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Enhancement of ciprofloxacin degradation in aqueous system by heterogeneous catalytic ozonation

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Abstract
Fluoroquinolones are extensively used in medicine due to their antimicrobial activity. Their presence in water inhibits microor-ganism activity in conventional wastewater treatment plants. This study aims to evaluate the technical feasibility of applying heterogeneous catalytic ozonation to eliminate ciprofloxacin (CIP) as a representative of fluoroquinolone antibiotics normally present in municipal wastewater discharges. Experiments were conducted in a semi-batch stirred slurry reactor, using 0.7 L of 100 mg L ^{1} CIP aqueous solution, at pH 3 and 30 °C. Experimental results show that single ozonation can easily oxidise CIP molecules (68%) within the first 5 min, leading to the generation of refractory oxidation by-products. However, when hetero-geneous catalytic ozonation is applied using iron oxide supported on MFI synthetic zeolite, total degradation of CIP is observed at 5 min and a higher mineralisation rate is obtained. A novel sequential process is developed for CIP mineralisation. In a first step, a flash single ozonation is applied and CIP molecules are broken down. Then, a catalytic ozonation step is conducted by adding the Fe/MFI catalyst into the reactor. As a result of catalyst addition, 44% of Total Organic Carbon (TOC) is eliminated within the first 15 min, compared to single ozonation where only 13% of TOC removal is reached in the same time. The application of this sequential process to a real wastewater effluent spiked with CIP leads to 52% of TOC removal.

Keywords Advanced oxidation process · Antibiotic · Catalyst · Ciprofloxacin · Ozonation · Wastewater treatment

Introduction

Over the last 15 years, pharmaceuticals have been receiving increasing environmental attention due to their negative effects. Thousands of tons of pharmaceuticals are used every year not only to treat human and animal diseases, but also in farming and aquaculture and these compounds have been becoming a serious threat to human health and environment (Gomes et al. 2017). Most of the pharmaceuticals designed to target specific metabolic pathways may become detrimental even at very low concentration. Such chemicals are very persistent and can often be found in wastewater treatment plants (Rivera Utrilla et al. 2013; Padhye et al. 2014; Andreu et al. 2016; Monteiro et al. 2016).

In particular, antibiotics have raised environmental concern because their presence even at low concentration can be harmful and toxic after prolonged exposure (Kümmerer 2003; Martínez 2008; Graham et al. 2010; Knapp et al. 2012; Larsson 2014; Li et al. 2016). Fluoroquinolones group antibiotics are extensively used in medicine due to their antimicrobial activity. Their presence in water inhibits microorganism activity in conventional wastewater treatment plants. After administration, most of the fluoroquinolones are incompletely metabolised and excreted in urine and faeces as a parent compound. Fluoroquinolones are strongly sorbing antibiotics tightly bound to organic matter in faeces, soil and clay minerals (Ötker and Akmehmet-Balcıoğlu 2005). As conventional wastewater treatment systems are unable to reliably remove a large amount of antibiotics (Kümmerer 2003; Rivera Utrilla et al. 2013), new ways of treatment have been developed for some decades.

In recent years, a considerable interest has been focused in the development and application of Advanced Oxidation Processes (AOPs) for the elimination of pharmaceuticals from contaminated waters (Oller et al. 2011; Lastre-Acosta et al. 2015; Sayed et al. 2016; Gomes et al. 2017; Adityosulindro et al. 2017; Velichkova et al. 2017). AOPs involve the generation of hydroxyl radicals that are able to degrade organic pollutants which are highly stable and very difficult to mineralise (Andreozzi et al. 1999; Legube and Leitner 1999; Kasprzyk et al. 2003). AOPs, such as H_2O_2/UV, photo-assisted Fenton, and ozonation at high pH values, have been used to oxidise micro-contaminants (Tay and Madehi 2015; Chávez et al. 2016; Ou et al. 2016). However, the efficiency of these homogeneous processes can be reduced by the presence of radical scavengers such as carbonates, bicarbonates, and natural organic matter due to the inhibition of radical chain reactions (von Sonntag and von Gunten, 2012). Therefore, it is necessary to find new process alternatives to overcome such drawbacks.

Recently, heterogeneous AOPs based on the combination of ozone with activated carbon or zeolites have been shown to improve the generation of free radicals. So the impact of inhibition effect produced by radical scavengers is less critical in such a process (Valdés and Zaror, 2006; Valdés et al., 2009 Reungoat et al. 2010; Valdés et al. 2010, 2012a, b; Sui et al. 2012; Aboussaoud et al. 2014; Jalali 2016). In such heterogeneous processes, chemical surface properties of microporous materials have been claimed to play an important role in the reaction mechanisms (Valdés and Zaror, 2006; Valdés et al., 2009; Merle et al. 2010; Valdés et al. 2012a, b). Consequently, heterogeneous catalytic ozonation with natural or synthetic zeolites has been receiving increasing attention in recent years (Martins et al. 2014; Ikhlaq et al. 2015; Vittenet et al. 2015; Gomes et al. 2018).

Lately, the use of zeolites containing iron species as catalysts has gained increasing interest because of the combination of their adsorptive and catalytic properties. Among catalysts, iron type catalysts can be recommended because of the abundance of this metal on earth. Iron type catalysts have already been used in ozonation processes to remove different compounds such as phenol, aniline, carboxylic acids, chlorobenzene, chlorophenols, dyes or natural organic matter (Beltran et al. 2005). Fe-containing zeolites are interesting candidates as heterogeneous catalyst because of their high catalytic activity in the oxidation of organic compounds, with minimal iron leaching (Chen et al. 2008; Gonzalez Olmos et al. 2011; Velichkova et al. 2017).

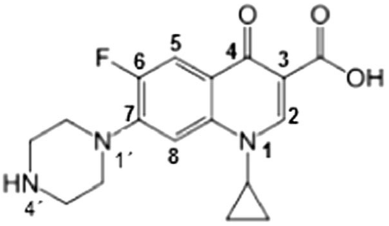
This work aims to study heterogeneous catalytic ozonation of antibiotic-contaminated waters, using ZSM-5 zeolite (Zeolite Framework Type ZS**M**-**FI**ve; abbreviation: **MFI**.) doped with iron oxide nanoparticles. CIP was used here as a representative of a group of fluoroquinolone antibiotics widely used in human and animal therapy. CIP is a non-biodegradable antibiotic that has been detected in wastewater treatment plant effluents in concentrations from 5.6 μg L ^{1} to 6.5 mg L ^{1} (Kümmerer et al. 2000; Hughes et al. 2012). As an antibiotic, CIP is of particular concern because its presence in natural waters could contribute to the rise of antibiotic resistance in microorganisms (Kümmerer 2003; Graham et al. 2010; Knapp et al. 2012; Martínez 2008; Larsson 2014). Very few studies have been found on CIP removal. Sorption on activated sludge and biodegradation catalysed by magnetite nanoparticles seem to give interesting results (Yang et al. 2017). More recently, membrane-based processes have been focused on (Sadhwani et al. 2018). However, information that deals with the elimination of CIP and its oxidisation by-products using processes based on the combination of ozone and zeolites is not abundant. In particular in this study, the effect of single ozonation, single adsorption, single heterogeneous catalytic ozonation, and the application of a sequential process comprising of two step (single flash ozonation followed by catalytic ozonation) are evaluated in terms of CIP mineralisation. Finally, all processes are assessed using real effluent spiked with CIP.

Materials and methods

Materials

Ciprofloxacin (1-cyclopropyl-6-fluoro-4-oxo-7-piperazin-1-ylquinoline-3-carboxylic acid, named here as CIP) was supplied by Sigma-Aldrich (St. Louis, MO, United States) with 99% purity. In a first step of this study, a synthetic wastewater: was used. It was prepared by dissolving CIP in deionised water. A complete geometric representation of the molecular structure of CIP, its solubility in water and its pK_a value are given in Table 1.

Table 1 Physical chemical properties of CIP

Structural formula	
Dimensions	13.2 Å; 7.8 Å; 3.7 Å (Stewart 2012)
Solubility in water (mg L ^{1}) at pH$_3$	3 × 10^4 (Nowara et al. 1997)
pK_a	3.64 (N1), 5.05(N1′), 6.95 (OH), 8.95 (N4′) (Lin et al. 2004; De Witte et al. 2007)

The adjustment of pH adjustment was carried out using 1 mol L^{-1} solution of HCl from Chem-Lab. Acetonitrile (HPLC quality) and o-phosphoric acid (85%) were provided by Merck (Darmstadt, Germany) and Fisher (Pittsburgh, United States), respectively, and were used in high-performance liquid chromatography (HPLC) analyses.

ZSM-5 zeolite with a framework type MFI doped with iron oxide (Fe_2O_3) nanoparticles (referred as Fe/MFI) was used here as a catalyst and was bought from Süd-Chemie AG (Munich, Germany) with a silicon/aluminium ratio of 27. This kind of ZSM-5 zeolite exhibits a three-dimensional pore network with 10-membered straight and sinusoidal ring channels and apertures of 5.3 × 5.6 Å and 5.1 × 5.5 Å, respectively (Pearce 1975). Physicochemical properties of Fe/MFI zeolite used in this study are listed in Table 2.

The physical-chemical characteristics of filtered real wastewater plant effluent sample, taken from Nailloux wastewater treatment plant (Occitanie, France), are shown in Table 3. Five-day biological oxygen demand (BOD_5) analyses were assessed at the Departmental Laboratory, LD 31, Toulouse, France. In the experiments where real wastewater was applied; it was spiked with 100 mg L^{-1} of CIP and used within 24 h after collection for assays of single ozonation and heterogeneous catalytic ozonation.

Experimental procedures

All experiments were performed at pH 3 and 30 ± 1 °C in a semi-batch stirred slurry reactor (Ø100 mm x 100 mm) containing 0.7 L of a CIP aqueous solution (100 mg L^{-1}). Figure 1 displays a schematic representation of the experimental ozonation setup. Ozone was produced from dry pure oxygen supplied by Air Liquide (Paris, France), using a 4-HC, WEDECO ozone generator rated at 1.44 $\text{gO}_3\ \text{h}^{-1}$. A continuous flow of ozone (30 L h^{-1}, 48 $\text{gO}_3\ \text{m}^{-3}$) was introduced into the reactor by means of a stainless steel diffuser. During single ozonation experiments at pH 3, no hydroxyl radical formation is expected (Hoigné 1998; Von Sonntag and von Gunten 2012). Under such conditions, radical oxidation route is almost inhibited and oxidation reactions are mainly due to direct action of ozone molecules. Samples were regularly collected in order to follow kinetic evolutions. Samples were filtrated and taken to determine the residual CIP concentration and Total Organic Carbon concentration (TOC).

Table 3 Physical chemical characteristics of real and spiked wastewater matrix with 100 mg L^{-1} CIP and adjusted to pH 3

Parameter	Unit	Wastewater plant effluent	Spiked wastewater
pH		6.5	3.0
TOC	$\text{mgO}_2\ \text{L}^{-1}$	15.28	76.03
BOD_5	$\text{mgO}_2\ \text{L}^{-1}$	< 2	110

Four different processes were studied. First, single ozonation (i) and heterogeneous catalytic ozonation using 1 g L^{-1} of Fe/MFI zeolite (ii) were conducted. After that, an original process was evaluated, with two different sequences: a quick ozonation step in order to break the CIP molecule (run during 5 minutes) followed by either an adsorption onto Fe/MFI zeolite (iii) or by a catalytic ozonation using Fe/MFI zeolite (iv). The influence of the catalyst dosage was assessed, applying different amounts of Fe/ZSM5 from 0 to 10 g L^{-1} (v). Experiments were run in triplicate.

Analytical methods

CIP concentration was determined by HPLC (Varian ProStar 310 model). A RP-18 column (Super Sphere 100 model, 250 mm × 4.6 mm; 5 μm) at 40 °C connected to an UV/VIS diode array detector and set at 278 nm was used for CIP detection. A mix of 15% of acetonitrile/acidified water (*v*/*v*) was applied as a mobile phase rated at 1.5 mL min^{-1}. A volume of 20 μL was injected and CIP-eluted at around 9 min. A calibration curve ($R^2 = 0.99$) was obtained using external standard, prepared with known concentrations of CIP.

Mineralisation of CIP was followed by TOC analysis, using a TOC-LCPN Shimadzu analyser equipped with a non-dispersive infrared detector. The injection volume was 50 μL. Combustion reaction was achieved in a quartz pipe at 680 °C with platinum as a catalyst. Oxygen was used as a carrier gas with a flow rate of 150 mL min^{-1}.

Results and discussion

CIP adsorption onto the Fe/MFI zeolite

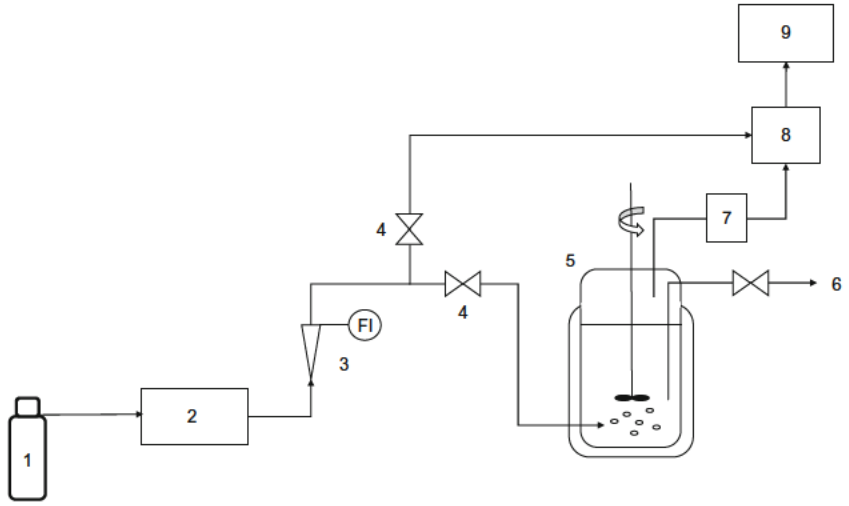
Preliminary experimental studies of kinetic adsorption show that the CIP adsorption onto the Fe/MFI zeolite is very slow.

Table 2 Physical chemical properties of Fe/MFI zeolite (Velichkova 2014)

Commercial name	SiO_2/ Al_2O_3	Fe (%)	S_{BET} ($\text{m}^2\ \text{g}^{-1}$)	V_{meso} ($\text{cm}^3\ \text{g}^{-1}$)	V_{micro} ($\text{cm}^3\ \text{g}^{-1}$)	pH_{PZC}[a]
Fe SH 27	27	3.4	329	0.05	0.13	2.6

[a] pH of the point of zero charge (pH_{PZC}) determined using the acidimetric–alkalimetric titration method proposed by Stumm and Morgan (1996)

Fig. 1 Schematic diagram of the experimental ozonation setup: (1) oxygen cylinder; (2) ozone generator; (3) gas flow meter; (4) ozone gas analyser/reactor bypass valves; (5) semi batch stirred slurry reactor; (6) sampling valve; (7) water collection trap; (8) ozone gas analyser; (9) ozone destruction system



Less than 5% of CIP removal is obtained in 1 h. This result could be explained by a size exclusion process because molecular dimensions of CIP are larger (13.2 Å; 7.8 Å; 3.7 Å) (Stewart 2012) than the dimensions of channels and pores of the zeolite 5.3 × 5.6 Å and 5.1 × 5.5 Å (Pearce 1975). At pH 3, the main part of CIP molecules carry on an overall positive charge (CIP^{3+}) with a pKa_1 value of 3.64. Taking into account the low pH_{PZC} (2.6), zeolite is able to exchange only a few cations in these conditions.

CIP homogeneous and heterogeneous ozonation

Figure 2 shows the variation of the dimensionless concentration of CIP and TOC as a function of time, during the application of single ozonation and heterogeneous catalytic ozonation promoted by Fe/MFI zeolite. A very fast degradation of the pharmaceutical compound is observed. A nearly total transformation (98%) of CIP is achieved in less than 15 min by single ozonation. However, an important amount of TOC (87%) still remains in the aqueous solution. The addition of 1 g L^{1} of Fe/MFI zeolite enhances the oxidation kinetics during the first 30 min. As it can be seen in Fig. 2, a total degradation of CIP is obtained after 5 min of reaction time. A 42% of the TOC is removed after 15 min in comparison to 13% obtained when single ozonation is applied. These results could be mainly due to two effects: (1) the formation of radicals due to the adsorption of ozone onto the catalyst surface and its further decomposition leading to the formation of surface-bound O-radicals and hydroxyl radicals, which are active oxidative species (Kasprzyk-Hordern et al. 2003), (2) and the enhancement in the adsorption of some of ozonation by-products with smaller size, being able to diffuse and being adsorbed onto zeolite active sites. Hence an increase in the removal rate of CIP takes place by catalytic ozonation at the solid–liquid interface, and by CIP homogenous oxidation reactions in the liquid phase closed to the zeolite surface.

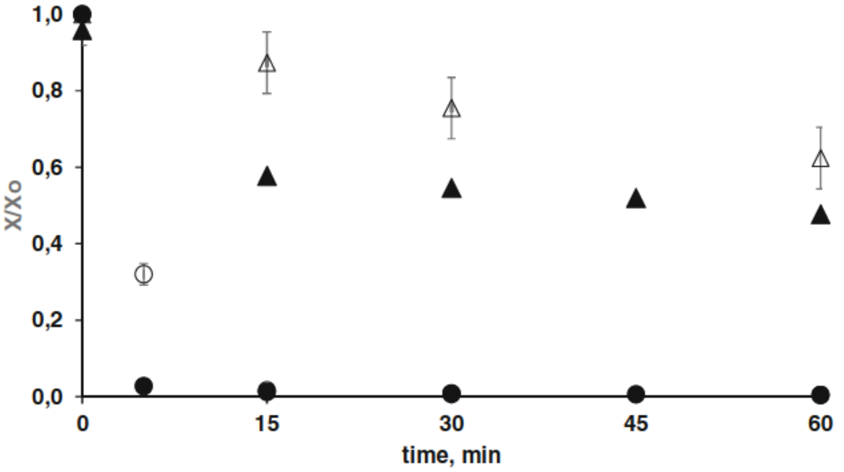


Fig. 2 Comparison of the variation of TOC and CIP concentrations during homogeneous and heterogeneous ozonation. Open markers represent single ozonation; filled markers mean heterogeneous catalytic ozonation promoted by Fe/MFI zeolite (1 g L^{1}): (○/●) dimensionless concentration of CIP and (Δ/▲) dimensionless concentration of TOC. Experimental conditions: 0.7 L of an aqueous solution of CIP with 100 mg L^{1} of initial concentration, continuous inlet flow of ozone (30 L h^{1}, 48 gO_3 m^{3}) at pH 3 and 30 °C

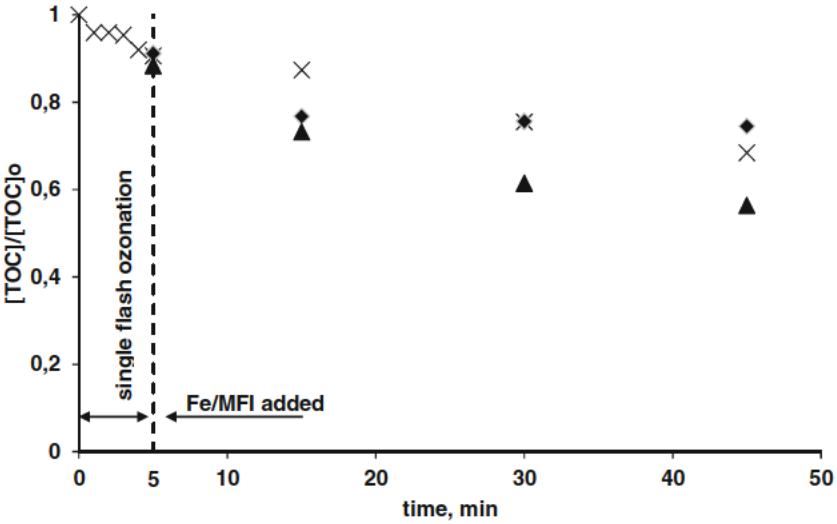


Fig. 3 Variation of TOC concentration (expressed as dimensionless concentration of TOC) during three different processes: (×) single ozonation during 45 min, (♦) 5 min flash ozonation followed by 40 min of adsorption onto Fe/MFI zeolite (1 g L^{-1}) and (▲) 5 min flash ozonation followed by 40 min of heterogeneous catalytic ozonation using Fe/MFI zeolite (1 g L^{-1}). Experimental conditions: 0.7 L of an aqueous solution of CIP with 100 mg L^{-1} of initial concentration, continuous inlet flow of ozone (30 L h^{-1}, 48 gO_3 m^{-3}) at pH 3 and 30 °C

Based on previous studies that reveal the formation of oxidation by-products during the ozonation of CIP molecule such as dealkylated and hydroxylated compounds, with smaller size and molecular mass than CIP molecule (De Witte et al. 2008; Liu et al. 2012), a sequential process was tested: a flash ozonation of the CIP solution during 5 min to transform large CIP molecules, followed by an adsorption process to remove small size oxidation by-products. Unfortunately, these ozonation by-products are hardly adsorbed, as it can be seen in Fig. 3. However, a better result is obtained when a catalytic ozonation process is applied instead of single adsorption. Under such conditions, a noticeable enhancement on the efficiency is found; up to 50% of TOC is removed after 40 min of catalytic ozonation.

Similar results were obtained by Sui and co-workers (Sui et al. 2012). A 38% reduction of TOC was achieved using catalytic ozonation promoted by MnO_2/MWCN, where a 30% of CIP remained adsorbed on the surface of MnO_2/MWCN. Therefore, the 25% of TOC removed from single ozonation compared to the 39% obtained after 25 min indicates that the presence of Fe/MFI zeolite increases TOC removal. Fe/MFI zeolite seems to provide a surface where CIP oxidation by-products are adsorbed and react with radicals generated from ozone interaction with active sites of zeolite surface.

In order to evaluate this behaviour, different Fe/MFI zeolite concentrations were used. Figure 4 shows the effects of the Fe/MFI zeolite concentration (0–10 g L^{-1}) in the TOC removal of

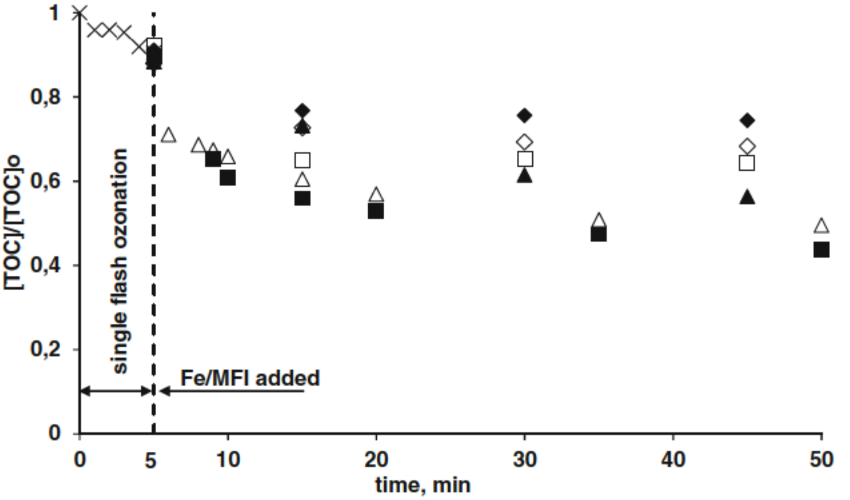


Fig. 4 Effect of the dosage of Fe/MFI zeolite during two different sequential processes (× stands for single flash ozonation during 5 min). Five minute single flash ozonation followed by 40 min of adsorption onto Fe/MFI zeolite using (♦) 1 g L^{-1}, (◇) (5 g L^{-1}) and (□) 10 g L^{-1}. Five minute single flash ozonation followed by 45 min of heterogeneous catalytic ozonation promoted by Fe/MFI zeolite using (▲) 1 g L^{-1}, (Δ) 5 g L^{-1} and (■) 10 g L^{-1}. Experimental conditions: 0.7 L of an aqueous solution of CIP with 100 mg L^{-1} of initial concentration, continuous inlet flow of ozone (30 L h^{-1}, 48 gO_3 m^{-3}) at pH 3 and 30 °C

the solution after 5 min of single flash ozonation. As it can be observed, TOC removal rate is improved as catalyst concentration is raised. TOC removal is enhanced for Fe/MFI zeolite load of 10 g L ^{1} (44%) within the first 15 min if compared with zeolite load of 1 g L ^{1} (27%).

During heterogeneous catalytic ozonation, TOC removal rate is increased to higher values than those obtained when a single ozonation process is followed by a single adsorption step, as it is shown in the Fig. 4. In this process, zeolite not only provides a contact surface where the CIP oxidation by-products and ozone are adsorbed, but also participates in ozone decomposition, yielding a higher quantity of hydroxyl radicals that increases TOC removal rate. Ozone could react with acid surface groups of metal oxide. Thanks to its resonance structure, ozone features high electron density on one of its oxygen atoms resulting in strong affinity to Lewis acid sites with the subsequent decomposition (Kasprzyk-Hordern et al. 2003). Adsorbed ozone on Lewis acid sites could convert to radicals (O_2 · or HO·), acting as initiators and/or promoters in free radical chain reactions (Valdés et al. 2010).

A kinetic study of CIP direct and heterogeneous catalytic ozonation with multi-walled carbon nano-tubes supported manganese oxides (MnO_2/MWCNT) as a catalyst has shown similar results, using Monte Carlo simulation, with respect to the effect of catalyst load (Jalali 2016). This method was applied with the purpose of modelling the experimental data for the ozonation of CIP over MnO_2 and MnO_2/MWCNT and (Sui et al. 2012). Under the experimental conditions investigated (pH 7, 25 °C, CIP concentration of 10 mg L ^{1}, and different initial amount of MnO_2 and MnO_2/MWCNT) a positive effect on CIP degradation is attained when the highest dose of MnO_2/MWCNT is applied. A lower pH value shows to be more favourable for CIP degradation in the catalytic ozonation. The efficiency of ozone treatment in the decontamination and regeneration of contaminated natural zeolite has also been evaluated by other research groups (Ötker and Akmehmet-Balcıoğlu 2005). Kinetic experiments for zeolite were performed using 200 mg L ^{1} of enrofloxacin solutions at pH values of 5, 7 and 10. It is claimed that a sufficient ozone concentration is able to decompose enrofloxacin adsorbed on natural zeolite, where enrofloxacin sorption interactions with natural zeolite are controlled by ionic functional groups resulting in ionic binding of the antibiotic and the zeolite (Ötker and Akmehmet-Balcıoğlu 2005). Catalytic ozonation in the removal of ibuprofen from water using ZSM-5 zeolites has been also investigated by Ikhlaq and collaborators (Ikhlaq et al. 2014). Different SiO_2/Al_2O_3 ratios were used. under different pH conditions in the range between 3 and 13 (490 mL of water spiked with 20 mg L ^{1} of ibuprofen, 5 g of catalyst, applying 0.5 mg min ^{1} of ozone flow rate, at 20°C). Results indicate that ibuprofen shows higher adsorption on zeolites at pH 3 than at pH 7.2 and 13. Furthermore, adsorption capacity of zeolite resulted to be dependant of the SiO_2/Al_2O_3 ratio. Catalytic ozonation using ZSM-5 zeolites is effective at pH 3 and 7.2, with the highest activity observed in the case of Z25 zeolites. However, zeolites did not show any activity at a basic pH of 13. This may be due to the high concentration of OH ions that are responsible for the high rates of aqueous ozone decomposition at pH 13 (Ikhlaq et al. 2014). Moreover, some other results show that heterogeneous catalytic ozonation using natural zeolite increases methylene blue removal rate with respect to the single ozonation process (Valdés et al. 2010, 2012a, b).

Kinetic modelling

In this section, a kinetic model was developed taking into account a synergistic mechanism that combines adsorption and oxidation reactions at the zeolite–liquid interface and oxidation reactions in the bulk-liquid phase. Similar approach has been proposed for cationic dye removal from contaminated waters using heterogeneous catalytic ozonation in the presence of natural zeolite, acid-treated natural zeolite and volcanic sand (Valdés et al. 2010, 2012a, b).

Hence, catalytic ozonation of CIP oxidation by-products (represented here as TOC) in the presence of Fe/MFI zeolite might include both direct reaction of molecular ozone and indirect reactions involving non-selective free radicals coming from ozone decomposition taking place in the bulk-liquid phase, adsorption of low molecular size CIP oxidation by-products at zeolite active sites and surface reactions of adsorbed complexes with molecular ozone and/or with free radicals. Assuming that the process rate is controlled by chemical reactions, ozonation of CIP oxidation by-products in the presence of Fe/MFI zeolite could be represented by a simplified and unbalanced reaction mechanism, comprising the two phases, as follows:

Bulk liquid phase reactions:

$$TOC + O_3 \quad \overset{k_2}{\rightarrow} \quad CO_2 + H_2O \; -\frac{d[TOC]_1}{dt} = k_1[O_3][TOC] \qquad (1)$$

$$TOC + R \quad \overset{k_2}{\rightarrow} \quad CO_2 + H_2O \quad -\frac{d[TOC]_2}{dt} = k_2[R][TOC] \qquad (2)$$

where, [TOC], [O_3] and [R] represent the concentration of CIP oxidation by-products analytically measured as Total Organic Carbon, dissolved ozone, and ozone decomposition reactive species in water (e.g. HO·, HO_2·/O_2· , O_3· , H_2O_2/HO_2), respectively.

Surface reactions at zeolite active sites (Z^*):

$$TOC + Z^* \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} Z^*-TOC \qquad r_3 = k_3\{Z^*\}[TOC] - k_{-3}\{Z^*-TOC\} \tag{3}$$

$$Z^*-TOC + O_3 \xrightarrow{k_4} CO_2 + H_2O \qquad r_4 = k_4[O_3]\{Z^*-TOC\} \tag{4}$$

$$Z^*-TOC + R \xrightarrow{k_5} CO_2 + H_2O \qquad -r_5 = k_5[R]\{Z^*-TOC\} \tag{5}$$

The overall rate of change of the surface complex concentration of CIP oxidation by-products $\{Z^*-\text{TOC}\}$ could be expressed as follows:

$$\frac{d\{Z^*-TOC\}}{dt} = k_3\{Z^*\}[TOC] - (k_{-3} + k_4[O_3] + k_5[R])\{Z^*-TOC\} \tag{6}$$

where $\{Z^*\}$ and $\{Z^*-\text{TOC}\}$ stand for surface concentration of zeolite active surface sites and surface complex of CIP oxidation by products, respectively. k_1 denotes rate constant of homogeneous reaction between CIP oxidation by-products and ozone (M^{-1} s^{-1}), k_2 is the rate constant of the homogeneous reaction between CIP oxidation by-products and radicals generated by ozone decomposition (M^{-1} s^{-1}), k_3 is the forward rate constant of surface complex formation of CIP oxidation by-products (M^{-1} s^{-1}), k_{-3} is the reverse rate constant of surface complex formation of CIP oxidation by-products (M^{-1} s^{-1}), k_4 is the surface reaction rate constant between CIP oxidation by-products and ozone (M^{-1} s^{-1}), k_5 is the surface reaction rate constant between CIP oxidation by-products and radicals generated by ozone decomposition (M^{-1} s^{-1}).

Applying the kinetic modelling recently proposed by Valdés and co-workers (Valdés et al. 2012a, b), the overall rate expression of catalytic ozonation of CIP oxidation by-products using ZSM-5 zeolite doped with iron oxide nanoparticles could be represented as a sum of bulk-liquid and surface reactions at zeolite active sites:

$$-r_{overall} = r_{bulk} + r_{surface} = \left(k_{bulk} + k_{surface}\{Z^*\}\right)[TOC] \tag{7}$$

Integrating, with initial conditions $[TOC]_t = [TOC]_0$ leads to:

$$\ln\frac{[TOC]_t}{[TOC]_0} = -k_{overall}t \tag{8}$$

with,

$$k_{overall} = k_{bulk} + k_{surface}\{Z^*\} \tag{9}$$

where, r_{bulk} and $r_{surface}$ are removal rates of CIP oxidation by-products in the bulk-liquid phase and at the active sites of zeolite surface, respectively. k_{bulk} and $k_{surface}$ represent pseudo-first-order rate constant of ozonation reactions taking place in the bulk-liquid phase and pseudo-second-order rate constant of the degradation of CIP oxidation by-products due to surface ozonation reactions, respectively. $[TOC]_t$ and $[TOC]_0$ are the concentration of CIP oxidation by-products globally determined as Total Organic Carbon at any time t and time zero, respectively. Such kinetic model is limited in this study to describe catalytic ozonation of CIP oxidation by-products using ZSM-5 zeolite doped with iron oxide nanoparticles without mass transfer limitations.

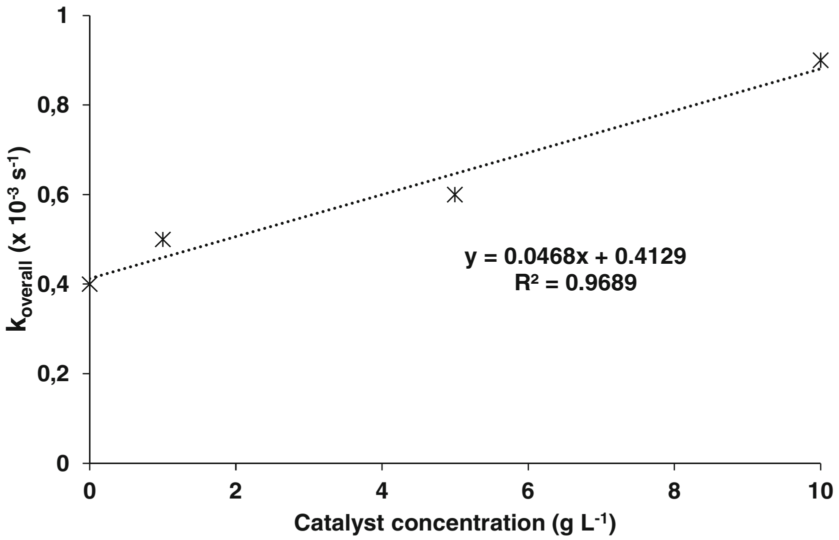


Fig. 5 Variation of pseudo first order rate constants of overall reactions of CIP oxidation by products ($k_{overall}$) as a function of zeolite concentration. Experimental conditions: 0.7 L of an aqueous solution of CIP with 100 mg L^{-1} of initial concentration, continuous inlet flow of ozone (30 L h^{-1}, 48 gO_3 m^{-3}) at pH 3 and 30 °C

Table 4 Variation of mineralisation and biodegradability indicators after each treatment process using real wastewater spiked with 100 mg L^{-1} of CIP

Treatment/time	TOC (mg O_2 L^{-1})	TOC removal (%)	BOD_5 (mg O_2 L^{-1})	BOD_5 removal (%)
Effluent	76		110	
Single ozonation of CIP (15 min)	41	46	< 2	> 98
Single flash ozonation of CIP (5 min) followed by the adsorption of CIP oxidation by products onto Fe/MFI (1 g L^{-1}) (15 min)	48	36	6	94
Single flash ozonation (5 min) followed by heterogeneous catalytic ozonation with Fe/MFI (1 g L^{-1}) (15 min)	36	52	< 2	98

The contribution of surface and bulk-liquid phase reactions to the catalytic ozonation of CIP oxidation by-products using Fe/MFI zeolite is estimated using Eq. (9), at pH 3. A series of experimental runs were performed with different zeolite concentration (see Fig. 5) and pseudo-first-order rate constants of overall oxidation reactions of CIP by-products, $k_{overall}$, were obtained from initial rate data.

Figure 5 illustrates the results of plotting the estimated $k_{overall}$ values as a function of zeolite concentration. Thus, the value of the pseudo-second-order rate constant of the degradation of CIP oxidation by-products due to surface ozonation reactions ($k_{surface} = 0.0468 \times 10^{-3}\ g^{-1}\ L\ s^{-1}$) and pseudo-first-order rate constant of ozonation reactions taking place in the bulk-liquid phase ($k_{bulk} = 0.4129 \times 10^{-3}\ s^{-1}$) are obtained from the line slope and the intercept of the line with "*Y*" axis, respectively.

Fe/MFI zeolite not only offers a contact surface for the adsorption and oxidation of CIP oxidation by-products but also takes part in aqueous ozone decomposition. Active surface sites of Fe/MFI zeolite could contribute to ozone decomposition, acting as initiators and/or promoters of radical chain reactions. Ozone could be adsorbed and decomposed at acidic sites of Fe/MFI zeolite such as acidic OH groups (Brønsted acid centres), "true" Lewis sites (aluminium-containing extra-framework species), generating surface radicals (Ni and Chen 2001; Einaga and Futamura 2005; Kwong et al. 2008; Valdés et al. 2012a, b) that react with adsorbed CIP oxidation by-products. A radical chain reaction continues in the bulk-liquid phase leading to the formation of an ozonide anion, $O_3^{\cdot -}$, by the transfers of an electron from $O_2^{\cdot -}$ to another ozone molecule, which is the chain reaction promoter and produces HO· radicals, contributing to organic oxidation in the liquid phase (Valdés et al. 2012a).

Influence of treatment process on effluent's mineralisation and biodegradability

Table 4 shows experimental results of TOC and BOD_5 analyses after different sequential treatment processes using real wastewater spiked with CIP and adjusted to pH 3. As it can be observed in Table 4, BOD_5 value increases when CIP is added, being CIP the major organic compound in this matrix.

Each sequential treatment process reduces the value of BDO_5 from 110 to less than 2 mg O_2 L^{-1} after 15 min. When wastewater sample is ozonated during 5 min and then adsorption onto the zeolite takes place, the BOD_5 is slightly superior with 6 mg L^{-1} compared to the other treatments. In the experiments, TOC is reduced from 41 to 36 mg O_2 L^{-1} when single flash ozonation (5 min)-followed by heterogeneous catalytic ozonation (15 min) is applied compared to single ozonation (15 min) corresponding in both cases to the reduction of the BOD_5 compared to the initial BOD_5 of the effluent. These experiments display in a better way the results than those obtained without matrix effect. It is well known that the stability of ozone is mainly determined by its reaction with organic matter, carbonates and bicarbonates normally presented in water. They could act as inhibitors or radicals scavengers, prolonging the lifetime of ozone at typical pH values of wastewater (pH ≤ 8.5) (Von Sonntag and von Gunten 2012).

Conclusions

The results presented here demonstrate that single ozonation treatment can easily oxidise CIP molecules; however, low TOC removal is obtained due to the generation of refractory CIP oxidation by-products. An improvement in the mineralisation rate is achieved when heterogeneous catalytic ozonation is applied, using ZSM-5 zeolite doped with iron oxide. An increase on TOC removal rate occurs, from 13% for single oxidation to 42% for catalytic oxidation. A new sequential process is proposed in order to improve the efficiency of the mineralisation. In a first step, a single flash ozonation breaks down ciprofloxacin molecules. Then, a catalytic ozonation step promoted by Fe/ZSM-5 zeolite leads to a noticeable enhancement on the efficiency, achieving up to 50% of TOC elimination after 40 min of heterogeneous catalytic ozonation. In this heterogeneous system, the elimination of CIP oxidation by-products could be described by a synergistic mechanism that combines adsorption and oxidation reactions at the zeolite–liquid interface and oxidation reactions in the bulk-liquid phase. A sequential process of two-steps, conformed by flash ozonation followed by catalytic ozonation, could be a hopeful advanced oxidation process for the removal of non-biodegradable complex molecules with a high molecular mass and size.

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