toward ofloxacin oxidation. The results are given in Fig. 4.

The oxidation efficiency is significantly influenced by the nature of impregnated metal. Iron presented the most important degradation capacity when compared to copper and silver. In the presence of iron, a conversion of 75% is reached within 2 hr whereas the Alg/Cu and Alg/Ag solids lead respectively to only 36% and 15% under the same conditions. This suggests that iron species are more appropriate to activate H₂O₂. It can be concluded that iron is the best choice for the degradation reaction. For this reason, ferrous ions were selected, for the rest of the work, as the best choice of impregnated metal on sodium alginate.

2.3. Oxidation process on CDTA-modified alginate

Several modifications were tested to improve the degradation capacity of Alg/Fe. Surprisingly, the solid modification with CDTA substantially improved the degradation capacities of the solid especially in the initial stage. The catalytic effect of virgin and modified support is compared and the results are given in Fig. 5.

The oxidation efficiency is enhanced in the presence of CDTA-treated support as compared with the untreated one. The modified solid proved to be more active in the initial time compared to virgin alginate for the same drug concentration and the same reaction time using the same solid mass. More than 64% of the equilibrium levels were achieved after only 30 min of contact time compared to only 37% for the virgin alginate which

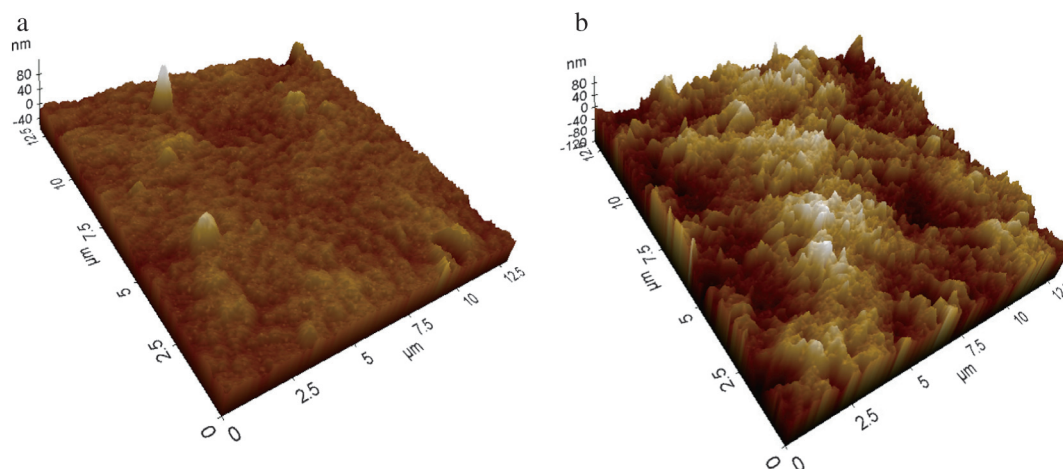


Fig. 2 – Atomic force microscopy (AFM) images in two and three dimensional organizations showing (a) the virgin alginate and (b) the composite material, Alg/CDTA/Fe. Alg: alginate CDTA: cyclohexane dinitrilo tetraacetic acid.

shows a relatively slow initial degradation yield. The addition of CDTA has a positive effect on the initial degradation rate but has no influence on final yields. The final degradation capacity of both materials exceeds 75%. Alginates have $-\text{COO}^-$ and $-\text{COOH}$ groups along the chain conferring different charge densities because of electrostatic attraction. With the decrease of pH, the number of dissociated carboxylic groups in alginate chains decreases, which makes alginate lose its hydrophilicity. Association with CDTA molecules can be attributed to hydrophobic interactions. Moreover, porosity in Ca-alginate allows CDTA molecules to diffuse into the beads. The attachment of CDTA chains onto the alginic matrix may induce profound changes in the physico-chemical behavior of the latter. This can explain the improvement of the oxidation process.

This experiment shows also that the degradation of OFL is substantially higher when using Alg/CDTA/Fe (77%) over Alg/CDTA (38%). This result proves the key role played by iron ions in the generation of $\cdot\text{OH}$ radicals.

2.4. Adsorption and oxidative behavior of the synthesized beads

In an attempt to discriminate between oxidation and simple adsorption of ofloxacin and to elucidate the part devoted to adsorption in the removal of the drug, we tested the influence of the presence of hydrogen peroxide for both solids (virgin and CDTA-modified). Fig. 6 resumes the obtained results.

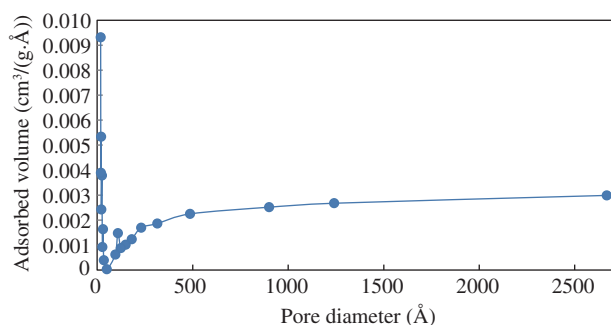


Fig. 3 – Pore size distribution of Alg/CDTA/Fe composite beads. Alg: alginate CDTA: cyclohexane dinitrilo tetraacetic acid.

It's clear that substantially different results were obtained in the presence and absence of H_2O_2 for the two synthesized solids. Even if the presence of CDTA allows, in both cases, better degradation yields which demonstrate the role played by CDTA addition, the absence of hydrogen peroxide induced a huge decrease of removal capacities of both solids. The removal capacity of the drug in the presence of Alg/CDTA/Fe passed from 19% (without H_2O_2) to 77% (in the presence of H_2O_2). This result clearly indicates the central role of hydrogen peroxide and the low adsorptive capacity of the solid. The antibiotic removal is mainly governed by the oxidation and the contribution of adsorption is negligible.

Also, if we compare between adsorption capacity (in the absence of H_2O_2) of virgin and CDTA-modified solid, we find that the latter lost a part of its capacity to incorporate in its structure OFL molecules. CDTA amendment clearly decreases the drug adsorption. This can be due to the fact that CDTA is likely to enter into competition with drug molecules toward active sites on alginate surface.

2.5. Optimization of operational parameters

The influence of H_2O_2 concentration, temperature, granule amount, and initial drug concentration on the degradation of ofloxacin in the presence of Alg/CDTA/Fe was studied and reaction rates were evaluated. The kinetic behavior analysis was illustrated using the first order kinetic model. This model is given by the well-known expression:

$$\frac{C}{C_0} = \exp(-K_1 t) \quad (2)$$

where C (mg/L) and C_0 (mg/L) are the concentrations of ofloxacin, respectively at time t and at the beginning of the experiment, and K_1 (min^{-1}) the pseudo first rate constant which represents in this study the apparent constant (K_{app}). Results are reported in Table 2 with the corresponding R^2 values.

2.5.1. Influence of H_2O_2 concentration and reaction temperature

The influence of the addition of oxidant in variable concentrations and the influence of temperature were investigated. Results are reported in Fig. 7a and b.

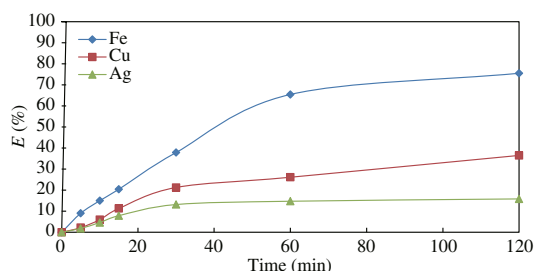


Fig. 4 – Evolution of ofloxacin oxidation using different impregnated metals. Ofloxacin concentration = 20 mg/L, H₂O₂ concentration = 40 mmol/L, granule mass = 1 g/L, pH = 3.

Fig. 7a clearly indicates that there is an important dependency of the oxidation capacity to the initial concentration of hydrogen peroxide. When working in the absence of oxidant, there is very little conversion of the drug, hardly 19%. As shown in the figure, an increase of the amount of hydrogen peroxide induces an improvement of the degradation capability of the solid until reaching a concentration of 10 mmol/L, but a supplemental increase of oxidant volume up on this value results in a decrease of the drug degradation. Oxidative capacity of hydrogen peroxide decreases indicating that it becomes less efficient for the molecule degradation. This can be explained by the fact that the excess of H₂O₂ reacts with the formed hydroxyl radical to give rise to water and another product. Hu et al. (2011) explained in their research that H₂O₂ is a powerful .OH scavenger at high dosages; hydroperoxyl radicals (HO₂·) are produced from hydroxyl radicals that are already formed. The hydroperoxyl radicals are much less reactive toward organic molecules (Aravindhan et al., 2006). Therefore, a high ofloxacin conversion at low oxidant dosage can be concluded.

Results also showed, for a chosen oxidant concentration of 10 mmol/L, a significant improvement of the oxidation efficiency upon increasing temperature (Fig. 7b). At 25°C, oxidation of the antibiotic was not complete. The free radical concentration usually increases with increasing reaction temperature, as reported by Bautista et al. (2010), allowing an improvement of molecule degradation. Kondru et al. (2009) observed similar results in their research work. It's established that increasing the working temperature allows

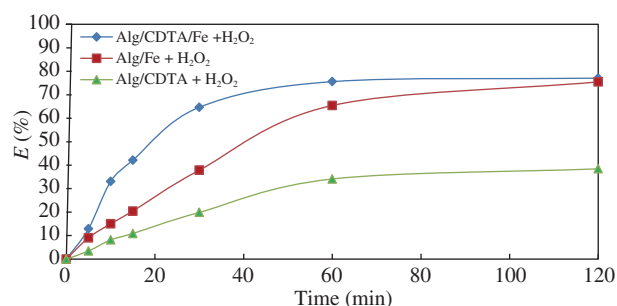


Fig. 5 – Evolution of ofloxacin oxidation in the presence of Alg/Fe, Alg/CDTA and Alg/CDTA/Fe. Ofloxacin concentration = 20 mg/L, H₂O₂ concentration = 40 mmol/L, granule mass = 1 g/L, pH = 3. Alg: alginate CDTA: cyclohexane dinitrilo tetraacetic acid.

reactant molecules to overcome the activation energy barrier by providing more energy which makes the oxidative reaction easy (Hassan and Hameed, 2011). Table 2 permits to compare the different kinetic constants calculated from the slopes of the kinetic plots given in Fig. 8a and b.

It is obvious that the drug degradation rate is highly dependent on hydrogen peroxide concentration. An increase of peroxide concentration causes an increase of the kinetic constant. Variation in H₂O₂ concentration from 2 to 10 mmol/L increased the initial degradation rate of ofloxacin by 1.9 folds. Higher peroxide concentrations yield to reduce oxidation rate. Temperature also had a beneficial effect on the reaction kinetics (Hassan and Hameed, 2011; Sun et al., 2009) and the straight lines in the plots (Fig. 8b) characterized by high regression coefficients indicate that the initial degradation rate of the drug follows well the first order kinetic model. The rate constant at 25°C was lower compared with the values at other temperatures (Table 2).

2.5.2. Influence of granule dosage and initial OFL concentration

Additional experiments were carried out to study the influence of the solid dosage and initial drug concentration on ofloxacin conversion efficiency. The mass was varied between 0.01 and 0.09 g and three different initial substrate concentrations (10, 20 and 30 mg/L) were tested. Results are respectively illustrated in Fig. 9a and b.

We observed from Fig. 9a that an increase of the introduced amount of granules improves the removal efficiency. An increase of 30% was observed when increasing the amount of added granules from 0.01 to 0.07 g. Other heterogeneous catalysts showed similar behavior in CWPO for organic wastewater treatment (Kondru et al., 2009; Aravindhan et al., 2006; Liou et al., 2005). This is probably due to the increasing number of active catalytic sites which positively influences the decomposition efficiency of hydrogen peroxide, but it is important to note that adding more than this mass does not induce a substantial increase in ofloxacin abatement.

It is clear from the inset of Fig. 8c that, similar to temperature, there is a close relationship between the rate of drug conversion and solid mass.

From Fig. 9b we observed that ofloxacin abatement decreased with the increase of initial drug concentration. Final drug conversion was only 66% for 30 mg/L of drug solution used initially and reached 94% for 10 mg/L. In fact, in the presence of high initial concentrations of drug, the produced active radicals become insufficient to treat all the target molecules. In addition, the active sites, where the radical reaction occurs, become limited when drug concentration is too high. As evidenced, the degradation rate constant increases by decreasing the substrate concentration (Fig. 8d) and higher pollutant concentrations need a longer treatment time as mentioned by Martin et al. (2009).

2.6. Evaluation of iron leaching from the beads

At this stage, the evaluation of the contribution of the homogeneous Fenton in ofloxacin removal is important. The possibility of iron leaching from the support to the liquid medium was evaluated by titration. It was determined by

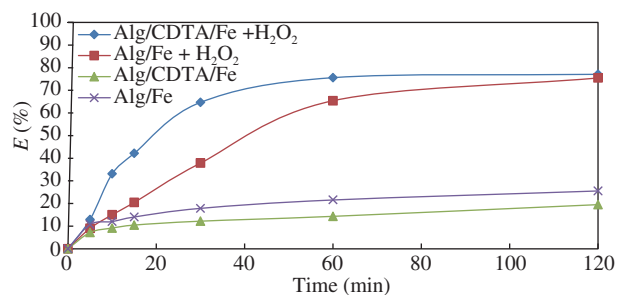


Fig. 6 – Evolution of ofloxacin conversion using virgin and modified material in the presence and absence of H_2O_2 . Ofloxacin concentration = 20 mg/L, H_2O_2 concentration = 40 mmol/L, granule mass = 1 g/L, pH = 3.

spectrophotometric method using 1,10-phenanthroline which forms a strong orange-red complex with iron species. This reaction is used for the quantitative analysis of low concentrations of $Fe^{2+}(aq)$ in solution. A degradation experience was conducted under optimal conditions and an aliquot was withdrawn from the solution after 2 hr of reaction time and filtered to be analyzed. It was found that only 0.8% of the initial incorporated quantities of iron were detected in the liquid medium showing good immobilization of the metal and high stability of the complex formed with CDTA. This value is lower than that found for virgin alginate which lost about 1.4% of the incorporated quantity. This result eliminates the contribution of homogenous process to the drug oxidation and evidenced that the composite synthesized material can be successfully used in heterogeneous catalytic oxidation.

Table 2 – Kinetic constants of the pseudo first order during the initial oxidation stage (30 min).

	K_{app} (min^{-1})	R^2
<i>H₂O₂ concentration (mmol/L)</i>		
2	0.0329	0.9866
4	0.0465	0.9522
10	0.0626	0.9309
40	0.0374	0.9942
160	0.0292	0.9895
320	0.0210	0.9937
400	0.0150	0.9975
<i>Temperature (°C)</i>		
25	0.0626	0.9309
45	0.1184	0.9984
65	0.1872	0.9755
85	0.2138	0.9909
<i>Granules loading (g)</i>		
0.01	0.0216	0.9845
0.03	0.0387	0.9899
0.05	0.0626	0.9309
0.07	0.0899	0.8519
0.09	0.1031	0.8067
<i>Ofloxacin concentration (mg/L)</i>		
10	0.1066	0.8954
20	0.0626	0.9309
30	0.0217	0.9967

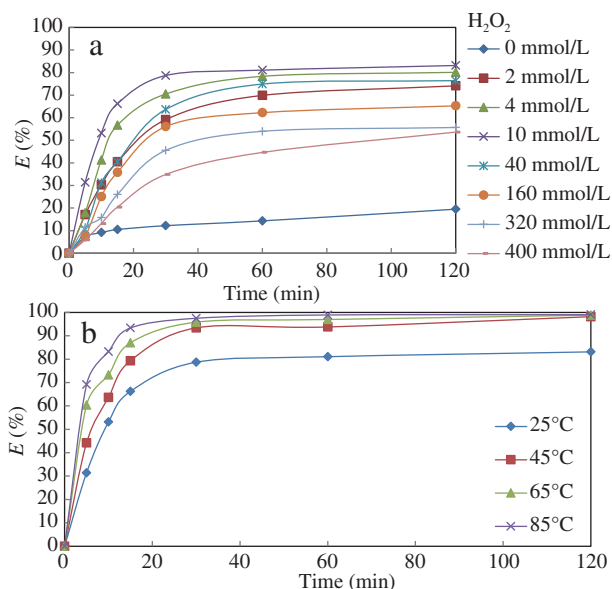


Fig. 7 – Evolution of ofloxacin oxidation for: (a) different H_2O_2 concentrations and (b) different reaction temperatures. Ofloxacin concentration = 20 mg/L, granule mass = 1 g/L, pH = 3.

2.7. Detection of $\cdot OH$ radicals by DPPH. test

To show the involvement of $\cdot OH$ radicals in the process, we used the well-known radical scavenger, DPPH. reagent. It is a rapid and simple method to detect the formation of radical species. Samples were withdrawn from reaction medium, at different time intervals, and added to DPPH. reagent. The obtained mixture was incubated for 30 min and then analyzed by absorbance measurement. This test is not quantitative. A qualitative signal of the reaction progress was a color change in the reaction medium (from purple to yellow green). The color degradation of DPPH. solution was evaluated at 517 nm. For a comparative purpose, a blank experience was conducted in the absence of hydrogen peroxide to assess the formation of radical species due to the association between H_2O_2 and iron. Fig. 10 resumes the results obtained from both experiences.

There is an important difference when working in the presence and absence of hydrogen peroxide. In the presence of oxidant, the absorbance of the initial DPPH. solution was dramatically reduced (90%) compared to the experience carried out without oxidant addition when the reduction percentage doesn't exceed 34%. This result indicates the formation of radical species in the first case which rapidly reacts with DPPH. reagent contributing in absorbance reduction.

2.8. Recyclability and evaluation of stability of the beads

Investigation of the synthesized support's stability in successive catalytic runs is important to evaluate the possibility of its re-use for industrial applications. The main goal of this

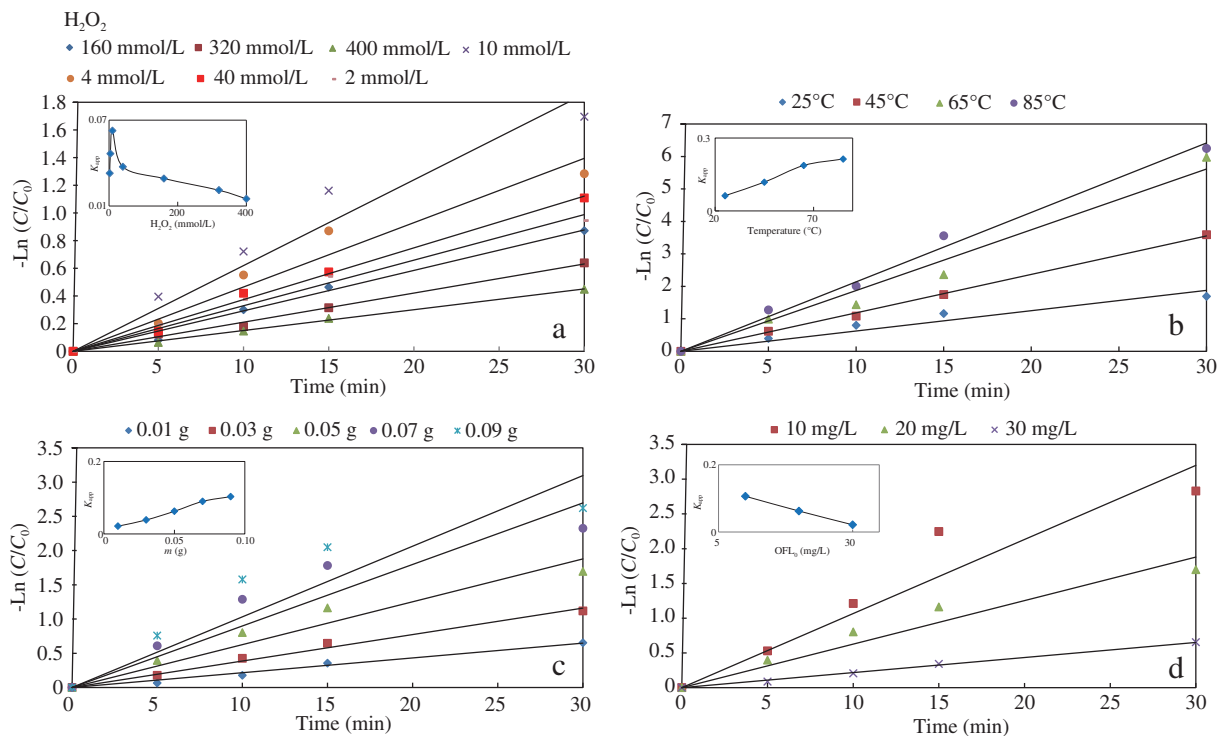


Fig. 8 – Plots of the pseudo first order model function of (a) hydrogen peroxide concentration, (b) reaction temperature, (c) granule mass and (d) initial drug concentration.

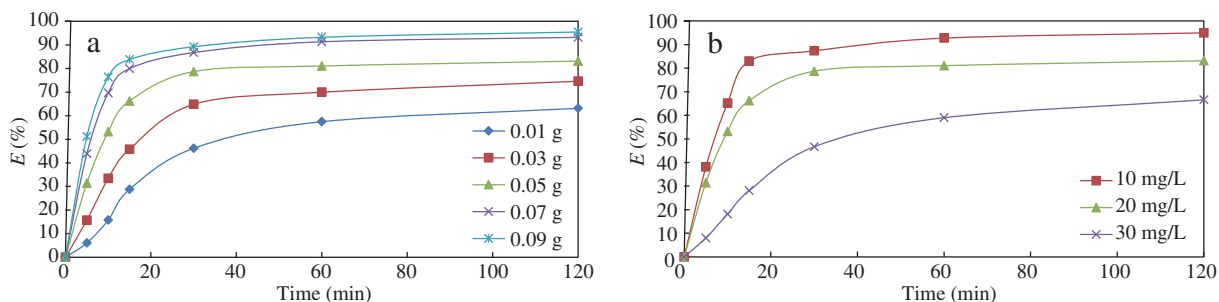


Fig. 9 – Evolution of ofloxacin oxidation for: (a) different granule masses and (b) different initial drug concentrations. H_2O_2 concentration = 10 mmol/L, pH = 3.

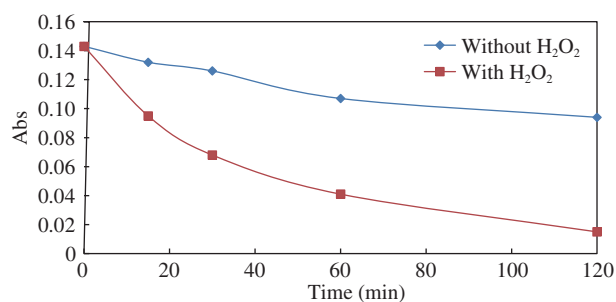


Fig. 10 – Evolution of DPPH absorbance in the absence and presence of H_2O_2 . Granule mass = 1 g/L, H_2O_2 concentration = 10 mmol/L, pH = 3. DPPH: diphenyl-picrylhydrazyl.

study was to study the capacity of the composite synthesized solid to be used in four successive experiments. The granules were recovered from the solution after the first oxidation run, simply washed with water and reused in a new experiment with fresh reactants under the same conditions. The procedure was repeated until the material was used four times. The obtained results are shown in Fig. 11.

It is observed, for the chosen concentration of the pollutant, that the catalytic support suffered a decrease of activity of only 9% after four successive runs and only 4% between the first and the third run. From the first to the second run, drug abatement was just dropped from 83% to 82%. From the fourth catalytic run, drug oxidation starts to be affected and just 74% of initial drug were transformed. These results indicate that the recycled solid could be used three

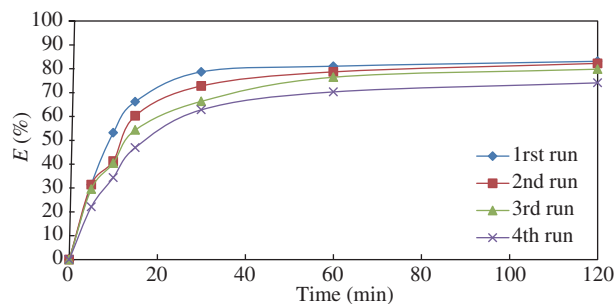


Fig. 11 – Evolution of ofloxacin oxidation during four consecutive runs of the catalytic support. Ofloxacin concentration = 20 mg/L, H₂O₂ concentration = 10 mmol/L, granule mass = 1 g/L, pH = 3.

times with no dramatic deactivation. One important factor of the deactivation of surface catalyst may be the adsorption of organic residual matter over its surface resulting in a partial blockage of used active sites.

2.9. High performance liquid chromatography analysis

HPLC was used to assess the real degradation rate of the target molecule since it separates molecules according to their affinity to stationary phase. The result of HPLC study, in terms of peak area function of time, is given in Fig. 12. The distribution curve of the most concentrated degradation product (DP1) is also presented.

It's observed that there was a sharp decrease in the ofloxacin antibiotic concentration which was completely removed by CWPO after only 10 min of reaction time contrary to the results obtained with UV analysis. This result can be explained by the fact that measuring absorbance may not represent absolutely the concentration of residual ofloxacin since some of the reaction intermediates may also absorb at 294 nm, thus contributing to the final absorbance which is rather regarded as a collective parameter (Hapeshi et al., 2010). The obtained result demonstrates that the used oxidation process was an efficient choice for treating ofloxacin contaminant.

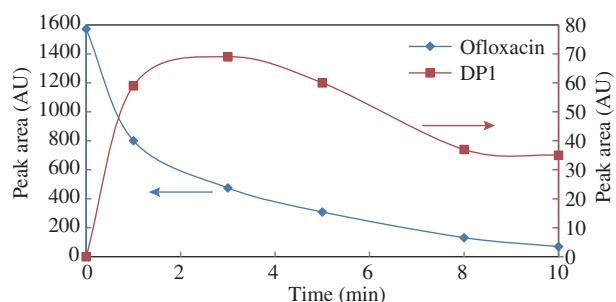


Fig. 12 – HPLC peak area distribution of ofloxacin and its relative degradation product. Ofloxacin concentration = 20 mg/L, H₂O₂ concentration = 10 mmol/L, granule mass = 1 g/L, pH = 3.

3. Conclusions

In the present study the heterogeneous oxidation of ofloxacin using a new composite material synthesized from sodium alginate and CDTA was investigated. The solid was successfully used in the drug degradation. The molecule degradation was directly proportional to catalytic support mass and to temperature, but decreases when the initial drug concentration increases. The process is highly dependent on the hydrogen peroxide amount and small quantities lead to more efficient oxidation. When a 10 mg/L drug solution was treated at pH 3 and ambient temperature, using only 10 mmol/L of H₂O₂ and in the presence of 1 g/L of granules, almost 94% of degradation occurred after treatment duration of 2 hr.

It was demonstrated that iron was well incorporated into the polymeric device and only a relatively low leached quantity of 0.8% was detected in the liquid medium. Also, the synthesized solid can be used for three successive runs without alteration of its activity toward the drug degradation.

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