UNIVERSITAT DE
BARCELONA

MASTER FINAL PROJECT

MASTER OF ENVIRONMENTAL ENGINEERING

Study of catalytic iron ozonation for the removal of emerging contaminants

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June 2019

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Agraïments

Fa uns deu mesos, recordo que estava presentant-me davant dels que anaven a ser els meus companys/es de classe, gent que no coneixes però que durant un temps comparteixen un mateix objectiu al teu. Ara, després d'aquest temps, sembla mentida que un cop presentem aquest treball que estic escrivint, tot s'acabi. Tot i ser curt, aquest curs ha sigut especial i he tingut la sort de conèixer gent molt interessant amb la qual em vull continuar trobant. Tot i així, sense la presència i ajuda de certes persones aquest treball no hagués estat possible.

Primer de tot, agrair al coordinador del màster, el Dr. Joan Dosta Parras per estar des del principi pendents de nosaltres i per, sempre que hi ha hagut algun dubte o problema, intentar solucionar-ho (i fer-ho) de la millor manera.

En segon lloc, a la Dra. Carme Sans Mazón per estar sobre meu, aclarir-me dubtes sobre el treball i tenir idees molt interessants sobre la investigació. També, és clar, a el Dr. Alberto Cruz Alcalde, que ha estat allà sempre que l'he necessitat i m'ha ensenyat pràctiques de laboratori útils que m'emporto pel futur.

En tercer lloc, no em puc deixar els/les companys/es de laboratori. Començant pel Lucas que, tot i que ja ens coneixíem de classe, el laboratori ens ha fet bons companys i amics. A la Núria, per tots els somriures que m'ha despertat i preocupar-se per ensenyar-me allò en el que dubtava. I, a l'Oriol, en Dimitri i en Rubén, per les estones compartides entre matrassos i les històries i aventures entretingudes que ens hem explicat.

Per últim, no vull deixar de donar les gràcies a totes aquelles persones que sempre estan; Gràcies família, amics i amigues!

Agraïments

Abstract and keywords

ABSTRACT: During last century, water has been consumed by human for agriculture, industrial processes and municipal use in huge amounts. This, together with the increase on the water quality standard, leads to water scarcity in many parts of the world. Emerging contaminants, which are organic recalcitrant compounds found recently in water, compromise nowadays the quality of the availability fresh water due to their unknown effect on human and environment health. This research was focused on the study of an Advanced Oxidation Process (AOPs), the Zero Valent Iron catalytic ozonation (O_3/ZVI), to treat spiked miliQ and bottled water at pH = 7.5 with a contaminant pesticide model: acetamiprid. Results showed that the type of water used had an effect on acetamiprid degradation being faster for miliQ water. These results were attributed to the concentration of bicarbonates present in bottled water which were demonstrated to have a scavenging effect of free hydroxyl radicals which are responsible of acetamiprid degradation. Also the presence of organic matter (NOM) showed a positive effect on single ozonation performance but an opposite outcome on O_3/ZVI degradation capacity. This research increases the knowledge about O_3/ZVI for further scientific research and technical applications.

Keywords: Water; Zero Valent Iron (ZVI); Advanced Oxidation Processes (AOPs); Ozonation; Catalyst; Bicarbonates; Organic matter

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1. Introduction

Water, which is responsible and necessary for the living in the Earth, is a very precious resource. Naturally water realises a cycle. It evaporates from the surface of the Earth, it condensates on the atmosphere and it precipitates creating accumulated parts of fresh water on the surface, subsurface or as ice or glaciers (AGUA.ORG.MX, 2010). Worldwide, availability of fresh water is 2.5% of the total, from which only a 0.77% is accessible for humans due to its difficult access (AGUA.ORG.MX, 2010).

Nowadays, globally around 70% of fresh water is used for agriculture and livestock, about 20% for industry and the remaining, 10%, for municipal use (Borràs, 2017). Although we can arrive to equilibrium between consume and the available reservoirs of fresh water, the growth of population and the industrialization during last century (Wang and Bai, 2017) drove to water scarcity in many parts of the world (Borràs, 2017). Concretely in Spain between 1975 and 2006 the fresh water consumption increased from 50% to 70% and it is predicted that in 2030 the 65% of Spanish population will suffer the consequences of water scarcity (Borràs, 2017).

This situation claims a development of new strategies for water resource management with the aim to obtain water that can be used again for a second purpose (regenerated water) or release into the environment without compromising the water quality standard which is getting more and more stringent (Wang and Bai, 2017). To achieve this aim, the strategies are focused on developing new tertiary technologies on wastewater treatment plants to remove trace organic pollutants (Meijide et al., 2018).

Emerging contaminants

Globally, emerging pollutants are some of the organic compounds that actually compromise the quality of water. These pollutants have this name due to the fact that they were discovered around twenty years ago coinciding with the enhancing of analytic technologies and they were found to be at low but increasing concentrations in water. These compounds come from widely used products and are released to the environment in huge quantities. In addition, they are not easily biodegraded (biorecalcitrant compounds) and nowadays their effect on human and environment

health are still not fully known. Within this group of contaminants there are pharmaceuticals and personal care products (PPCPs), endocrine-disrupting chemicals (EDCs), and pesticides (Wang and Bai, 2017).

Pesticides, which are chemicals or organic substances used to kill, repel or control any kind of plant or animal that is considered to be pest (NATIONAL INSTITUTE OF ENVIRONMENTAL HEALTH SCIENCES, 2018), are widely used and released to the environment. Farmers in Spain, one of the main fruits and vegetables exporting country in Europe, use many of these substances for their crops (MINISTERIO DE AGRICULTURA, PESCA Y ALIMENTACIÓN, 2017). This massive use has led to consider their release to the nature as a matter of environmental concern (Meijide et al., 2018).

Insecticides are pesticides that prevent insects (NATIONAL PESTICIDE INFORMATION CENTER, 2018). A group of them are the neonicotinoid compounds. Their effect is based on the attack on the insect nervous system (Meijide et al., 2018). Due to the fact that they are responsible of the colony collapse disorder (CCD) on bees and the devastation of honeybee colonies, some of them (clothianidin, thiamethoxam and imidacloprid) were banned in Europe by the European Food Safety Authority (EFSA) (Murano et al., 2018). However, some as acetamiprid, (1E)-N-[(6-chloro-3-pyridinyl)methyl]-N'-cyano-Nmethylethanimidamide (Figure 1), are still approved for agriculture use (Murano et al., 2018).The use of these compounds present thus a significant environmental problem due to their high solubility in water, their persistence on the environment (Meijide et al., 2018; Marcelo et al., 2016) and their low octanol/water partitioning coefficient indicating its low potential to be absorbed to soil (Murano et al., 2018).
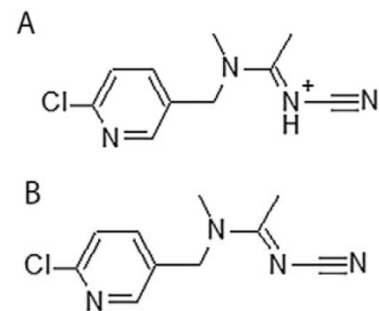
Figure 1. Acetamiprid structure at low pH (A) and at high pH (B) (Murano et al., 2018).

New technologies: Iron catalytic ozonation

Advance Oxidation Processes (AOPs), which have been well studied (Wang and Bai, 2017), have emerged as promising solutions (Ziylan and Ince, 2015) and efficient technologies for the removal of these emerging contaminants from water (Beltrán,

2005). They are based on the attack to organic pollutants by non-selective free hydroxyl radicals.

Ozonation is considered one of these AOPs (Wang and Bai, 2017). It is based on the use of ozone, a molecule discovered in 1839 by Christian Friedrich Schönbein formed by three oxygen atoms. Its name comes from Greek "ὄζειν" (smell) and Schönbein put it due to its strong smell. Naturally, it is formed on the upper zones of the atmosphere where there are atomic oxygen and biatomic oxygen that react by the action of ultraviolet light (UV) and electrical discharges within the Earth atmosphere (Beltrán, 2005).

In 1839 Schönbein attributed to ozone high oxidizing properties caused by the electronic configuration of the molecule (Table 1). Its redox potential (E_o), its capacity to give electrons, is of 2.07 V. For this reason during the late 19th century ozone was mainly used as disinfectant together with chloride (Beltrán, 2005). Despite some air disinfection and purification applications (Xiong et al., 2016), nowadays ozone is applied in water treatment plants for three reasons: to disinfect, to remove organic pollutants and in some pre- or post-treatment processes to improve the efficiency of other steps in the plant (Beltrán, 2005). In the role of removing some organic compounds, ozone uses two routes: 1) direct degradation for pH < 4, where ozone has high stability and directly

Table 1. Physico-Chemical Properties of Ozone (Beltrán, 2005).

Property	Value
Melting point, ºC	−251
Boiling point, ºC	−112
Critical pressure, atm	54.62
Critical temperature, ºC	−12.1
Specific gravity	1.658 higher than air
	1.71 gcm^{-3} at −183ºC
Critical density, kgm^{-3}	436
Heat of vaporization, $calmol^{-1}$ [a]	2,980
Heat of formation, $calmol^{-1}$ [b]	33,880
Free energy of formation, $calmol^{-1}$ [b]	38,860
Oxidation potential, V[c]	2.07

[a] At the boiling point temperature. [b] At 1 atm and 25ºC. [c] At pH = 0.

oxidise the compounds due to its high reactivity (Equation (1)), and 2) indirect degradation for pH > 10, where ozone suffers a decomposition process into free hydroxyl radicals (·OH) with higher redox potential (E_o= 2.33 V) that reacts with organic compounds (Equations (2) and (3)) (Wang and Bai, 2017; Li et al., 2018). When the pH is near neutrality, such as water, there is a contribution of both types of degradation.

Although ozonation is an effective oxidation process and it has been well studied and applied (Wang and Bai, 2017), there are several disadvantages that limit its application and lead to search other alternatives. The main and important limitation is that ozone reaction is selective and thus it does not react with all the organic pollutants present in water. Moreover, the solubility of ozone in water is relatively low (Wang and Bai, 2017; Xiong et al., 2016) and it is able to produce harmful by-products, especially in waters with bromide creating bromate (Beltrán, 2005). These limitations could be avoided by using higher amounts of ozone and enhancing the indirect degradation to produce more hydroxyl radicals. However, production of ozone is really expensive and its massive use does not prevent the production of bromate but enhances it.

$$M + O_3 \rightarrow M_{OX} + O_3^{-} \quad {}_1 \tag{1}$$

$$O_3^{-} \underset{\leftarrow}{\rightarrow} O_2 + O^{\cdot -} \tag{2}$$

$$O^{\cdot -} + H_2O \underset{\leftarrow}{\rightarrow} \cdot OH + OH^{-} \tag{3}$$

In recent years, to overcome the ozonation process problems, catalytic ozonation has emerged as an effective technology for water and wastewater treatment plants because of its capacity to increase ozone decomposition and thus free hydroxyl radicals' production (Wang and Bai, 2017; Wu et al., 2016; Xiong et al., 2016). Ozone catalytic mechanisms could be homogeneous, where the catalyst is soluble, and heterogeneous, where the catalyst has a different phase of the aqueous medium (Wang and Bai, 2017). For the heterogeneous, one metal-based catalyst (Mn, Al, Ti...) are commonly used having iron (Fe) more advantages than other materials due to the fact that it can be found on the nature and it is almost a non-toxic metal (Wang and Bai, 2017), only at high concentrations. Many iron ions and oxides were investigated as ozonation catalyst (Xiong et al., 2016). Although zero valent iron (ZVI or Fe^0) is an effective reductant (E_o = -0.44 V) (Xiong et al., 2016), it has been recently studied as a catalyst for the ozonation process (Wang and Bai, 2017) and as an environmental process to treat water contaminated with dyes, phenolic compounds, nitroaromatics or heavy metals (Xiong et al., 2016). During the catalytic process, some Fe-based

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[1] M represents organic matter; M_{ox} represents oxidized organic matter.

species are formed on the surface of ZVI: FeOOH, Fe_2O_3 and Fe_3O_4, which act as Fe-based catalysts and react with O_3 to produce hydroxyl radicals, leading to a heterogeneous catalytic ozonation. Moreover, the O_3/ZVI catalyst reaction is based on homogeneous catalytic ozonation of Fe^{2+}/Fe^{3+}, Fenton-like reactions and, finally, adsorption and precipitation compounds such as $Fe(OH)_2$ and $Fe(OH)_3$ (Figure 2) (Xiong et al., 2016).
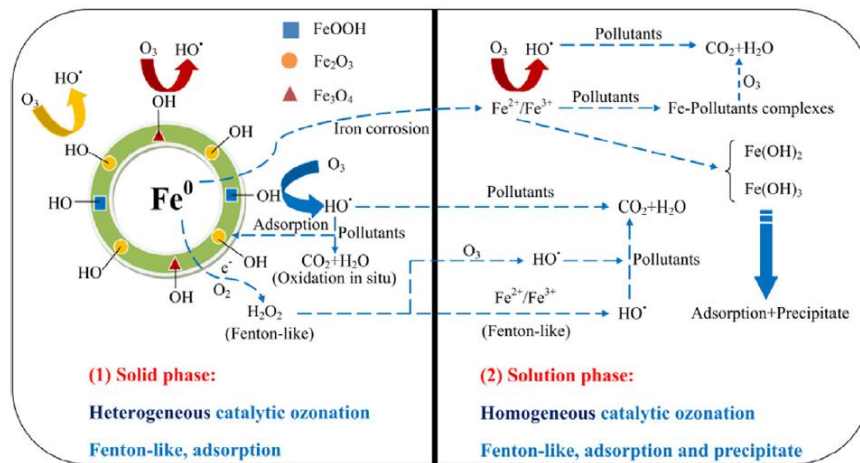

Figure 2. Reactions mechanism of ZVI/O_3 heterogeneous catalytic process (Xiong et al., 2016).

1.1. Aims of the study

The general objective of this work is to study the performance of ZVI as catalyst on the ozonation process in a lab-scale reactor. The pesticide acetamiprid, which has low reactivity with ozone and thus is a good choice as a hydroxyl radical probe compound, has been selected to perform the research. More specifically, this study intended to:

- Study the viability of O_3/ZVI process to eliminate and/or reduce the presence of acetamiprid using miliQ water at pH = 7.5.
- Evaluate the effects of aqueous medium (miliQ water and real bottled water) on the catalytic ozonation process O_3/ZVI at pH = 7.5.
- Test the influence of different compounds present in aqueous medium (bicarbonates concentration, presence of organic matter…) on the catalytic ozonation process O_3/ZVI at pH = 7.5.
- Study the evolution of dissolved iron during the process and its potential relationship with the process performance.

2. Material and methods

2.1. Material

Water

The experiments were done using miliQ water and bottled water. In all cases, water was adjusted to pH = 7.5 using a solution of NaOH 0.1 M.

MiliQ water was obtained from a MiliQ® system machine which filtrates through a 0.22 μm membrane filter and purifies deionised water to create ultrapure water with a resistivity of 18.2 MΩ·cm at 25 °C.

Bottled water was purchased from a bottled water brand (i.e. Solán de Cabras). The characteristics of this water were obtained from the brand website (Taula 2).

Table 2. Water composition concentration in parts per million (ppm) (SOLÁN DE CABRAS, 2019).

	COMPOSITION (mg/L)
	BOTTLED WATER
Bicarbonates	284
Calcium	60
Chlorine	8.3
Sulphates	21.8
Sodium	4.8
Silica	7.5
Potassium	4
Magnessium	26.7

Chemical reagents

Iron (ZVI) was added to the reactor as powder, made of particles sized less than 44 μm. Depending on the experiment, the final concentration was different. For miliQ water experiments the iron used was from 5 to 500 mg/L whereas for experiments with bottled water the concentrations were higher: from 500 to 5000 mg/L.

Sodium hydrogen carbonate ($NaHCO_3$, 99% purity) was added to the experiments in which the bicarbonates in water were needed to be changed. To change the amount of organic matter in water, humic acids were used at a final concentration in water of 2 mg/L, which corresponds to the amount found in water from a clean river.

2.2. Methods

Semi-batch ozonation

The catalytic ozonation process was performed in a semi-batch reactor setup. The installation has an ozone generator that creates ozone from dry pure oxygen.

Water at pH = 7.5 were spiked with acetamiprid at a final concentration of 0.1 mg/L on a final volume of 750 mL. When bicarbonates or organic matter, they were added before spiking the water and adjusting the pH. The solution was put inside the jacketed glass reactor that kept the solution during all the experiment at 20 ± 1 ^{0}C. Ozone was injected to the solution through a diffuser at 105 mL/min flow rate (Table 3). To ensure a homogeneous and a proper contact between the liquid phase and the gas phase, inside the reactor there was a mechanical mixing system which was kept for all the experiments at 300 rpm.

Table 3. Ozone conditions in the inlet for the different experiments performed.

Ozone conditions in the inlet							
MiliQ water		Bottled water		MiliQ water + bicarbonates		MiliQ water + humic acids	
Flow rate (mL/min)	$[O_3]$ (mg/L)	Flow rate (mL/min)	$[O_3]$ (mg/L)	Flow rate (mL/min)	$[O_3]$ (mg/L)	Flow rate (mL/min)	$[O_3]$ (mg/L)
105	30	105	20	105	20	105	20

When conducting ZVI experiments, after weighing the proper amount, the iron was added to the reactor, while the mechanical mixing was on, ten minutes before starting the experiment. The experiments started when the ozone was put in contact with the solution. All the experiments lasted 30 minutes.

The installation provides manometers to control the pressure inside the system and two ozone gas-phase analysers; for the entrance to and the exit from the reactor (Figure 3). A logger was connected to these systems to get the continuous measurements of inlet and outlet gas concentrations to later assess the ozone mass balance and thus ozone consumption during experiments.
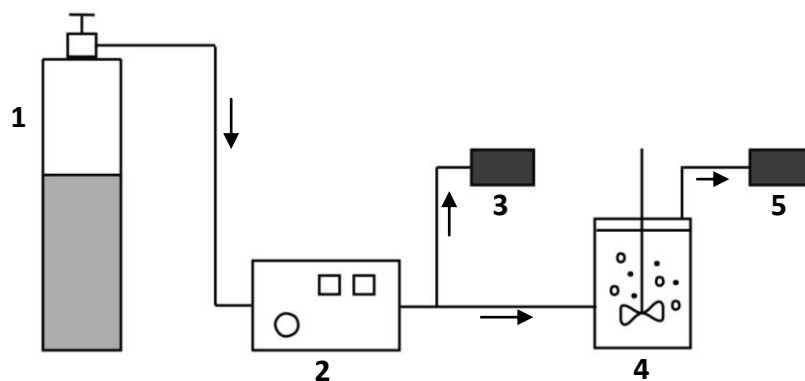
Figure 3. Simplified scheme of the lab-scale, semi-batch ozonation setup.
1. Oxygen bottle; 2. Ozone generator; 3. Ozone inlet analyser (gas-phase);
4. Reactor with mechanical stirrer; 5. Ozone outlet analyser (gas-phase).

Analytical techniques

Each sample, after enough time to assure that the ozone has completely reacted with the liquid medium, was filtered throw a 0.45 μm and analysed by using High Performance Liquid Chromatography (HPLC). The exact concentration of acetamiprid for all the experiments was determined by HPLC and a calibration curve previously obtained (Figure 4).

For the measurement of dissolved Fe^{2+} and total Fe, a colorimetric method based on ISO 6332 (1988) was used. To measure the Fe^{2+} this method is based on the reaction between Fe^{2+} and o-fenantroline which forms an orange complex, $[(C_{12}H_8N_2)Fe]^{2+}$, which has absorbance at 510 nm. To measure the total dissolved iron the method is based on the iron with ascorbic acid which also forms a complex that presents some absorbance at 510 nm.

For this reason, the samples at fixed experimental times, were taken and filtered through a 0.45 μm syringe filter. Then 4 mL were put in contact with a solution of o-fenantroline. After one minute, the absorbance at
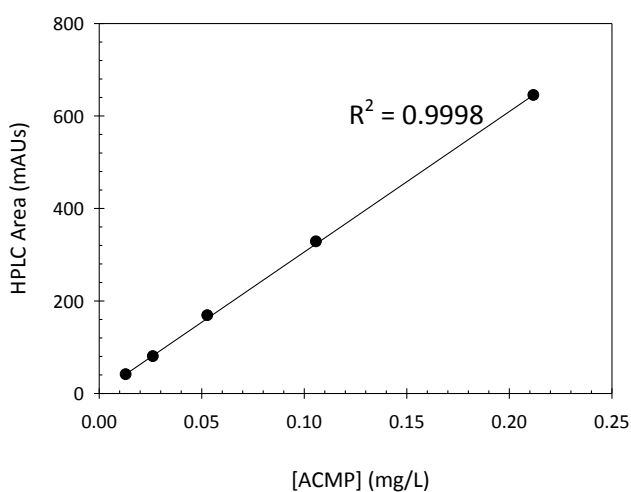
Figure 4. Acetamiprid (ACMP) calibration curve used to relate the HPLC integration signal with the acetamiprid concentration in the solution.

510 nm of the solution was determined by using a spectrophotometer and the final dissolved Fe^{2+} concentration was calculated by using a dissolved Fe^{2+} calibration curve previously prepared. Due to the experimental time and the procedure, samples at time three and seven minutes were not analysed.

After this, samples were saturated with ascorbic acid and after 24 hours their absorbance was measured at 510 nm. The concentration of total Fe was determined by using a total Fe calibration curve previously prepared.

Transferred Ozone Dose

To know exactly how much ozone was transferred to the liquid medium and thus consumed by the system, it was necessary to calculate the Transferred Ozone Dose (TOD) (Equation (4)). TOD takes into account the concentration of ozone on the inlet $[O_3]_{in}$ and on the outlet $[O_3]_{out}$ on the gas flow F and per liquid volume V inside the reactor. To calculate the total TOD during the thirty minutes of the experiment, a trapezoidal method of numerical integration with a step size of ten seconds was implemented.

$$TOD \left(\frac{mg}{L}\right) = \int \frac{F}{V} \cdot ([O_3]_{in} - [O_3]_{out}) \, dt \tag{4}$$

To compare experiments this calculation was necessary due to the fact that all the experiments were done using different inlet ozone concentration, $[O_3]_{in}$ (Table 3).

3. Results and discussion

3.1. O_3/ZVI in miliQ water and in bottled water

To study the catalyst process O_3/ZVI to reduce or eliminate the concentration of acetamiprid in water, semi-batch ozonation experiments with spiked miliQ and bottled water were realised.

In miliQ water, the experiments were done without the addition of ZVI to the system and with ZVI at different final concentrations: 5, 50 and 500 mg/L. Although four treatments influenced acetamiprid degradation, results showed differences between them, as it can be seen in Figure 5.
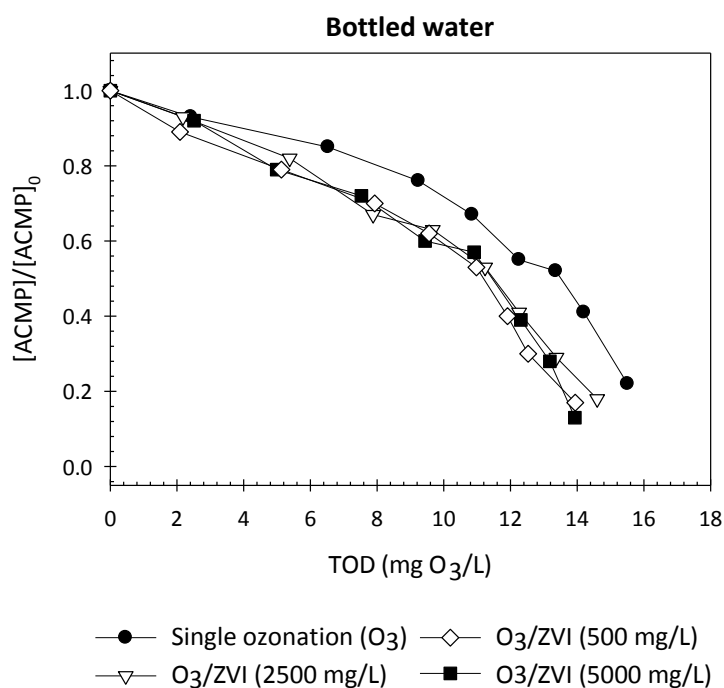
MiliQ water
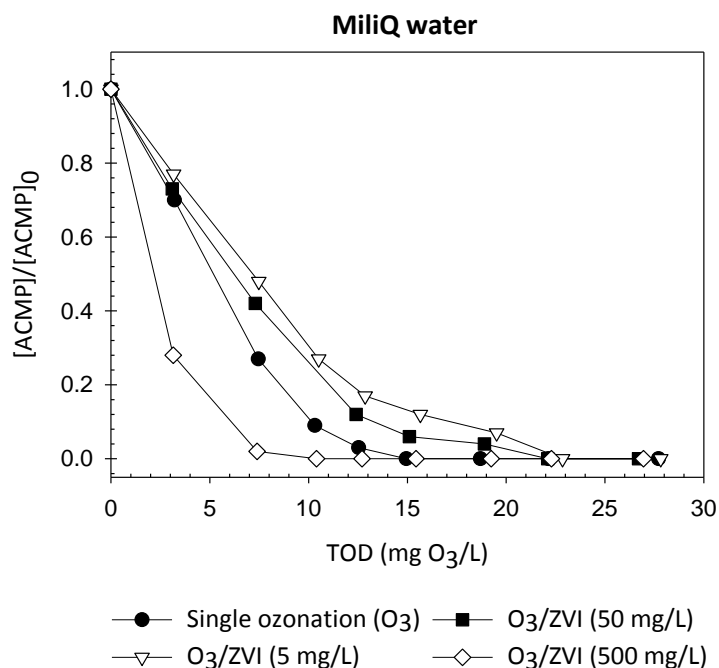
Figure 5. Experiments' data using miliQ without and with catalyst ZVI at different concentrations. The data represent relative concentration of acetamiprid (ACMP) against the consumption of ozone (TOD) inside the reactor.

For single ozonation, there was a total degradation of acetamiprid after a consumption of 15 mg O_3/L. Comparing these results with the catalyst ozonation processes, the results showed that for lower concentrations of ZVI catalyst (i.e. 5 and 50 mg/L), the degradation of acetamiprid was slower, needing more consumption of ozone to have a total degradation of acetamiprid. However, in the case of higher ZVI concentration

(i.e. 500 mg/L) acetamiprid degradation was faster than single ozonation, arriving to a total degradation at about 7 mg O_3/L consumed by the solution.

In the case of bottled water, some semi-batch experiments were done without and with catalyst ZVI at different concentrations: 500, 2500 and 5000 mg/L.

Results on Figure 6 showed that acetamiprid concentration was decreasing while there was a consumption of ozone by the solution. For the four treatments performed, the results showed differences between the single ozonation and the ones with the utilization of catalyst, having in the case of using the catalyst faster acetamiprid degradation. However, between the treatments with ZVI at different concentrations the results did not show significant differences, being the final concentration and the acetamiprid degradation's trend similar.
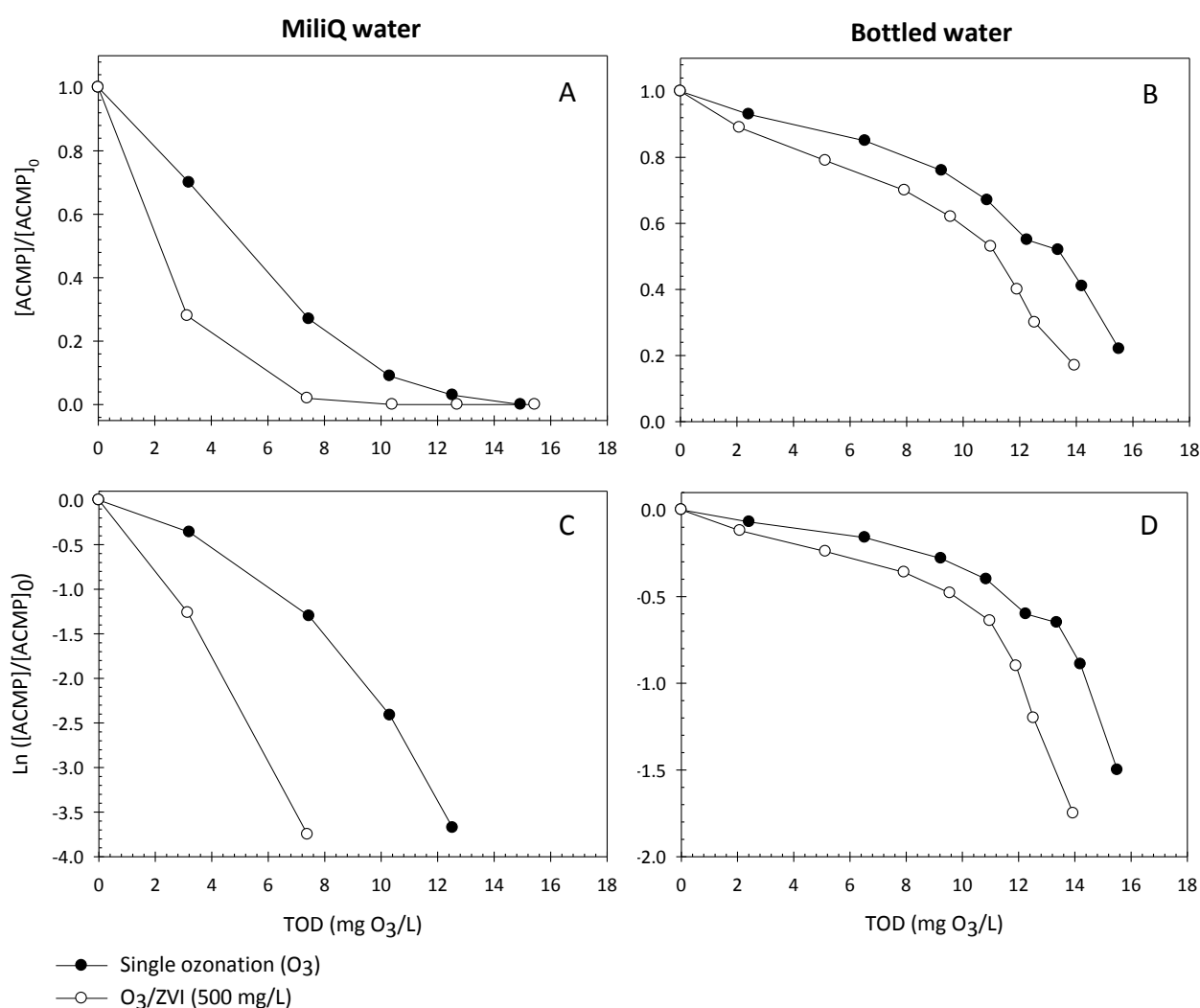

Figure 6. Experiments' data using bottled water without and with catalyst ZVI at different concentrations. The data represent relative concentration of acetamiprid (ACMP) against the consumption of ozone (TOD) inside the reactor.

Although in miliQ water higher concentration of ZVI seemed to lead to a faster degradation results, the results obtained in experiments using bottled water (Figure 6)

showed that more ZVI concentration did not involve more acetamiprid degradation. For this reason, 500 mg/L were used for the following experiments.

To compare better both types of water, results obtained without and with 500 mg ZVI/L are shown in Figure 7. There, for miliQ water the degradation followed almost a first order degradation whereas the contaminant degradation in bottled water could be divided in two steps: first the degradation rate is significantly slowly compared with deionized water, but kinetics improved after the consumption of about 10-12 mg O_3/L. At the end, results showed better acetamiprid degradation when using miliQ water than bottled water.

Figure 7. Experiments' data using miliQ (A, C) and bottled water (B, D) without and with 500 mg ZVI/L. **A and B**: Represent relative concentration of acetamiprid (ACMP) against the consumption of ozone (TOD). **C and D**: Represent the logarithm of the relative concentration of ACMP against TOD.

For bottled water, iron was also analysed and it is plotted together with acetamiprid degradation in Figure 8. When using 500 mg ZVI/L, the concentration of total dissolved iron on the solution was unstable ranging from almost 0.07 mg/L to around 0.7 mg/L.
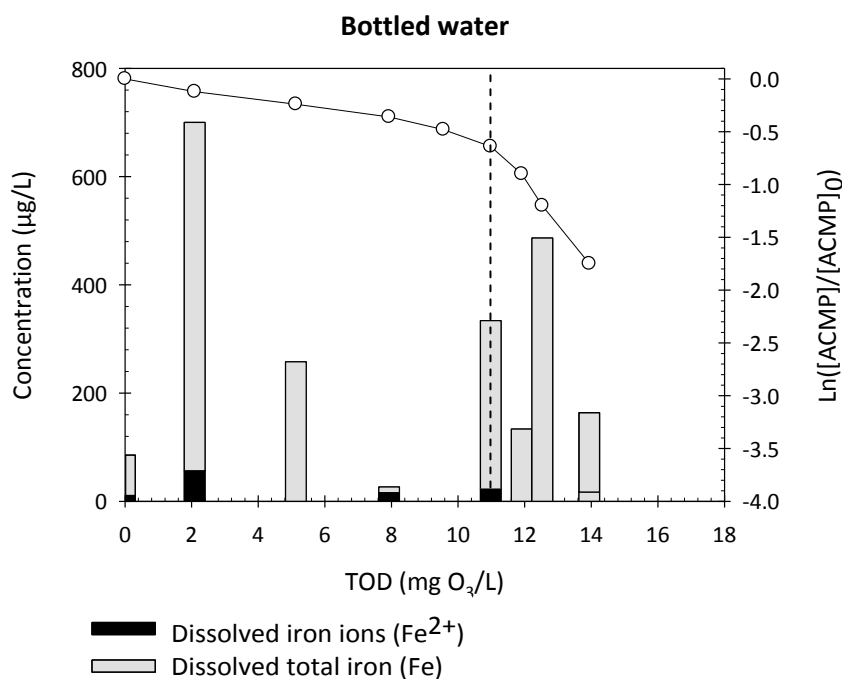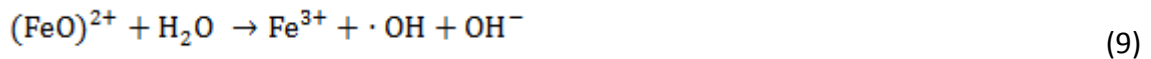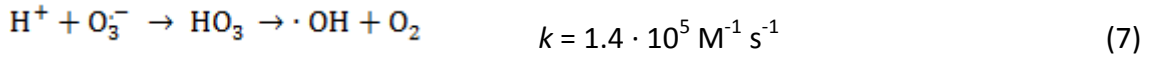

Figure 8. Experiments' data using bottled water with 500 mg ZVI/L. White rounds represent the logarithm of relative concentration of acetamiprid (ACMP) against the consumed ozone (TOD). Bars represent the concentration of dissolved total iron and the iron ions (II) in solution against TOD. Striped line shows the start of the change on acetamiprid degradation kinetics.

Iron in water led to unstable concentrations of dissolved total iron and dissolved iron ion (II) (Fe^{2+}). From the point where there was the change on acetamiprid degradation kinetics, the concentration of Fe^{2+} was null. Although the concentration of iron added to the system was high, it is important to highlight that the maximum dissolved iron value obtained was of 0.65 mg/L, less than what it is allowed by law (i.e. 10 mg Fe/L).

All the results obtained on miliQ and bottled water for the O_3/ZVI catalyst process could be explained by the plenty of reactions that take place inside the reactor. As it has been above explained, and as it has been before reported and explained by some studies, O_3/ZVI catalyst procedure is based on four different pathways, mainly the homogeneous and the heterogeneous catalyst ozonation. During homogeneous procedure, ZVI is oxidised by ozone leading to the release of Fe^{2+}/Fe^{3+} species to the reactor (Wang and Bai, 2017; Xiong et al., 2016) and thus generating free hydroxyl

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radicals (·OH) (Xiong et al., 2016). The reactions are following described (Xiong et al., 2016):

$$\text{Fe} + 2\text{O}_3 \rightarrow \text{Fe}^{2+} + 2\text{O}_3^- \tag{5}$$

$$\text{Fe}^{2+} + \text{O}_3 \rightarrow \text{Fe}^{3+} + \text{O}_3^- \tag{6}$$

$$\text{H}^+ + \text{O}_3^- \rightarrow \text{HO}_3 \rightarrow \cdot\text{OH} + \text{O}_2 \qquad k = 1.4 \cdot 10^5 \text{ M}^{-1}\text{ s}^{-1} \tag{7}$$

$$\text{Fe}^{2+} + \text{O}_3 \rightarrow (\text{FeO})^{2+} + \text{O}_2 \tag{8}$$

$$(\text{FeO})^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \tag{9}$$

$$\text{Fe}^{3+} + \text{O}_3 \rightarrow \text{FeO}^{2+} + \cdot\text{OH} + \text{O}_2 + \text{H}^+ \tag{10}$$

Together with the ·OH and some oxidation compounds formed on the surface of ZVI during the heterogeneous procedure, the Fe-compounds were responsible of the degradation of the contaminant (Xiong et al., 2016). Since one mole of iron needs to react with two moles of ozone to produce iron ions (II) (Equation (5)), when applying more ZVI catalyst to the system the results were the same, so in this case ozone is the limiting reactant.

For bottled water, although it is difficult to relate the degradation and the concentration of dissolved iron ions (II), it seemed that the lack of dissolved Fe^{2+} inside the system coincided with the change on the degradation kinetics (Figure 8). This phenomenon, together with the almost non acetamiprid degradation at first, could be related to the presence of free hydroxyl radicals' scavengers.

3.2. Effect of bicarbonates

Bicarbonates and carbonates have been reported to have a free hydroxyl radical scavenging effect, which consists of the reaction with free hydroxyl radicals with some compounds avoiding then their reaction with the contaminant. To study the influence of carbonates and bicarbonates on the O_3/ZVI catalyst process some experiments were done using spiked miliQ water at pH = 7.5 with different concentrations of bicarbonates: 0, 50, 150 and 300 mg HCO_3^-/L, without and with ZVI at a final concentration of 500 mg/L. The bottled water had a bicarbonate concentration of 284 mg HCO_3^-/L.
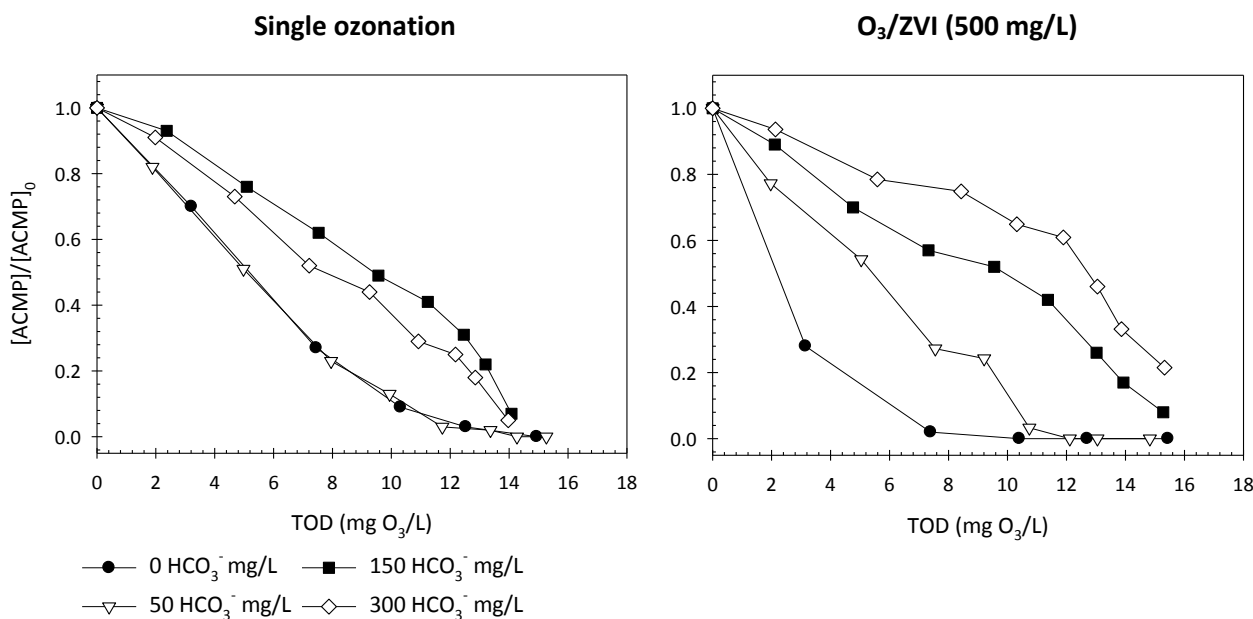
Figure 9. Experiments' data using miliQ water without and with 500 mg ZVI/L and different concentrations of bicarbonates (HCO$_3^-$). Results represent relative concentration of acetamiprid (ACMP) against the consumption of ozone (TOD).

Results, in Figure 9 left, showed that for single ozonation, there were differences depending on the amount of bicarbonates present. For 0 mg HCO$_3^-$/L and for 50 mg HCO$_3^-$/L the results were similar: the acetamiprid degradation was almost equal while the ozone was consumed. However, with 150 and 300 mg HCO$_3^-$/L, the degradation was slower and similar for both concentrations, so it needed to consume more ozone to attain comparable degradation levels of the model compound.
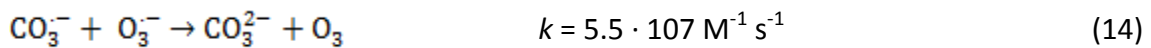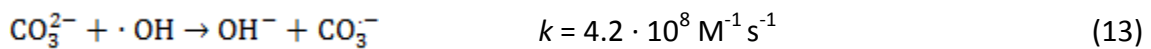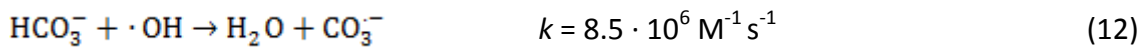
When using ZVI catalyst (Figure 9; right), the differences between the diverse concentrations of bicarbonates were more remarkable. In this case, when the concentration of bicarbonates was 50 mg/L, the degradation was slower than 0 mg/L. For waters with higher bicarbonates concentration, the degradation was much slower and, comparing with single ozonation process, higher concentration of bicarbonates lowered the degradation and increased the consumption of ozone. In addition, as it was seen for bottled water (Figure 7), there was a change on the degradation kinetics after around 9-12 mg O$_3$/L consumed.

The results obtained can be explained by the reactions that occur inside the system. In water with a pH near neutrality, such the water used, dissociation of bicarbonates to

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carbonates and protons has a low constant (Ka) (i.e. high pKa) (Equation (11)) (Mook, 2002) and thus, the reaction is primarily shifted to the not dissociation form of the compound.

$$HCO_3^- \underset{\rightarrow}{\leftarrow} CO_3^{2-} + H^+ \qquad\qquad pK_a = 10.33 \qquad\qquad (11)$$
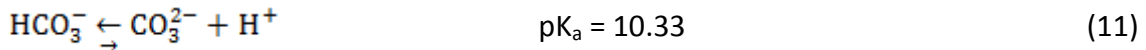
Despite the fact that both ions (bicarbonate and carbonate) do not react with ozone, they are able to consume free hydroxyl radicals (Equations (12) and (13)) (Gardoni, Vailati and Canziani, 2012), leading to a scavenging effect. The mentioned reactions, as they occur fast, have high reaction rate constants (k), being for the scavenging effect of carbonates higher than for bicarbonates. Although this effect could explain the (bi)carbonates effect on ozonation process, it has been reported that the product CO_3^- formed on carbonates reaction also react with O_3^- radical leading to the generation of carbonates and ozone (Equation (14)) (Gardoni, Vailati and Canziani, 2012).

$$HCO_3^- + \cdot OH \rightarrow H_2O + CO_3^- \qquad\qquad k = 8.5 \cdot 10^6 \, M^{-1} s^{-1} \qquad\qquad (12)$$

$$CO_3^{2-} + \cdot OH \rightarrow OH^- + CO_3^- \qquad\qquad k = 4.2 \cdot 10^8 \, M^{-1} s^{-1} \qquad\qquad (13)$$

$$CO_3^- + O_3^- \rightarrow CO_3^{2-} + O_3 \qquad\qquad k = 5.5 \cdot 107 \, M^{-1} s^{-1} \qquad\qquad (14)$$

Our results showed for single ozonation and O_3/ZVI (500 mg/L) faster and more efficient degradation, and thus less ozone consumed, when having less bicarbonates concentration in the system. These results then confirmed the effect of (bi)carbonates as free hydroxyl radicals' scavengers.
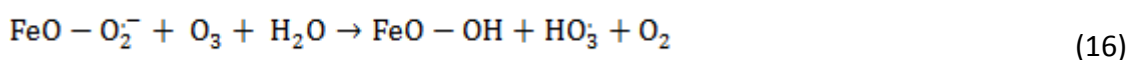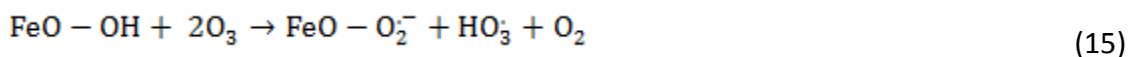
If we analysed the total and iron ions (II) dissolved in the system during the experiment, plotted in Figure 10, results showed that the amount of dissolved total iron and dissolved iron ions (II) were unstable during the experiment and different for the different concentration of bicarbonates used, being higher at less bicarbonates concentration. However, although the iron results obtained for bottled water and for miliQ water with 300 mg HCO_3^-/L are not reproducible, the phenomenon of change on the degradation kinetics also coincided with the lack of dissolved iron ions (II).
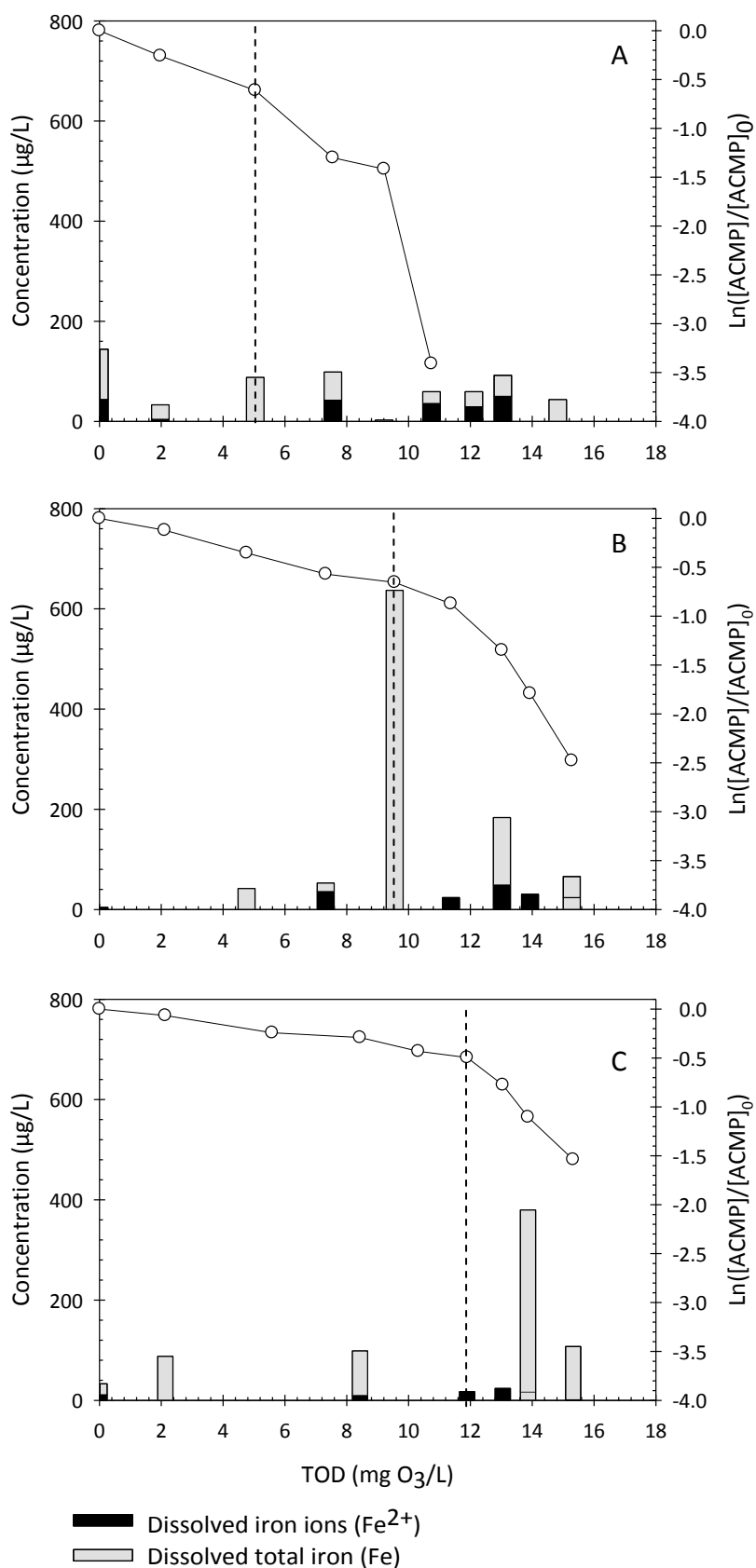
Figure 10. Experiments' data using miliQ water with 500 mg ZVI/L and different concentrations of bicarbonates (HCO_3^-). Bars represent total dissolved iron and dissolved iron ions (II) against the consumption of ozone (TOD) and white rounds the logarithm of the relative concentration of acetamiprid (ACMP) in solution. **A**: 50 mg HCO_3^-/L. **B**: 150 mg HCO_3^-/L. **C**: 300 mg HCO_3^-/L. Striped lines show the start of the change on the degradation kinetics.

Equations could also help us to understand what happened. During the homogeneous catalyst process (Equations (5) to (10)), iron ion (II) and ion (III) are responsible of the production of $\cdot OH$ and $O_3^{\cdot -}$. When there are (bi)carbonates in the system, there is a scavenging effect of $\cdot OH$ and $O_3^{\cdot -}$ (Equations (12) to (14)), leading to a lower hydroxyl radicals generation (Equation (7)), decreasing the degradation rate of the contaminant. This can explain that at first there is a low degradation of acetamiprid on the solution when having (bi)carbonates and iron in the system. The initial degradation that is observed in these cases is caused by the effect of some Fe-contaminant complexes that can react with ozone without the participation of free hydroxyl radicals (Xiong et al., 2016).

The coincidence of the lack of dissolved iron ions (II) with the change on acetamiprid degradation kinetics, could be explained by the different reactions in which iron ions are involved (Equations (5) to (10)). While ozone was consumed, scavengers consumed all the radicals hydroxyl as above explained. There was a moment that the scavengers of the system were exhausted and led to free hydroxyl radicals which could react with the contaminant and then, degrade it. However, the degradation was too fast and this amount of free hydroxyl radicals was not enough to see the increase on degradation observed. In this case, together with the homogeneous catalyst ozonation, there was a heterogeneous catalyst ozonation based on the formation of oxidative complex FeOOH on the surface of catalyst able to react with ozone and generating $\cdot OH$ (Equations (15) and (16)) (Xiong et al., 2016). Both catalyst processes, together with Fenton-like reactions and absorption-precipitation processes (Wang and Bai, 2017; Xiong et al., 2016) were responsible of the high acetamiprid degradation.

$$FeO - OH + 2O_3 \rightarrow FeO - O_2^- + HO_3^{\cdot} + O_2 \tag{15}$$

$$FeO - O_2^- + O_3 + H_2O \rightarrow FeO - OH + HO_3^{\cdot} + O_2 \tag{16}$$

The differences on the behaviour for bottled water and the miliQ water with 300 mg HCO_3^-/L could be related to the other parameters present in bottled water that also could have a scavenging effect and/or the final amount of bicarbonates in bottled water that maybe was less than it was expected.

3.3. Effect of organic matter

To test the effect of organic matter in water, some experiments with miliQ water at 2 mg/L of organic matter were performed. Experiments were conducted without and with catalyst at a concentration of 500 mg ZVI/L. The pH was adjusted at the beginning of the experiment at 7.5 but during the experiment it was unstable being around 5.
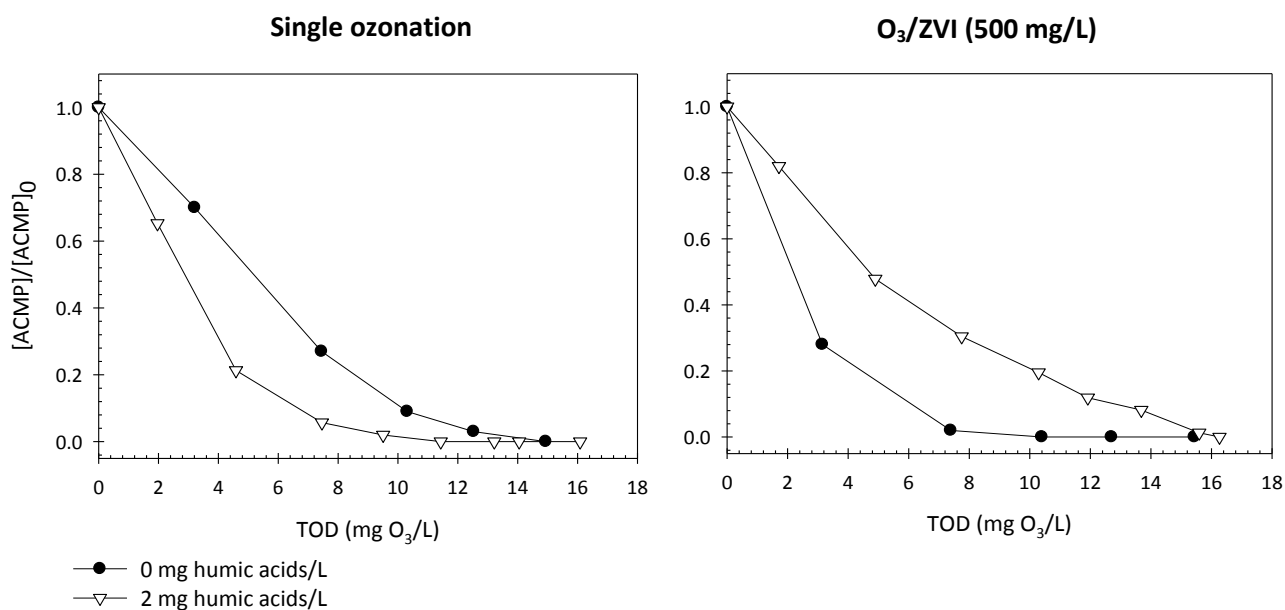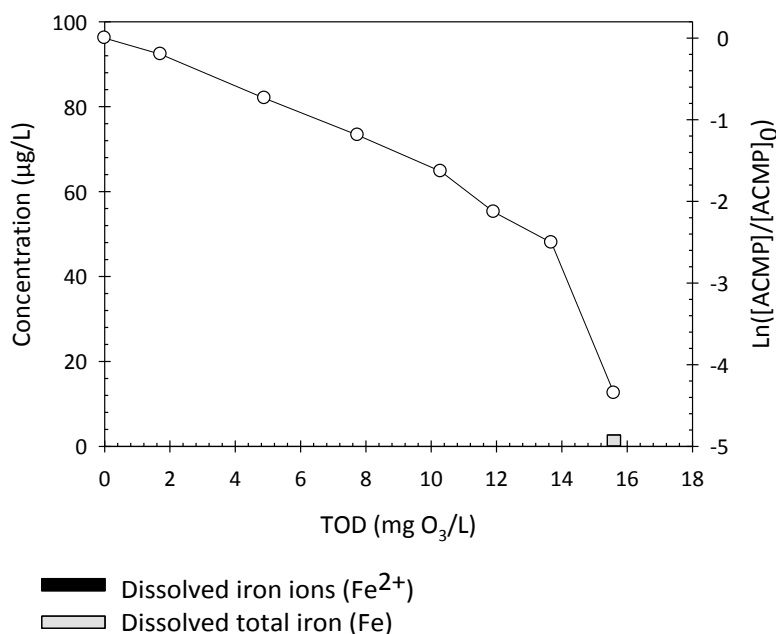

Figure 11. Experiments' data using miliQ water without and with 500 mg ZVI/L and with and without 2 mg humic acids/L. Results represent relative concentration of acetamiprid (ACMP) against the consumption of ozone (TOD).

Results plotted in Figure 11 showed that for single ozonation acetamiprid degradation was faster when having little organic matter inside the system. However, for experiments with catalyst, the results showed that the ozonation effect was better to degrade or eliminate the contaminant in the absence of humic acids in the solution. In addition, as shown iron results plotted in Figure 12, dissolved iron ions (II) lacked during all the catalytic experiment and very little dissolved total iron was only present at the end of the experiment.

Natural Organic Matter (NOM), which is generally referred as humic acids, is formed by humic substances, polysaccharides, aminosugars, proteins, peptides, lipids and small hydrophilic acids (Gardoni, Vailati and Canziani, 2012). Its structure consists of alkyl

and aromatic units linked to functional groups (Gardoni, Vailati and Canziani, 2012) and a vast unsaturated bonds, electron-rich aromatic systems, amines and sulphides with which ozone preferentially and directly reacts (Van Geluwe, Braeken and Bruggen, 2011).

Dissolved iron ions (Fe^{2+})
Dissolved total iron (Fe)

Figure 12. Experiments' data using miliQ water with 500 mg ZVI/L and 2 mg humic acids/L. White rounds represent the logarithm of concentration acetamiprid (ACMP) against Transferred Ozone Dose (TOD). Bars represent the concentration of dissolved total iron and the iron ions (II) in solution against TOD.

During the direct reaction between ozone and NOM during the initial phase of ozonation, a high amount of hydroxyl radicals are formed due to the promotion of ozone decomposition (Equations (17), (18) and (7)). For this reason, when having NOM present in the system acetamiprid degradation was faster than only applying ozone.

$$O_3 + NOM \rightarrow NOM^+ + O_3^{\cdot-}$$
(17)

$$O_3^{\cdot-} + H^+ \rightarrow HO_3^{\cdot-}$$
(18)

In the case of having the catalyst ZVI in the system, our results showed that humic acids had a negative effect on the ZVI catalyst process. A possible explanation could be the absence of soluble iron during the experiment probably for the formation of NOM-Fe complexes which disabled the catalytic effect of both iron and organic matter during ozonation.

4. Conclusions

In this research, catalytic iron ozonation (i.e. O_3/ZVI) was applied to test its efficiency eliminating and/or reducing the concentration of a model contaminant, acetamiprid. Spiked waters with the contaminant were used in a lab-scale semi-batch ozonation setup. During the research some parameters and characteristics, such as the amount of bicarbonates and the organic matter present in water, were tested. In addition, the effect of dissolved iron during the process was studied. Therefore, the conclusions of this research were:

- The water matrix (i.e. miliQ and bottled water) at pH = 7.5 had an influence on the catalytic iron ozonation being acetamiprid degradation in miliQ water faster and more efficient at the same ozone consumed than in bottled water.

- The concentration of bicarbonates in bottled water at pH = 7.5 could be the responsible of these differences between waters, due to their hydroxyl radicals scavenging effect.

- Test performed in miliQ water in the presence of bicarbonates at pH=7.5 demonstrated their effect on the ZVI catalyst processes; a lower bicarbonates concentration presented more efficient and faster acetamiprid degradation demonstrating their hydroxyl radicals scavenging effect.

- During ZVI catalyst process in the presence of bicarbonates, dissolved iron was unstable. This could have an influence on the increase on acetamiprid degradation after around 10-12 mg O_3/L consumed due to the homogeneous and heterogeneous catalytic reactions.

- The presence of organic matter (NOM) in miliQ water at pH = 7.5 improved the single ozonation process to degrade the contaminant but for catalytic iron ozonation better acetamiprid degradation was obtained in the absence of organic matter.

- Creation of NOM-Fe complexes during O_3/ZVI catalyst could disable the contaminant degradation process.

These conclusions increase the knowledge about the iron catalytic ozonation process for further scientific research and technical applications.

For further scientific research it would be interesting to deeply understand what happens with the iron during the O_3/ZVI processes, by testing the O_3/ZVI process with an increase on the organic matter. Depending on the results obtained, and after doing replicates, it would be interesting to apply the mechanism to treat a real secondary effluent.

If this technique finally has a technical application, it is remarkable that it has some advantages. First, the released water to the environment after reaction (at least, at the concentration tested in this research) would have less amount of iron than the value limited by law. Secondly, the O_3/ZVI leads to a less consume of ozone and thus, less production, which is one of the most economical limitation in a wastewater treatment plant. And, thirdly, if some research are done on the capability of waste steel shavings from the metallurgical industry as catalyst for the ozonation process and it has a waste water treatment application, this would make the process more economically viable and contribute to the circular economy.

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