EVALUATION OF HETEROGENEOUS CATALYTIC OZONATION PROCESS FOR DICLOFENAC DEGRADATION IN SOLUTIONS SYNTHETICALLY PREPARED

Jenny Castro[1], Santiago Paz[1], Natali Mena[2], Julián Urresta[2], Fiderman Machuca[1]

Abstract

Sodium diclofenac (DCF) is a common analgesic and anti-inflammatory drug, due to its growth and accumulation into water bodies it has become an environmental problem. In this work technical and analytical DCF mineralization by means of heterogeneous catalytic ozonation was studied. The process was carried out with magnetite (Fe_3O_4) as a catalyst, which preserve its physical and chemical properties during the process. The best results of mineralization were obtained after a 40 minutes treatment of 35 mg/L analytical DCF solution, with a 0.5 g/L catalyst concentration. These results showed the highest organic load decrease, measured as dissolved organic carbon (DOC) and chemical oxygen demand (COD), with 94% and 89%, respectively. In addition, the percentage of organic load decrease was compared between the conventional and the catalyzed process. Besides, reaction products were identified by Gas Chromatography–Mass Spectrometry (GC-MS) and the catalytic properties were identified by Mössbauer spectroscopy, which showed catalyst maintained its nature after the process. Finally, the results obtained show that the heterogeneous catalytic process could be an efficient degradation treatment for emerging contaminants such as DCF.

Keywords

Ozonation, diclofenac, magnetite, heterogeneous catalysis, wastewater, catalytic activity, emerging pollutants.

1. Introduction

Many commonly drugs such as sodium diclofenac, DCF (Fig1), are not completely retained and eliminated from conventional wastewater treatment systems, being discharged directly into water bodies. In Colombia, about 7569 tons of pharmaceutical waste are generated per year (IDEAM, 2014-2015), and the last decade, the group of 28 countries that comprises the European Union, reported discharges to the water around 25350 tons of analgesics per year (CEVIME, 2016), where DCF has reached concentrations of 3.02 μg/L (Jiménez, 2011); its increase could cause human health affectations, especially of living beings that inhabit aquatic environments, with alterations in mitochondrial activity and DNA changes (Feito et al., 2012).

1. Grupo de Investigación de Procesos Avanzados para Tratamientos Químicos y Biológicos (GAOX)-
Universidad del Valle, Calle 13 No. 100-00
jenny.castro@correounivalle.edu.co
santiago.paz@correounivalle.edu.co
fiderman.machuca@correounivalle.edu.co

2. Laboratorio de Investigación en Catálisis aplicada y Procesos (LICAP)
Universidad del Valle, Calle 13 No. 100-00
natali.mena@correounivalle.edu.co
julian.urresta@correounivalle.edu.co

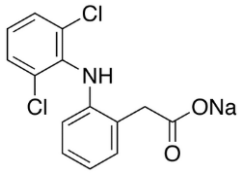


Fig1. DCF molecular structure.

Despite of this situation, the organic compounds degradation into the water is not yet regulated in some third world countries like Colombia, and there is no legislation that establishes the maximum allowed values of drug concentration in wastewater. However, in this country the 2676 decree of December 22 and the Technical Regulation of Drinking Water and Basic Sanitation (RAS) of 2000, establishes the regulations for the collection, transportation, and integral management of hospital waste, in order to regulate the presence of pharmaceutical waste into aquatic environments and drinking water.

To mitigate the impact caused by pharmaceutical waste, especially DCF into aquatic ecosystems and drinking water systems, several advanced oxidation processes have been evaluated in order to reduce organic polluting substances to CO_2 and H_2O. Moreira et al. (2015), evaluated DCF degradation using advanced oxidation processes, such as conventional ozonation, photolysis and photolytic ozonation. Photolysis and ozonation never reached TOC decrease higher than 6% and 41%, respectively, during a 180 minutes treatment. It was concluded that, although ozone is a powerful oxidant of aromatic compounds, it reacts slowly with other species, leading to the byproducts accumulation, such as carboxylic acids and carbonyls compounds that ozone cannot oxidize easily. On the other hand, with the photocatalysis process, approximately 15% of non-oxidizable organic compounds such as oxalic acid remained after 180 minutes. In the photolytic ozonation case, TOC decrease kinetic was slow, even reaching 95% degradation, but after 300 minutes, and using photocatalytic ozonation it was reached a completed DCF mineralization after 120 minutes.

Another combined method of advanced oxidation, among which heterogeneous catalytic ozonation stands out, have been used for the DCF decomposition and degradation study. Photocatalysis, using TiO_2 as a catalyst, reached 45% DCF mineralization in 30 minutes of degradation, due to NH_4^+ ions generation and, to a lesser extent, NO_3^-, which reduced CO_2 formation (Calza et al., 2006). Zhao et al. (2009), studied DCF electrochemical degradation using boron-doped-diamond (BDD) with a 4V potential reaching 72% of mineralization after a 240 minutes treatment, due to the intermediates presence such as benzoic acid, which reduced the DCF degradation rate. Barbosa et al. (2015), reached a 70% COD reduction using a current density of 30 mA/cm^2 for 360 minutes.

The heterogeneous catalytic ozonation using iron oxides as catalysts has proved to be a highly efficient process in the pollutants reduction in wastewater, since it allows improving the direct reaction between ozone and DCF. Thanks to its redox properties, Fe_3O_4 is widely used in oxidation processes of organic compounds, such as phenols, dyes and polycyclic aromatic hydrocarbons (Pouran et al., 2014). Mena (2014) used an active Fe_3O_4

surface as a reaction medium between ozone and organic molecules, improving the organic matter degradation rate and allowing high efficiencies of the process, with COD and DOC decrease up to 60%. Additionally, catalytic ozonation is more profitable compared with conventional techniques due to the low cost related to the process, equipment maintenance, catalyst separation and especially low sludge formation.

The reactions with ozone are characterized by the high interaction with several compounds, leading to direct reactions with the polluting agent, or indirect reactions by means of hydroxyl radicals. In this investigation the ozonation process was carried out at an acidic pH (3-5), allowing the direct oxidation of ozone with the unsaturated bonds present in the DCF molecule in a more selective way, due to the bipolar structure of the ozone, which makes it a strong electrophile and allows it to react in the highest electron density positions; while the reactions initiated by the interaction between radicals are more aggressive and there is no control over the reaction. (Eriksson, 2015)

2. Materials and methods

2.1. Chemicals

Technical injectable sodium DCF, from Genfar, 25mg/mL. Analytical sodium DCF powder, from Sigma. Analytical potassium iodide (KI) powder, from Panreac. Technical Fe_3O_4 powder, 95%, from Aldrich. Sodium thiosulfate solution ($Na_2S_2O_3 \cdot 5H_2O$) 0.1N. Starch solution 5%. Sulfuric acid solution (H_2SO_4) 2N. Solutions were prepared using deionized water, and based on the Iodometric Method I 4500-Cl B (Eaton et al., 2012). For the experiments carried out at basic pH, the pH of the solution was adjusted with sodium hydroxide (NaOH).

2.2. Fe_3O_4 catalyst activation

For the catalyst activation, Fe_3O_4 and H_2SO_4 2N solution were added with 6mg/mL proportion. To ensure continuous contact with the surface of the catalyst, a PTFE mechanical stirrer at 250 rpm was used for two hours and then a vacuum filtration was performed to remove the remaining acid.

2.3. Experimental procedure

Ozonation experiments were performed within a 2750 cm^3 glass reactor. Ozonation equipment scheme is shown in Fig2. An ozone generator, from Pacific Ozone, adapted in a local laboratory at Universidad del Valle, using pressurized oxygen as a feed gas, obtained from a CRYOGAS cylinder, with 2900 psia of internal pressure. The ozone produced was regulated by a rotameter, and a 24.18 mg/min ozone flow was directed to the reactor, which contained 250 mL of DCF solution and Fe_3O_4; it was distributed uniformly throughout the solution by means of a porous glass diffuser. The catalyst was stirred with a magnetic field given by a magnet. The

ozonation time was 40 minutes. To quantify the process performance, the non-reactive or residual ozone was directed towards an ozone trap.

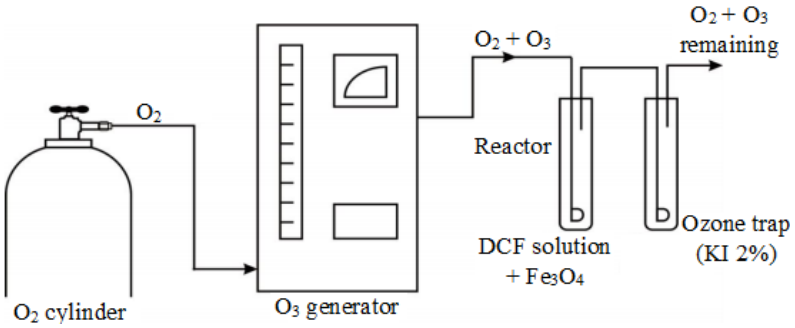


Fig2. General scheme of ozonation (Mena, 2014)

2.4. Ozone trap

The ozone trap was prepared with a 2% KI solution, which reacted with ozone; 2 mL of H_2SO_4 2N solution was added, and it was titrated with $Na_2S_2O_3 \cdot 5H_2O$ solution until it turned yellow. Finally, 2 mL of a 5% starch solution was added, and it was titrated until obtaining a translucent solution. $Na_2S_2O_3 \cdot 5H_2O$ spent allowed to calculate the residual ozone using of Eq1, thus the efficiency of the process was determined.

2.5. Analytical methods

DOC measurement was carried out using a SHIMADZU TOC VCPH Total Organic Carbon Analyzer. The samples were prepared and analyzed according to the 5310-B analysis from the Standard Method. The samples were filtered with 0.45 μm membranes to ensure the effectiveness of DOC measurement.

For COD measurement, a reactor was initially used to digest the samples during 120 minutes at 150°C ± 2°C, as established in the 5220 standards; then, a SHIMADZU UV 1800 spectrophotometer was used at 360 nm wavelength.

Tests which obtained the highest percentages of organic load reduction (COD and DOC) were analyzed in a Shimadzu gas chromatograph model QP2010 Plus, with UV-Vis G1314A detector, selective mass detector, electrons bombardment at 70 eV and 200°C as injection temperature.

Infrared spectrophotometer FT-IR Jasco was used with an ATR cell to analyze the vibrational spectra and remnant compounds on the Fe_3O_4 after the heterogeneous catalytic ozonation process. An equipment for Fe Transmission Mössbauer spectroscopy was used with a Co source with 100 mCi of initial activity, inside a Rh matrix. The isometric deviation value and the speed scale was calibrated with respect to α-Fe at 300K, (δ =

0.12). The different samples were adjusted with the MOSF program, based on an independent model of distribution of hyperfine fields or quadrupole splits.

2.6. Experimental design

A random 2x3x3 experimental factorial design (18 tests) with trials was used, with two levels for the quantitative variables: DCF concentration and Fe_3O_4 concentration; and a level for the qualitative variable: DCF type (technical and analytical), in order to evaluate the conditions that generate the greatest effect in DCF concentration decrease. The response variables were fixed as parameters of final water quality (COD and DOC).

2.7. Residual ozone quantification

To determine the process efficiency, the non-reactive ozone was measured, according to the iodometric method described of the Standard Methods 2350B, using the residual ozone dose equation in mg/min, as shown in Eq1.

$$\text{Ozone Dose } \left(\frac{\text{mg}}{\text{L}}\right) = \frac{(\text{A}+\text{B})*\text{N}*24}{\text{T}}$$

Eq1. Residual ozone dose in the process

Where:
A: $Na_2S_2O_3$ used in trap A (mL)
B: $Na_2S_2O_3$ used in trap B (mL)
N: Normality of $Na_2S_2O_3$
T: Ozonation time (minutes)

In this study, only one ozone trap (Trap A) was used for the process, therefore, in the Eq1, B is equal to zero; the normality calculated for Na_2SO_4 was 0.0976.

3. Results and discussion

3.1. DCF and Fe_3O_4 characterization

The initial characterization of technical and analytical DCF samples (10, 35 and 60 mg/L) was performed related to DOC and COD, as shown in table 1.

Table 1. Initial characterization of DCF solutions

[DCF] (mg/L)	DCF type	DOC (mg/L)	DQO (mg/L)	pH
10	Technical	259.35	1501.81	4.55
	Analytical	230.59	807.26	4.37
35	Technical	606.15	1944.88	4.38
	Analytical	283.60	1441.93	4.19
60	Technical	1065.65	2950.78	4.40
	Analytical	407.10	867.13	4.40

Additionally, analytical and technical DCF samples were characterized using FTIR. In the FTIR spectrum of analytical DCF characteristic peaks were evidenced at 3385 cm^{-1} (NH secondary amine stretching), 3217 cm^{-1} (OH group tension), 1574 cm^{-1} (–C=O carboxyl ion stretching), 1557 cm^{-1} (C=C ring stretching), 1548 cm^{-1} (C-O bond tension), 943 cm^{-1} (OH group flexion) and in 746 cm^{-1} (C-Cl stretching) (Baena, 2011 and Kebebbe et al., 2010), as shown in Fig3a and Fig3b. Mass spectra were performed using electrons bombardment where characteristic signals, based on charge/mass (m/z) relation, of analytical DCF (295, 242, 214, 179, 151, 107, 89 and 78 m/z) (Yilmaz et al., 2015) and technical DCF (327 281, 267, 230, 195, 167, 139 and 109 m/z). (NIST Standard Reference Data, 2017) samples were evidenced.

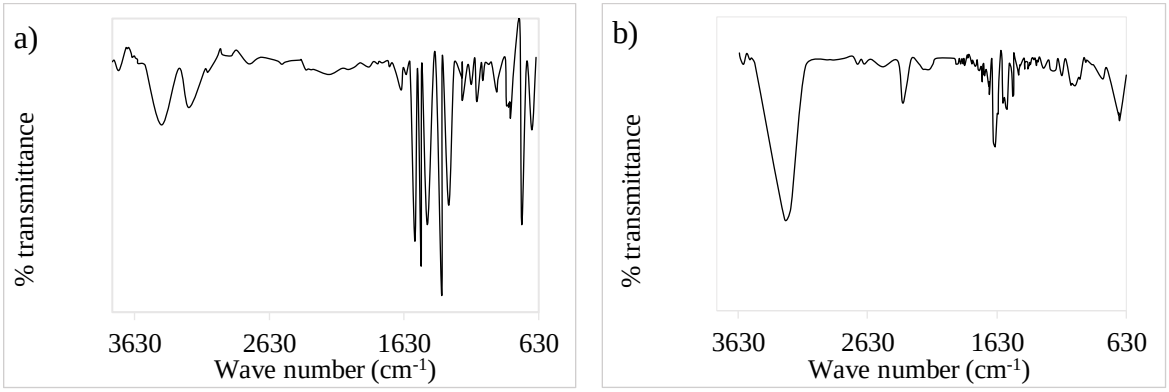


Fig3. Initial FTIR for a) analytical DCF. b) technical DCF.

On the other side, iron oxide was characterized, this material has an intrinsic magnetic field due to its atomic structure, and the magnetic moments that depend on the spin-orbit coupling are oriented in a preferential direction, causing its own magnetic field. In this study, a Mössbauer spectroscopy was performed on the initial catalyst (Fe_3O_4), (Fig4a), and recovered catalyst (Fig4b), that presented the best results of organic load decrease after the ozonation process. Fig4b shows there were no deviations in the preferential direction of the spins, these deviations could be produced by a possible adsorption of another particles in the Fe atom neighborhood (Pérez et al., 1993). Additionally, even when there was molecular adsorption on the catalyst during the process, these

molecules were desorbed to the medium, which could demonstrate why the catalyst preserved its magnetic and catalytic properties after the process, according to the Mössbauer spectroscopy.

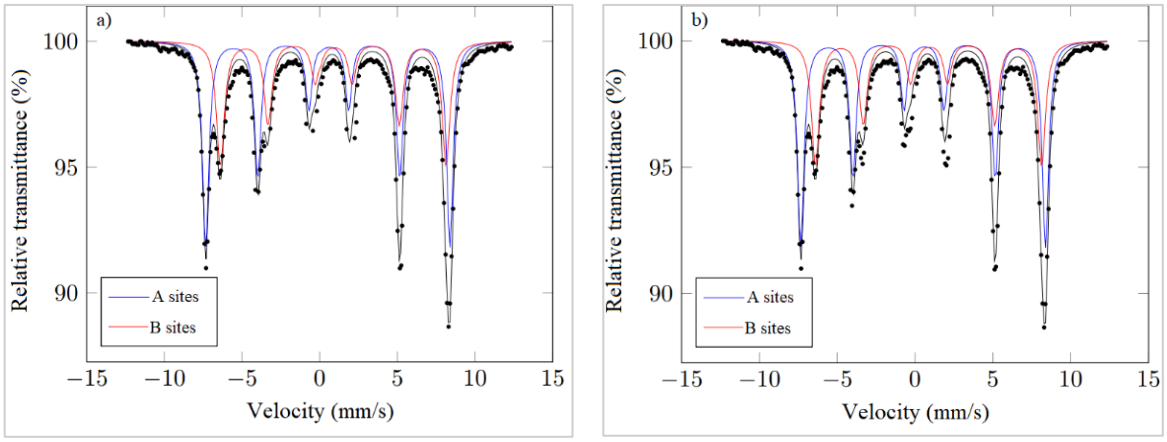


Fig4. Mössbauer spectroscopy (a) before ozonation process, (b) after ozonation process.

Besides, Fe_3O_4 is characterized within iron oxides by having an atomic structure of inverse spinel. Within this atomic arrangement exist sites A and sites B, where sites A contains iron atoms with valence +3 and sites B contains two iron atoms, one with valence +3 and another with valence +2 (Chean et al., 2007). These characteristics were maintained after ozonation process (Fig4), which showed that the catalytic solid did not change its nature, and it was preserved as 95% Fe_3O_4 (valence +3) and 5% maghemite (valence +3 and valence +2).

3.2. Analysis of organic load measured as COD and DOC

The highest percentages of organic load decrease measured as COD and DOC, after the heterogeneous catalytic ozonation process, were obtained using the highest catalyst concentration, 0.5 g/L, (Fig5).

.

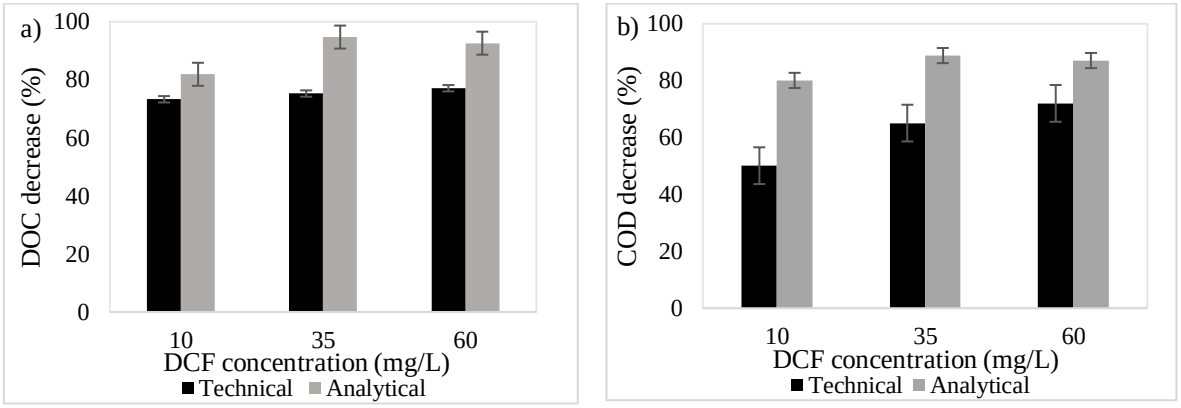


Fig5. a) DOC decrease. b) COD decrease.

Percentage of DOC decrease was lower than COD decrease, as shown in Fig5, possibly due to the presence of chloride ion or residual chlorine after the DCF ozonation, which interfered within COD measurement. GC-MS showed signals related to a peak of 35 m/z, corresponding to the Cl molecular weight with intensity of 55 (Fig6).

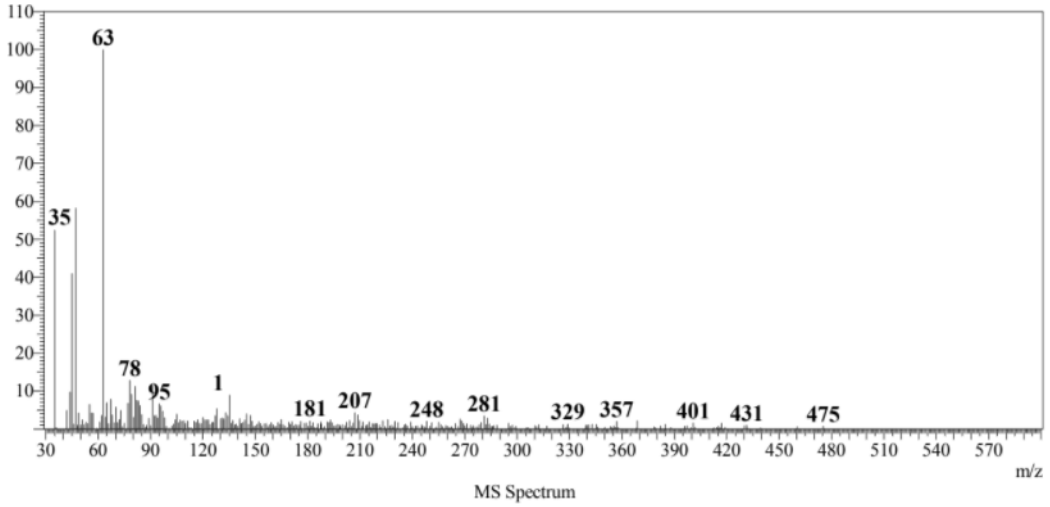


Fig6. Mass spectra after DCF ozonation process.

Organochlorinated species are formed by chlorine-hydrocarbons union, these compounds are classified within persistent environmental contaminants. For this reason, advanced oxidation processes such as ozonation tend to reach the mineralization of this type of molecules to minimize the chlorinated byproducts formation, among others, and to obtain only H_2O and CO_2 as products of the process. Although Zhihui et al. (2015), established that some oxidation process conditions lead to the C-Cl bond breakdown (347.27 ± 4.18 kJ/mol) (Arunan, 1997) which is energetically easier to break compared to C-OH bond (377 ± 13 kJ/mol) (Darwent, 1970). Coelho et al. (2009), showed that among the byproducts of DCF ozonation, long chain compounds such 2-[2,6-dichlorophenyl)amino]-5-hydroxyphenylacetic acid and 2,6-dichloro-4-hydroxybenzenamine were identified, in which chlorine remained stable. On the other hand, Alimoradzadeh et al. (2012) analyzed 4-chlorophenol degradation and established that high values of COD are related to the presence of persistent chlorinated compounds in the process.

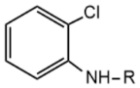
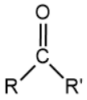
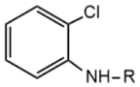
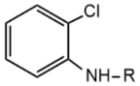
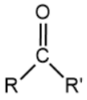
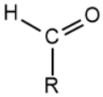
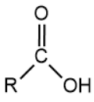
The synthetic solutions characterization before the heterogeneous catalytic ozonation process showed an initial pH of 4.32 and 4.11 for analytical and technical DCF, respectively. These pH values decreased after the process until around 3.4. Harttmann et al. (2008), concluded after a DCF oxidization by TiO_2 catalyzed sonolysis that the final products from complete mineralization were HCl and CO_2. According to Yang et al. (2007) and Alimoradzadeh et al. (2012) the pH decrease is related to the union of chlorine atom with H^+ ion, which come from water, allowing the acid compounds formation such as HCl, as shown in Reac1.

$$ClC_6H_4OH + \frac{13}{2} O_2 \rightarrow 6CO_2 + HCl + 2H_2O$$

Reac1. HCl formation (Rao et al. 2003)

Other chemical species such as saturated hydrocarbons, azo compounds (R-N=N-R´), halogenated aromatic nitrogen compounds, ketones, aldehydes and carboxylic acids were found after ozonation process by GC-MS, as shown in Table 2.

Table 2. Chemical species found by GC-MS after ozonation process

[DCF] (mg/L)	DCF Type	[Fe_3O_4] (g/L)	DOC decrease (%)	COD decrease (%)	Identified species	GC-MS Retention time (min)	Area (%)
10	Technical	0.1	33.52	66.36		3.99	40.84
						4.03	26.33
	Analytical	0.3	34.49	54.51	R═R'	3.97	42.13
					R—R'	4.04	31.05
					R—Cl	4.00	26.82
35	Technical	0.5	65.09	75.27	R═R'	4.04	35.37
					R—R'	3.97	28.84
	Analytical	0.5	88.84	94.73		3.99	44.03
60	Technical	0.5	72,03	77,1		4.01	41.92
	Analytical	0.3	79,9	37,52		3.99	36.35
						4.03	17.65
						4.22	4.40

In this study it was used the Pareto chart of standardized effects, shown in Fig7, which determined the catalyst concentration ([Fe_3O_4]) and DCF type as the greatest influence variables during the process, similar as it was shown in Fig5.

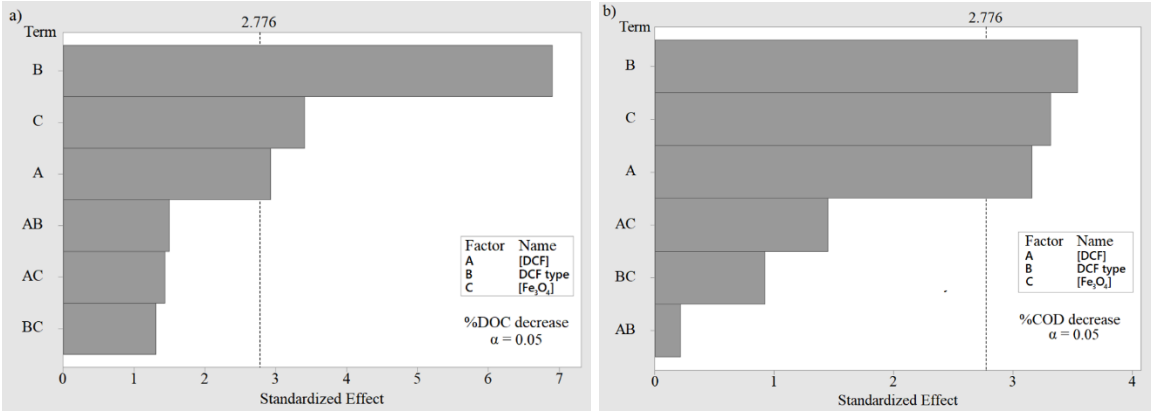


Fig7. Pareto chart of standardized effects related to (a) DOC, (b) COD.

Organic load decrease efficiency was higher as the catalyst concentration increased, since it allowed a greater contact surface between DCF and ozone, facilitating the DCF breaking up. On the other hand, analytical DCF is excipient free, unlike technical DCF, which can contain benzyl alcohol (C_7H_8O), sodium metabisulfite ($Na_2S_2O_5$), propylene glycol ($C_3H_8O_{12}$), sodium hydroxide (NaOH) and water. These compounds can increase organic load of the solutions for study, causing possible oxidation route changes, during the ozonation process, which could lead to several reaction mechanisms and different type of intermediaries and byproducts that could be harder to degrade, affecting the mineralization percentage, after ozonation.

For analytical DCF, the highest mineralization result reached was 89% after 40 minutes and 0.5 g/L of Fe_3O_4. Mössbauer spectroscopy determined that did not occur detectable organic matter adsorption on the catalyst surface (Fig4), hence the intrinsic nature of the heterogeneous catalyst was not modified.

3.3. Influence of pH

pH has a great influence on the catalytic ozonation due to its effect in the ozone decomposition on the catalyst surface, since pH determines the stability of the ozone molecules dissolved in water and also indicates the way in which the ozonation process occurs (Hikmat et al., 2017). With a pH increase towards an alkaline value, indirect ozonation is favored, surface density of hydroxyl groups becomes larger and more OH• are generated. Although, it is possible that the degradation efficiency is affected. This negative effect can be attributed to the disappearance of OH•, since ozone generates more radicals such as HO_2•, HO_3• and O_3^-•, which reacting between them, result in the disappearance of the OH• radical. On the other side, the effect of an acidic pH allows the DCF degradation and mineralization to be carried out by the direct reaction of the ozone. In addition, ozone reacts selectively with some organic compounds such as aromatic rings and substituted aromatic compounds, because they present unsaturated bonds. Thus, oxidation is more controlled, and it is more efficient to reduce the organic load (Gunten, 2003). In this study, tests were performed at low pH (3-5), favoring the direct reaction of ozone with DCF on the catalyst surface, these conditions allowed the formation of short-chain organic species, as it was shown in Table 2.

3.4. Viability of oxidation process using catalyst

In order to determine the viability of the ozonation process by using Fe_3O_4 as a catalyst, conventional ozonation tests without catalyst were performed (Fig 8), and the results were compared to the process catalyzed by Fe_3O_4.

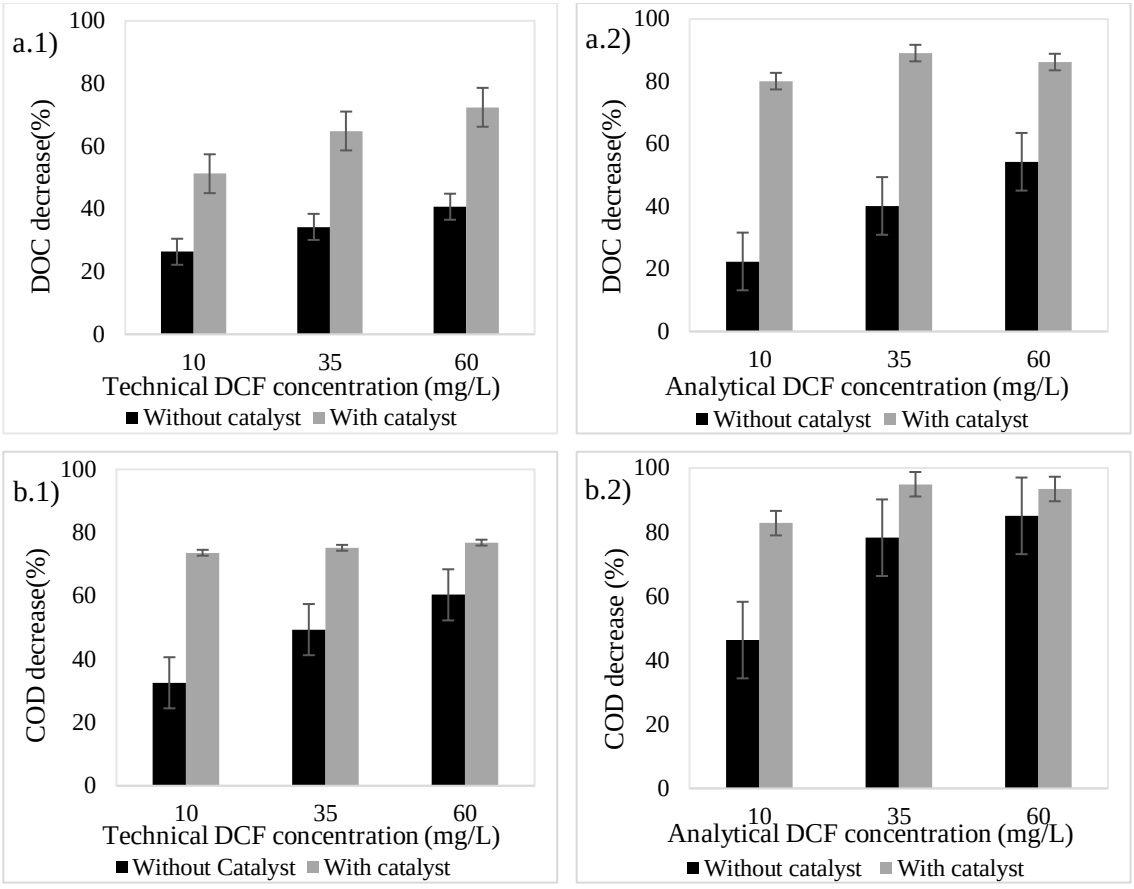


Fig8. Conventional and catalytic ozonation process comparison, a.1) DOC decrease using Technical DCF, a.2) DOC decrease using Analytical DCF, b.1) COD decrease using Technical DCF, b.2) COD decrease using Analytical DCF.

By keeping the catalyst suspended homogeneously, due to the ozone bubbling into the reactor and the magnetic field generated by a magnet, a possible stable distribution of the catalyst and a greater contact surface with the DCF solution were generated, reaching percentages of COD and DOC decrease about 89% and 95%, respectively, in a 40 minutes treatment, which indicates a fast reaction rate. In this way, using catalyst decreased the amount of ozone and process time, improving the percentages of organic load decrease compared with the conventional process, which allows proposing the implementation of Fe_3O_4 on a large scale without additional economic costs associated with its subsequent separation. (Huang et al., 2012)

Mena (2014), evaluated possible economic costs associated with heterogeneous catalytic ozonation process finding that, although it is more expensive than traditional wastewater treatment, processes such as flocculation,

wetlands and oxidative lagoons, could compete with ion exchange, electro-oxidation and photocatalytic processes.

3.5. Catalyst stability over time

Fe_3O_4 is a mixed iron oxide, which chemical structure is $(Fe^{3+})_{tet}[Fe^{2+}Fe^{3+}]_{oct}O_4$, constituted by 31.03% of FeO and 68.97% of Fe_2O_3. Through FTIR analysis of Fe_3O_4 powder before experimental tests (Fig9), it was observed that its characteristic absorption bands are between 630 and 930 cm^{-1}, these peaks are caused by vibration of Fe-O bonds presents in Fe_3O_4 structure (Ivashchenko et al., 2016).

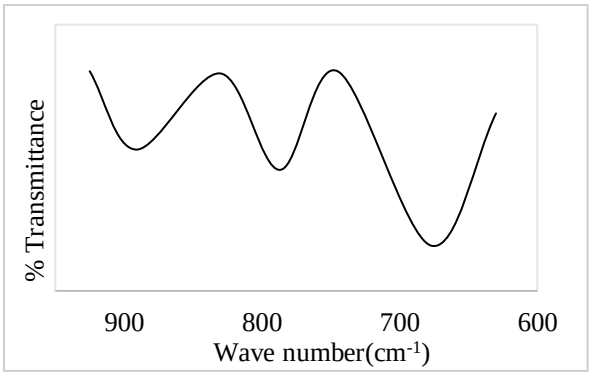


Fig9. Fe_3O_4 FTIR before ozonation process.

After the heterogeneous catalytic ozonation process all the samples of experimental design (18 tests) performed the same behavior, conserving their nature as catalysts; due to there was no evidence of changes in the absorption bands in the FTIR spectra corresponding to the vibrations of Fe-O bonds from FeO and Fe_2O_3 molecules present into the Fe_3O_4 (Fig10).

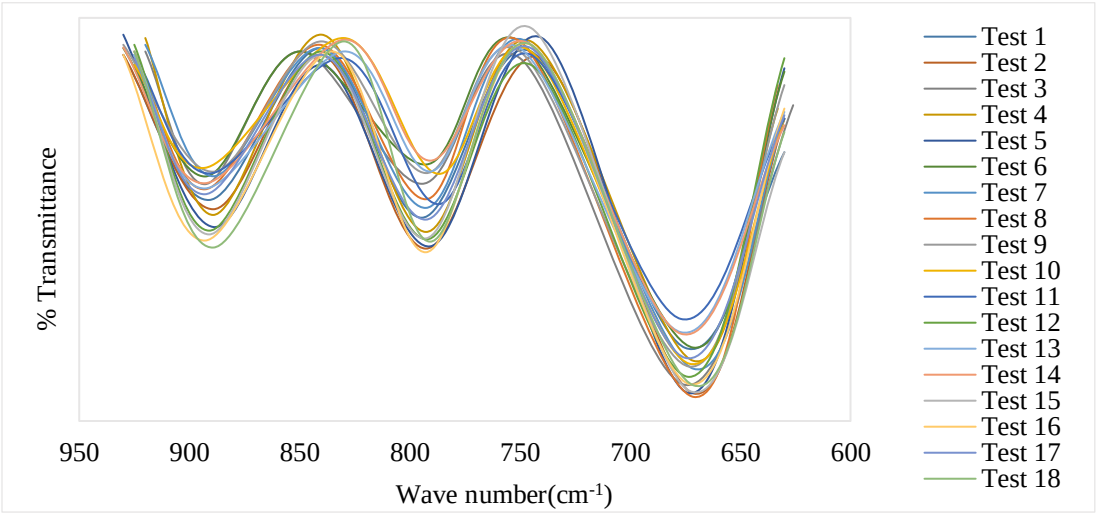


Fig10. Fe_3O_4 FTIR of all experiments after ozonation process.

Catalyst contains Fe^{2+} and Fe^{3+} species, with a magnetic moment of 4.90 and 5.92 (Parks et al., 1968), respectively, which allows it to attract other compounds to its surface by means of electrostatic forces; moreover, since Fe_3O_4 is in its highest oxidation state, it reaches a stable state where it is not oxidized with the ozone of the medium, so it could be used as a catalyst without presenting physical or chemical changes in its structure and/or catalytic activity. Studies of its implementation in the alkylation process of amines (Martínez et al., 2009) show that the catalyst remains active up to 10 cycles without loss of its properties.

The activity, stability and catalyst reuse are important factors in its application. If it is unstable or easily deactivated, its practical application is not viable. Therefore, the study of stability and continuous use of the same catalyst sample in several catalytic cycles was carried out using the solid sample during three consecutive experimental tests under the same process conditions. No significant loss of activity was observed, due to the rate of organic load reduction measured as DOC and COD remained similar throughout the sequential experiments (Fig 11).

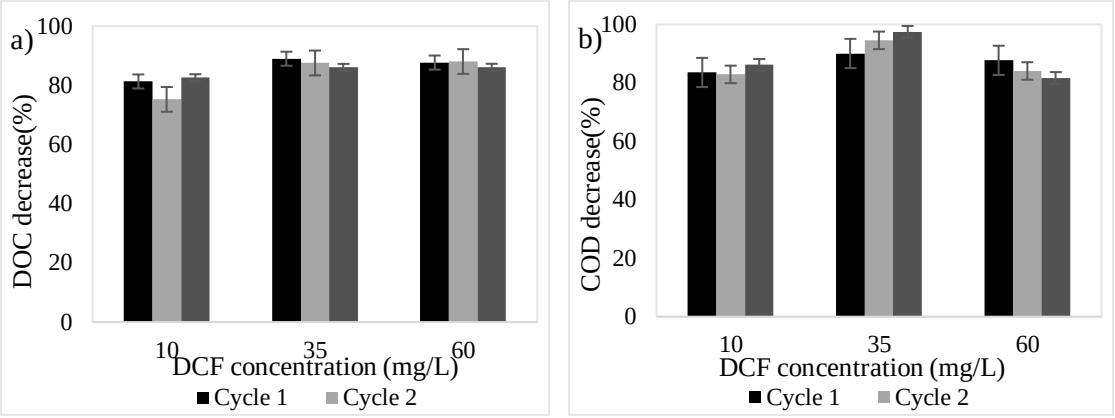


Fig11. Catalytic cycles of reused Fe_3O_4 evaluated with a) DOC decrease. b) COD decrease

Furthermore, the structure of the catalyst was observed after the process by FTIR (ATR) technique (Fig12), and no differences were observed in its characteristic spectrum of absorption band, associated to the Fe-O bonds vibration, compared to a sample taken before the ozonation process, showing that the catalyst remained stable.

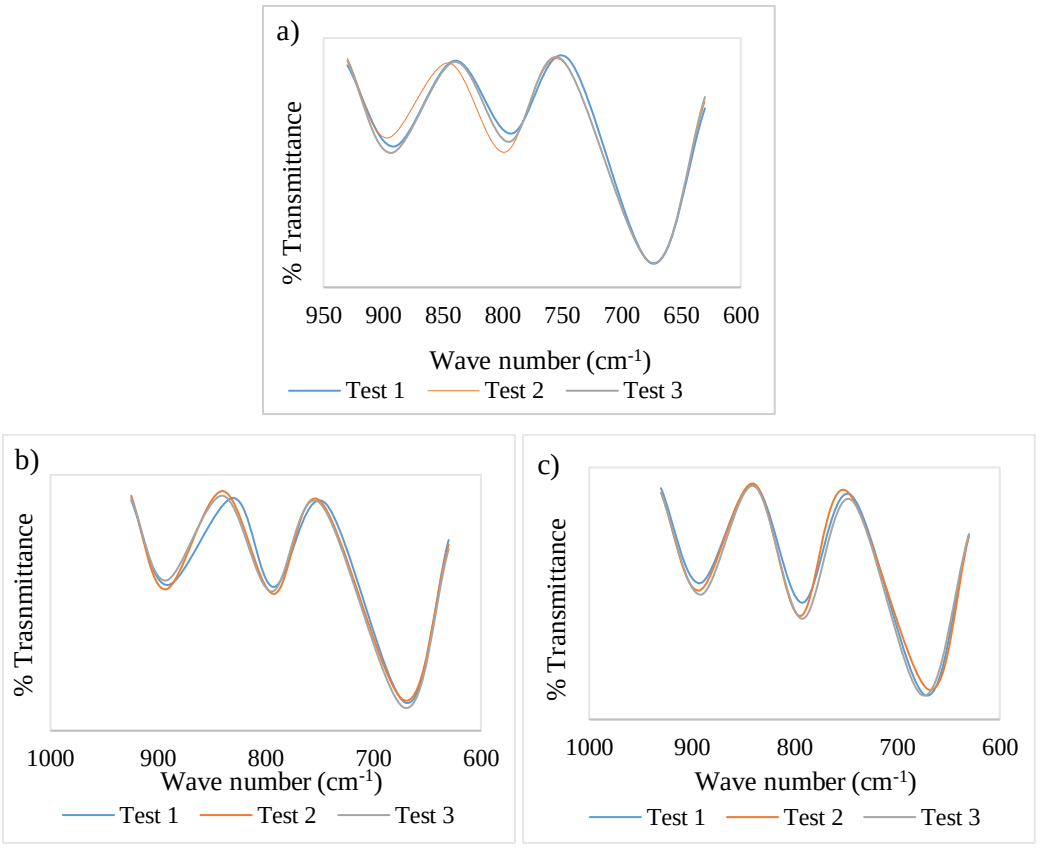


Fig12. Re-used catalyst FTIR spectra after three tests into DCF aqueous solutions of a) 10 mg/L, b) 35 mg/L and c) 60 mg/L.

4. Process efficiency

During ozone quantification, it was used 71.43 mL of Na_2S_2O, on average, for KI trap titration, to determine residual ozone of 4.18 mg/min using Eq1, and then the process efficiency. Material balance was realized based on around 80% ozone generator theoretical efficiency, 60% generator output regulation and a constant reactor inlet flow of 24.18 mg/min, obtained according to the calibration curve (Fig13) which allowed to calculate the reactant ozone with the DCF on the catalyst surface and an overall process efficiency of 82.71%.

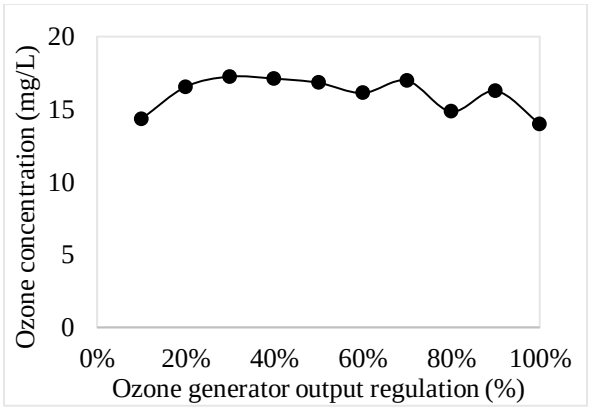


Fig13. Ozone calibration curve using a fixed inlet flow of 1.5 L/min.

5. Controversies related to catalytic ozonation process

The mechanisms of catalytic ozonation process are still largely unknown (Nawrocki et al., 2010). Mechanisms of catalytic ozonation of aqueous solutions are not easy to investigate and determine mainly due to the several reaction pathways depending on conditions such as pH, molecular polarity of organic compounds, catalyst nature and its surface properties (Guo et al., 2012). However, several mechanisms have been proposed for homogeneous and heterogeneous catalysts. For homogeneous catalysis, two major mechanisms are found: Decomposition of ozone by metal ions leading to the generation of free radicals and Complexes formation between organic molecule and the catalyst and subsequent oxidation of the complex to more simple molecules (Beltrán et al., 2005). For heterogeneous catalysis the most widely catalyst used are metal oxides, metals and metal oxides on supports. Two representatives mechanisms are: interfacial reaction mechanism, in which the main function of catalysts is to act as adsorptive material, and OH• mechanism, which proposes that the metal oxide catalysts can increase the solubility of ozone and initiates the ozone decomposition (Guo et al., 2012).

Catalytic activity is usually justified using the catalyst just in one experiment, but it is not enough to ensure that it preserves its catalytic properties. It is necessary to use the same catalyst sample in several experiments, to prove the "catalytic" activity is not caused by impurities or a reaction between catalyst and substrate (Nawrocki, 2013). In this investigation, catalytic activity was studied by using the same catalyst sample in three consecutives experiments, and it was demonstrated, by FTIR and Mössbauer spectroscopy, that its nature was not altered.

Reactions of ozone with organic matter usually lead to the formation of aldehydes and carboxylic acids, both of which do not react with ozone (Nawrocki et al., 2010). The formation of these compounds is well established in literature (Nawrocki et al., 2003), and it is related to the ozone dose and pH process. The higher ozone dose, higher the aldehyde formation, which becomes into carboxylic acids when it is oxidized. Related to pH, the most influential mechanism in the aldehydes formation occurs with the pH increase, and the oxidation from aldehydes to carboxylic acids is favored with pH decrease (Rodríguez, 2003). In this study, pH process was between 3.4 and 4.3, which allowed the aldehydes and carboxylic acids formation as DCF degradation products, hence it did not have a complete mineralization.

The usage of catalysts in aqueous solutions will lead to competition between ozone and organic compounds for catalytic (adsorptive) active sites (Nawrocki et al., 2010). Studies with several catalysts have demonstrated that some organic compounds and even ozone are adsorbed into active sites of catalyst surface due to the polarity, while nonpolar organics are not adsorbed on the surfaces (Nawrocki, 2013). In this study, it was used Fe_3O_4 as catalyst, which has a surface that allows a possible adsorption of other particles in the Fe atom neighborhood, and their subsequent complete desorption. This was demonstrated by Mössbauer spectroscopy.

6. Conclusions

The obtained results indicate that the heterogeneous catalytic ozonation could be an efficient treatment to degrade the DCF, reaching percentages of organic load decrease around 89% and 94% of COD and DOC respectively, under experimental conditions of 35 mg/L analytical DCF in aqueous solution, with a 0.5 g/L of catalyst concentration, during 40 minutes of process.

After the process, shorter chain organic compounds such as C_3, C_4 and C_6 were found due to DCF degradation and free radicals substitution during oxidation.

Introducing a heterogeneous catalyst improved the results of organic load decrease measured as DOC, with an increase around 40% for technical DCF and 60% for analytical DCF, compared to the process without catalyst, since it provided greater contact surface between the solution and ozone. It was proved by stability analysis with FTIR, Mössbauer spectroscopy, and COD and DOC results that Fe_3O_4 preserves its catalytic properties when it is reused in several experimental tests.

Despite of there are several proposed mechanisms for catalytic ozonation process, there is still a lack of understanding concerning to a unified mechanism, due to the several conditions, which affect the process, generating different pathways and reaction products. Catalytic ozonation still remains as a focal point of modern advanced oxidation process into the laboratory field.

7. Acknowledgments

The authors thank to investigation group Procesos Avanzados para Tratamientos Químicos y Biológicos (GAOX) and to Laboratorio de Investigación en Catálisis Aplicada y Procesos. (LICAP) from Universidad del Valle, Cali-Colombia for their financial and scientific support.

8. References

Alimoradzadeh, R., Assadi, A., Nasseri, S., and Mehrasbi, MR. (2012). Photocatalytic degradation of 4-chlorophenol by UV/H_2O_2/NiO process in aqueous solution. *Iranian Journal of environmental health science & engineering*, 9(1), 1-8. https://doi.org/10.1186/1735-2746-9-12

Arunan, E. (1997). The C-C bond is stronger than the C-Cl bond in CH_3COCl. *Journal of Physical Chemistry A*, 101(27), 4838-4839. http://dx.doi.org/10.1021/jp970576j

Baena, Y. (2011). *Estudio fisicoquímico de la liberación del diclofenac a partir de complejos polielectrolito-fármaco* (Doctoral Thesis). Universidad Nacional de Colombia, Colombia.

Barbosa, A., Santos, D., Ciríaco, L., Pacheco, M., and Lopes, A. (2015). Identificação dos metabolitos da oxidação anódica do diclofenac por HPLC. *Coletânea Interdisciplinar em Pesquisa, Pós-Graduação e Inovação*, 4, 149-167.

Calza, P., Sakkas, V., Medana C., Baiocchi, C., Dimou, A., Pelizzetti, E., and Albanis, T. (2006). Photocatalytic degradation study of diclofenac over aqueous TiO_2 suspensions. *Applied Catalysis B: Environmental*, 67(3-4), 197-205. https://doi.org/10.1016/j.apcatb.2006.04.021

CEVIME. (2016). *Farmacontaminación. Impacto ambiental de los medicamentos*. 24(10). Recovered from http://files.sld.cu/medicamentos/files/2017/01/INFAC_Vol_24_n_10_farmacontaminacion.pdf [Accesed: 27-Aug-2017]

Chen, Y.-L., and Yang, D.-P. (2007) Mössbauer Effect in Lattice Dynamics: Experimental Techniques and Applications. *WILEY-VCH Verlag GmbH & Co. KGaA*, Germany. doi: 10.1002/9783527611423.ch4.

Coelho, A., Sans, C., Agüera, A., Gómez, M., Esplugas, S., and Dezotti, M. (2009). Effects of ozone pre-treatment on diclofenac: Intermediates, biodegradability and toxicity assessment. *Science of the Total Environment*, 407, 3572-3578.

Darwent, B. (1970). *Bond Dissociation Energies in Simple Molecules*. Recovered from http://nvlpubs.nist.gov/nistpubs/Legacy/NSRDS/nbsnsrds31.pdf

Eaton, A., Clesceri, L., Greenberg, A., and Franson, M. (2012). *Standard methods for the examination of water and wastewater*. 22th ed. Washington, DC: American Public Health Association.

Eriksson, M. (2005). *Ozone chemistry in aqueous solution – Ozone decomposition and stabilization* (Licentiate Thesis). Royal Institute of Technology, Switzerland.

Feito, R., Valcárcel, Y., and Catalá, M. (2012). Biomarker assessment of toxicity with miniaturised bioassays: Diclofenac as a case study. *Ecotoxicology*, 21(1), 289–296. https://doi.org/10.1007/s10646-011-0790-2

Gunten, U. (2003). Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Research*, 37(7), 1443-1467. https://doi.org/10.1016/S0043-1354(02)00457-8

Hartmann, J., Bartels, P., Mau, U., Witter, M., Tümpling, W., Hofmann, J., and Nietzschmann, E. (2008). Degradation of the drug diclofenac in water by sonolysis in presence of catalysts. *Chemosphere*, 70(3), 453-461. https://doi.org/10.1016/j.chemosphere.2007.06.063

Hikmat, K., Miessner, H., Mueller, S., Kalass, D., Moeller, D., Khorshid, I. and Rashid, M. (2017). Degradation of pharmaceutical diclofenac and ibuprofen in aqueous solution, a direct comparison of ozonation, photocatalysis, and non-thermal plasma. *Chemical Engineering Journal*, 313, 1033-1041. https://doi.org/10.1016/j.cej.2016.10.137

Huang, D., and Feng, C. (2012). Use of iron oxide nanomaterials in wastewater treatment: A review. *Science of the Total Environment*, 424, 1-10. https://doi.org/10.1016/j.scitotenv.2012.02.023

IDEAM. (2014-2015). *Informe Nacional Generación y Manejo de Residuos o Desechos Peligrosos en Colombia*. Recovered from http://www.ideam.gov.co/documents/51310/1929967/Informe+Nacional+de+generacion+y+manejo+de+residuos+y+desechos+peligrosos.pdf/158efdc8-e8dc-4775-b377-6f2239b36d21?version=1.0. [Accesed: 23-Aug-2017]

Ivashchenko, O., Jurga-Stopa, J., Coy, E., Peplinska, B., Pietralik, Z., and Jurga, S. (2016). Fourier transform infrared and Raman spectroscopy studies on magnetite/Ag/antibiotic nanocomposites. *Applied Surface Science*, 364, 400-409. https://doi.org/10.1016/j.apsusc.2015.12.149

Jiménez, C. (2011). Contaminantes orgánicos emergentes en el ambiente: Productos farmacéuticos. *Lasallista de Investigación*, 8(2), 143–153.

Kebebe, D., Belete, A., and Gebbre-Mariam, T. (2010). Evaluation of two Olibanum resins as rate controlling matrix Forming Excipients in Oral Sustained Release Tablets. *Ethiopian Pharmaceutical Journal*, 28, 95-109. http://dx.doi.org/10.4314/epj.v28i2.4

Martínez, R., Ramón, D., and Yus, M. (2009). Selective N-monoalkylation of aromatic amines with benzylic alcohols by a hydrogen autotransfer process catalyzed by unmodified magnetite. *Organic & Biomolecular. Chemistry*, 7(10), 2176-2181. https://doi.org/10.1039/b901929d

Mena, N. (2014). *Tratamiento de lixiviados mediante ozonización catalítica heterogénea* (Master's Thesis). Universidad del Valle, Colombia.

Moreira, N., Orge, C., Ribeir,o A., Faria, J., Nunes, O., Pereira, M. and Silva, A. (2015). Fast mineralization and detoxification of amoxicillin and diclofenac by photocatalytic ozonation and application to an urban wastewater. *Water Research*, 87, 87-96. https://doi.org/10.1016/j.watres.2015.08.059

NIST Standard Reference Data, Secretary of Commerce on behalf of the United States of America. All rights reserved, 2015. Original licence Universidad del Valle, Cali- Colombia, 2017

Parks, G., and Akthar, Salim. (1968). Magnetic moment of Fe_2^+ in paramagnetic minerals. *The american mineralogist*, 53, 406-415.

Pérez, G., and Bohórquez, A. (1993). *Espectroscopia Mössbauer*. Cali, Colombia: Universidad del Valle.

Pouran, S., Abdul, A. and Ashri, W. (2014). Review on the application of modified iron oxides as heterogeneous catalysts in Fenton reactions. *Journal of Cleaner Production*, 64, 24-35.

Rao, N., Dubey, A., Mohanty, S., Khare, P., Jain, R., and Kaul, S. (2003). Photocatalytic degradation of 2-chlorophenol: a study of kinetics, intermediates and biodegradability. *Journal of Hazardous Materials*, 101(3), 301-314. https://doi.org/10.1016/S0304-3894(03)00180-8

Yang, R., Wang, M., Shen, Z., Wang, W., Ma, H., and Gu, J. (2007). The degradation and mineralization of 4-chlorophenol in aqueous solutions by electron beam irradiation in the presence of TiO_2 nanoparticles. *Radiation Physics and Chemistry*, 76(7), 1122-1125. https://doi.org/10.1016/j.radphyschem.2006.10.008

Yilmaz, B., and Ciltas, U. (2015). Determination of diclofenac in pharmaceutical preparations by voltammetry and gas chromatography methods. *Journal of Pharmaceutical Analysis*, 5(3), 153-160. https://doi.org/10.1016/j.jpha.2014.10.005

Zhao, X., Hou, Y., Liu, H., Qiang, Z., and Qu, J. (2009). Electro-oxidation of diclofenac at boron doped diamond: Kinetics and mechanism. *Electrochimica Acta*, 54(17), 4172-4179. https://doi.org/10.1016/j.electacta.2009.02.059

Zhihui, A., Peng, Y., and Xiaohua, L. (2005). Degradation of 4-Chlorophenol by microwave irradiation enhanced advanced oxidation processes. *Chemosphere*, 60(6), 824-827. https://doi.org/10.1016/j.chemosphere.2005.04.027