Improving biotreatability of hazardous effluents combining ZVI, electrolysis and photolysis

M. Barbosa Ferreira¹, M. Muñoz-Morales², C. Sáez², P. Cañizares², C.A. Martínez-Huitle¹, M.A. Rodrigo²,*

¹Institute of Chemistry, Federal University of Rio Grande do Norte, Campus Universitario 3000, 59078-970 Natal-RN, Brazil
²Department of Chemical Engineering, Faculty of Chemical Sciences and Technologies, University of Castilla-La Mancha, Campus Universitario s/n. 13071 Ciudad Real, Spain

Abstract

In this work, nine types of combination advanced oxidation processes / zero-valent iron (AOP-ZVI) were tested, in order to determine if any of these combinations demonstrate good chances as pretreatment for the biological degradation processes of organochlorinated pollutants. To do this, the changes undergone in the respirometric behavior, toxicity and short-term biodegradability were compared. The three AOPs studied were anodic oxidation with mixed metal oxides anodes (AO-MMO), with boron doped diamond anodes (AO-BDD) and photolysis and they were evaluated in three different modes: without any addition of ZVI, with ZVI-dehalogenation as pre-treatment and with ZVI-dehalogenation simultaneous to the AOP treatment. Clopyralid has been used as a model of chlorinated hydrocarbon pollutant. Results show that technologies proposed can successfully treat wastes polluted with clopyralid and the biological characteristics of the waste are significantly modified by dehalogenating the waste with ZVI, either previously to the treatment or simultaneously to the treatment, being the information provided by the three techniques very important in order to
evaluate later combinations of the advanced oxidation technologies with biological treatments.

Keywords

ZVI; electrolysis; photolysis; biodegradability, toxicity
Highlights

- Important dehalogenation and high impact on biological characteristics
- Addition of ZVI modifies importantly the characteristics of wastes
- Great changes between the use of ZVI as pre-treatment or simultaneous to the AOP
- Better respirometric behavior after photolysis treatments
- Lower toxicity with ZVI dehalogenation
- Higher biodegradability of the effluents of BDD-electrolysis
**Introduction**

Treatment of liquid wastes polluted with hazardous pollutants is a topic of the major interest. Generally, the use of biological processes for the treatment of wastes is advised when the species contained can be degraded by microorganisms in a robust and efficient way. This is because costs associated to these treatments are known to be much lower than those associated to other oxidation technologies. However, sometimes the application of these technologies fails and there is no other choice than the use of advanced oxidation processes (AOPs). Within this group, characterized by the production and use of hydroxyl radical as the primary oxidant, electrochemical advanced oxidation processes (EAOPs) joint one of the most efficient set of technologies, involving very different processes based on the use of electrolysis (Bebelis et al., 2013; Dewil et al., 2017; Oturan and Aaron, 2014; Sirés et al., 2014).

Results obtained by EAOPs depends on the anode material and operation conditions used (Malpass et al., 2010; Mena et al., 2017; Scialdone et al., 2009; Zhou et al., 2011). Thus, depending on the anode material, the oxidation conditions can be harsher or softer. The first type of conditions is obtained with non-active electrodes, such as the diamond coatings (especially boron-doped diamond, BDD), which lead to important mineralization degrees and small production of stable intermediates. Conversely, the second type of conditions leads to lower mineralization percentages and to the formation of many intermediates and, among the electrodes that attain them, it is worth to mention the mixed metal oxides (MMO) anodes containing ruthenium or iridium oxides (Fóti et al., 1999; Panizza and Cerisola, 2005; Panizza and Cerisola, 2008; Panizza and Cerisola, 2009).

Regarding the operating conditions, electrolytic processes can be divided into two categories, namely anodic oxidation and enhanced mediated oxidation
processes (Martínez-Huitle et al., 2015). In the first, the direct and mediated electrochemical processes are developed during the treatment, although the second group is not promoted, but just occur naturally. In the second, the addition of oxidant precursors is applied to enhance the results obtained, moving the oxidation zone from the nearness of the electrode surface to the bulk of the solution. The most important process belonging to this group is the electro-Fenton (Brillas et al., 2009; Garcia-Segura et al., 2015; Randazzo et al., 2011; Özcan et al., 2008; Üstün et al., 2010), that reach very high efficiencies in the degradation of many types of organics.

One of the most important types of pollutants that must be treated with these technologies are chlorinated hydrocarbons. These compounds have a wide variety of applications, ranging from pesticides to industrial solvents and, unfortunately, they are contained in many waste flows. Hazardousness of pollutants is directly related to the chlorine content of the molecule and because of that, dehalogenation with different technologies has been proposed as a good possibility to be included in the overall treatment (Rodrigo et al., 2014). At this point, the use of zero-valent iron (ZVI) is seen as promising (Crane and Scott, 2012; Dominguez et al., 2016a; Dominguez et al., 2016b; G et al., 2016; Kim et al., 2010; Pardo et al., 2016; Xu and Wang, 2011) and previous works about the combination of this technology with EAOP have been recently published, in which it is demonstrated that, from the viewpoint of electrochemical treatment, a pre-treatment with ZVI does not show important advantages (Carvalho de Almeida et al., 2019b), although it was suspected that the system could improve the biological treatability. Because of that, further research was carried out and, in this work, we aim to evaluate if this improvement is real. To this, different combinations of electrochemical and ZVI processes have been proposed, including electrochemical tests with active and non-active electrodes. In addition, for the sake of comparison, results have been compared to those obtained using photolysis,
a well-known AOP. As a model compound the organochlorine pesticide clopyralid was selected. Two ZVI-dehalogenation conditions were used in combination with the electrochemical and photolytic treatments, and results were compared with the same treatments without the use of the ZVI reagent. In the first, dehalogenation with the ZVI is applied as a previous treatment, followed then by the electrochemical or photolytic treatment. In the second ZVI-dehalogenation process, the ZVI was added directly to the reactor, where the electrochemical or photolytic treatments develop, trying to see the effect of the simultaneous dehalogenation and advanced oxidation processes. Hence a total of 9 combinations of treatments dehalogenation-AOP are compared, trying to shed light on the benefits of their potential further combination with biological oxidation technologies.
Material and Methods

Chemical reagents. Clopyralid (99%) (CAS number: 1702-17-6, C₆H₃Cl₂NO₂, 72% purity, solubility > 1 g L⁻¹ at 20°C, Kₐw = 2.34-3 at pH 7 and 20°C) purchased from Sigma Aldrich, was selected as a model of organic compound. The micro iron (≥99%, granular, 10-40 mesh, > 99.99% trace metal base, CAS number 7439-89-6) was purchased from Sigma Aldrich and it was used as received (average size is 568 µm).

Methanol HPLC grade and formic acid (Sigma-Aldrich, Spain) were used for the mobile phase of HPLC. Sulfuric acid (98%) (Scharlab, Barcelona) were used to control pH and sodium sulphate from Sigma Aldrich as electrolyte. Double deionized water (Millipore Milli-Q system, resistivity: 18.2 MΩ cm at 25°C) was used to prepare all solutions. Clopyralid solutions used as synthetic wastes were prepared at a concentration of 30 mg dm⁻³ with 10³ mg dm⁻³ of Na₂SO₄.

Dehalogenation conditions. To compare the efficiency of the ZVI reagent in the dehalogenation of the organochlorine pesticide, three different methodologies were developed for the effluent mitigation process. The first was a single electrochemical treatment, carried out in a single flow cell (SFC) as it was explained elsewhere (Carvalho de Almeida et al., 2019a) without the presence of ZVI, before or simultaneous to the AOP. The current density was 50 mA cm⁻² and two different anodes (MMO and BDD), with an area of 78.6 cm², were evaluated. The second methodology consists of a pretreatment of the effluent with 45 g L⁻¹ of ZVI and then, the application of the electrochemical treatment in the same conditions stated before. Finally, the third methodology consists of the simultaneous dehalogenation/electrolysis attained with the addition of ZVI in situ to the electrochemical tank. Photochemical treatments with a UV lamp of 11 W were also carried out with the three methodologies mentioned, to provide more information on the ideal conditions for the use of ZVI as a dehalogenation agent. Experimental conditions were summarized in Table 1.
Table 1. Experimental conditions of photolysis and electrolysis using DSA and BDD anodes.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Photolysis</th>
<th>MMO-Electrolysis</th>
<th>BDD-Electrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>No ZVI</td>
<td>$W_{irradiation} = 11\text{W}$</td>
<td>$J = 50 \text{ mA cm}^{-2}$</td>
<td>$J = 50 \text{ mA cm}^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$V = 1 \text{ dm}^3$</td>
<td>$V = 1 \text{ dm}^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$W_{electrolysis} = 17.05 \text{ W}$</td>
<td>$W_{electrolysis} = 16.66 \text{ W}$</td>
<td></td>
</tr>
<tr>
<td>ZVI Pretreatment</td>
<td>$W_{irradiation} = 11\text{W}$</td>
<td>$J = 50 \text{ mA cm}^{-2}$</td>
<td>$J = 50 \text{ mA cm}^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$V = 1 \text{ dm}^3$</td>
<td>$V = 1 \text{ dm}^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$W_{electrolysis} = 10.78 \text{ W}$</td>
<td>$W_{electrolysis} = 15.28 \text{ W}$</td>
<td></td>
</tr>
<tr>
<td>ZVI in situ</td>
<td>$W_{irradiation} = 11\text{W}$</td>
<td>$J = 50 \text{ mA cm}^{-2}$</td>
<td>$J = 50 \text{ mA cm}^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$V = 1 \text{ dm}^3$</td>
<td>$V = 1 \text{ dm}^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$W_{electrolysis} = 10.38 \text{ W}$</td>
<td>$W_{electrolysis} = 14.50 \text{ W}$</td>
<td></td>
</tr>
</tbody>
</table>

Pretreatment lasted for 72 hours, where the synthetic effluent was maintained under constant stirring, 150 rpm and pH 3 in a thermostatic bath at a temperature of 40°C during the whole process. Temperature of the system is kept constant (25°C) by means of a thermostatic bath (JP Selecta, Digiterm 100) and a heat exchanger.

**Analytic Techniques.** Selected samples were collected and filtered with 0.22 µm Nylon Supelco filters before analysis. The concentration of the clopyralid and their dehalogenated intermediates were quantified by HPLC (Agilent 1200 series) using a ZORBAX Eclipse Plus5 C18 analytical column. The mobile phase consisted of 30% methanol / 70% water with 0.1% of formic acid (flow rate: 0.8 cm$^3$ min$^{-1}$). The DAD detection wavelength was 280 nm, the temperature was maintained 25 ºC and the injection volume was 20 µL. The Total Organic Carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytic Jena Analyser. Chemical oxygen demand (COD) was measured with Spectroquant® kits and it was determined by a Pharo 100 Merck spectrophotometer analyzer. Water samples toxicity were determined along the different stages of the electrochemical pre-treatment by means of a BioTox™ Kit supplied by Aboatox. The inhibitory effect of the sample on the light emission of luminescent bacteria, Aliivibrio fischeri, formerly Vibrio fisheri (Urbanczyk et al., 2007), is measured with a luminometer (Junior LB 9509 of Berthold Technologies). This test provides a rapid, easy to use method for measuring toxicity of aqueous
samples (Rodriguez et al., 2013). The sample toxicity was evaluated as EC50 by measuring the effective concentration at which 50% of the light is lost due to the toxicity (Salles et al., 2010; Sarria et al., 2002).

The respirometry was performed by measuring dissolved oxygen consumption (mg O₂ L⁻¹ h⁻¹) by the microorganisms contained in active sludge after adding the treated samples. The active sludge used in this work was collected from the Aquona Water Treatment Plant, located in Ciudad Real/ES. After their collection, they were stored in a tank with constant supply of oxygen through an air pump. The rate of oxygen uptake, called the "respiration rate" (mg O₂ L⁻¹ h⁻¹), is determined by analytical measurements performed using a portable dissolved oxygen meter pHenomenal® OX 4100 H. Measurements were performed under continuous stirring at 200 rpm, and in an enclosed container. The active sludge has a requirement of oxygen necessary for its respiration, that is, the oxidant necessary for the functioning of the cells of its microorganism, which is called endogenous sludge respiration rate (Andreottola et al., 2005). Thus, before these tests, the sludge was kept one-night bubbling oxygen without adding any substrate to reach this endogenous state. Experiments have compared the oxygen consumption in the endogenous stage before and after adding the treated samples. In addition, a modified test allows the calculation of the short-term biological oxygen demand, obtained by adding samples for which the total consumption of oxygen associated to the substrate can be measured during a single batch test.
Results and discussion

General oxidative behavior. Figures 1, 2 and 3 show the changes undergone in the clopyralid, TOC and COD concentrations after 0, 2 and 4 h of treatment in the three different conditions studied for each technology: no addition of ZVI, pre-treatment with ZVI-dehalogenation and simultaneous ZVI-dehalogenation/oxidation. The three parameters monitored give different information about the progress of the treatment: the changes in the herbicide concentration informs only about the oxidation or dehalogenation reactions underwent by any of the functional groups of the raw molecule and this information is less valuable than that of COD or TOC, which inform, respectively, about the global oxidation state of the pollutants contained in the in-treatment waste or the mineralization attained.

As seen, from the viewpoint of the oxidative technologies, there are important differences between the removals attained here, being more effective the use of BDD-electrolysis, which does not only remove the raw pollutant, but it is also capable to mineralize a very important fraction of the pollution contained in wastewater within the reaction time fixed. Considering the current density applied (50 mA cm\(^{-2}\)), electric charges passed in 4 h are 15.6 Ah dm\(^{-3}\), more than 130 times the faradaic values required (0.12 Ah dm\(^{-3}\)). This means that efficiencies obtained in the experiments are lower than 0.75%. This low efficiency can be explained in terms of the very low initial concentration of the pollutant in the waste and it is within the values expected according to the Comninellis’ model (Rodrigo et al., 2001), considering that the COD\(_{\text{limit}}\) of the cells used, for the flow rates used, is around 1750 mg dm\(^{-3}\) as well as the average COD concentration during the test is near 15 mg dm\(^{-3}\) (COD\(_{\text{average}}$/COD_{\text{limit}} = 15/1750 = 0.8\%$) (Aquino et al., 2014). Electrolysis with MMO electrodes is even less efficient and the results obtained are very similar to those of photolysis. However, despite the low
removals, the results confirm that the three oxidation technologies are able to attack
clopyralid, attaining the mineralization and, hence, that they can treat wastes containing
this herbicide.

Regarding the effect of the addition of ZVI, there are no significant differences between
the three cases of study in the BDD-electrolysis, just an improvement in the oxidation
rate, which allows the complete removal of COD within the 4 h of treatment in the tests
with the ZVI pre-dehalogenation and simultaneous dehalogenation. It is important to
point out that, although the same waste has been used in all tests, measured values of
TOC and COD change in an important way with the dehalogenation treatment. This is
because the effect shown in the figures is the direct result of the application of the
analytical technique and the dehalogenated intermediates affect significantly both
parameters, in particular the COD, not representing the theoretical expected value but
the IR absorption by gases produced during a catalytic oxidation, in the case of the
TOC, or the color of a reaction media in which species contained react with dichromate,
in the case of the COD, and both are clearly affected by the dehalogenation of the raw
molecule. Because of that, data should be handled with care and what is really important
is the comparison of the changes observed in the parameters and not the numerical
values, which are not representing exactly the theoretically expected value.

Taking into account this observation, regarding the other two technologies evaluated,
the MMO-electrolysis seems to be improved with the ZVI dehalogenation strategies and
higher mineralization and oxidation rates are observed as compared to the single
technology. This indicates that the electrolysis, which is still very inefficient after the
addition of the ZVI (with both strategies), is more effective for non-halogenated species
than for the raw chlorinated species. Meanwhile, the photolysis undergoes a very
different effect and it works better in process without ZVI dehalogenation, indicating
that the dehalogenated intermediates have less photolytic activity than the non-dehalogenated species.

Figure 1. Removal of Clopyralid by: A) single technologies, without ZVI addition; B) ZVI-dehalogenation pretreatment; C) ZVI-dehalogenation simultaneous with the AOP. Symbols: Electrolysis MMO ○; Electrolysis BDD ●; photolysis ○.

Figure 2. Mineralization by: A) single technologies, without ZVI addition; B) ZVI-dehalogenation pretreatment; C) ZVI-dehalogenation simultaneous with the AOP. Symbols: Electrolysis MMO ○; Electrolysis BDD ●; photolysis ○.
Figure 3. Oxidation by: A) single technologies, without ZVI addition; B) ZVI-dehalogenation pretreatment; C) ZVI-dehalogenation simultaneous with the AOP. Symbols: Electrolysis MMO ○; Electrolysis BDD ●; photolysis ●.

Respirometric tests. Respirometry is based on measuring the rate of oxygen consumption of microorganisms when they degrade an organic substrate, ammoniacal nitrogen or, even, themselves (what it is known as endogenous breathing). The respiration rate (also called as oxygen uptake rate, OUR) consists of the amount of oxygen consumed by bacteria per unit of time and it is expressed in mg O$_2$ L$^{-1}$ h$^{-1}$. Its value only depends on the state of the biomass and the quantity and biodegradability of the substrate that is available. Figure 4 shows as example two different respirometries made with non-acclimated activated sludge obtained from a municipal wastewater treatment plant and they correspond to the respirometric behavior of the active sludge before (endogenous respiration) and after adding the treated waste with the herbicide coming from 240 min of photolysis or electrolysis (BDD and MMO). In each case 5 mL were added to 20 mL of suspension containing a concentration of SSV of around 400 mg L$^{-1}$. 
Figure 4. Respirometries made to activated sludge feed with water coming directly from the municipal WWTP of Ciudad Real in which it is added 20 mL of treated wastewater \([\text{ZVI-dehalogenation previous to 4 h MMO electrolysis} \quad \text{ZVI-dehalogenation previous to 4 h BDD electrolysis.}]\)

Results show that effluents of the different treatments are biodegradable, because the addition of a small volume produces a very rapid increase in the respiration rate. This is important, because in case of refractority or inhibition the value of the slope should be kept constant or decrease, respectively. Values of the OUR calculated for the nine tests are summarized in Table 2.

<table>
<thead>
<tr>
<th>Time / s</th>
<th>Dissolved oxygen / mg L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>OUR(_0)</td>
</tr>
<tr>
<td>200</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. OUR (mg O\(_2\) L\(^{-1}\) h\(^{-1}\)) before and after the addition of clopyralid waste and relative variation (%)
Changes observed indicate the rapid biodegradability of the clopyralid waste treated with the different technologies. Photolysis is the technology that attains the higher enhancements in the metabolic activity of microorganisms followed by MMO electrolysis, being the electrolysis with the non-active electrode the technology in which the improvement in the activity seems to be the worst (although still very positive). Regarding the dehalogenation, it seems to follow a different pattern for each technology. For photolysis is negative, that is, pre-dehalogenation, or simultaneous dehalogenation, does not improve respiration rate of microorganism. For MMO electrolysis, almost no effect is observed and for BDD-electrolysis, dehalogenation has a positive impact on the respiration rate, especially the pre-dehalogenation treatment.

**Changes in toxicity.** The increase in the slope observed in the respirometries, when adding the treated waste, suggests that toxicity of the effluents should not be very high. Otherwise, instead of an increase in the slope a decrease should be expected. However, in order to understand better the process, it was considered interesting to measure this parameter with an standard test using photoluminescent of Vibrio Fisheri (MicroTox Test). This test is known to be more time-saving and sensitive than other biological test that have been proposed in the literature. Figure 5 shows the changes in the EC50 undergone by the fluid during the progress of the 9 tests, calculated as the relative volume that it is necessary to cause a 50% reduction in light after 30 min of exposure.

<table>
<thead>
<tr>
<th></th>
<th>Photolysis</th>
<th>MMO-Electrolysis</th>
<th>BDD-Electrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>No ZVI</td>
<td>4.48/7.71</td>
<td>4.58/6.87</td>
<td>5.72/5.84</td>
</tr>
<tr>
<td></td>
<td>(+41.9%)</td>
<td>(+33.3%)</td>
<td>(+2.1%)</td>
</tr>
<tr>
<td>ZVI Pre-treatment</td>
<td>7.03/7.98</td>
<td>8.81/11.91</td>
<td>10.11/13.28</td>
</tr>
<tr>
<td></td>
<td>(+11.3%)</td>
<td>(+26.0%)</td>
<td>(+23.9%)</td>
</tr>
<tr>
<td>ZVI in situ</td>
<td>7.64/10.88</td>
<td>9.38/12.95</td>
<td>2.81/3.43</td>
</tr>
<tr>
<td></td>
<td>(+29.8%)</td>
<td>(+27.6%)</td>
<td>(+18.1%)</td>
</tr>
</tbody>
</table>
time. Samples were taken at different times and, in most cases, toxicity is reduced despite the herbicide is not fully removed.

Figure 5. Changes in the EC50 during: A) single technologies, without ZVI addition; B) ZVI-dehalogenation pretreatment; C) ZVI-dehalogenation simultaneous with the AOP. Symbols: Electrolysis MMO ○; Electrolysis BDD ●; photolysis ⬜.

In the case of the single treatment (without ZVI dehalogenation), higher toxicity is detected after the electrochemical treatment due to the oxidants produced, because in the case of the BDD-electrolysis a very important part of the organic content is mineralized, so the inorganic species should account for the reduction in toxicity. Contrary, in the case of photolysis, the toxicity detected is reduced by around 3 times, which indicates that the soft changes observed during the treatment, in terms of oxidazability and mineralization, leading to the formation of intermediates that are less toxic than the raw pollutants. In the case of oxidation carried out with a previous dehalogenation process, the results obtained are clearly much better. In addition, maximum reduction of toxicity is obtained with BDD anodes (close to 4-times reduction). Regarding the simultaneous ZVI-dehalogenation, toxicity is also reduced, with similar values in all cases, being a little bit higher the reduction of toxicity with BDD anodes (1.76 times). In comparing the respirometry and the EC50, it is important
to take in mind that the first technique gives information about the influence of the
treated waste to a consortium of microorganism while in the second case the
information is limited to the photoluminescence microorganisms tested. This means that
despite the second test is more standard, the first gives more valuable information
because it is the sludge that has to treat the waste if this waste is discharge to sewers
(Coelho et al., 2009; Li et al., 2016; Malpass et al., 2011; Van Aken et al., 2015).

Changes in Short-term Biodegradability. A modification of the respirometric test
shown in the previous section can be used to measure the short-term biological oxygen
demand, that is the amount of oxygen required to oxidize a given amount of wastewater.
This parameter can be related to DBO₅, TOC or COD in order to give a biodegradability
index of the wastewater, which indicates the percentage of substrate that can be easily
metabolized (Mouset et al., 2014). Figure 6 shows, for three of the 9 cases evaluated
in this work, how this measurement can be carried out. As seen, the decay rate observed
before the SWE sample added is recovered after some time. Distance between the two
lines indicates in concentration units of oxygen the DBO₅st. This value must be corrected
with the dilutions made in order to calculate the real DBO₅st of the sample measured.
Figure 6. Three examples of the calculation of DBO$_{st}$ with samples obtained in this study. Main: photolysis without ZVI dehalogenation. Onset left: ZVI pre-dehalogenation with MMO electrolysis. Onset right: Simultaneous ZVI dehalogenation-photolysis.

With this calculation, Figure 6 shows the changes in the DBO$_{st}$/TOC ratio undergone by the waste during the progress of the 9 tests. In these figures, it is shown the evolution of the DBO short time with the time in different treatment approaches studied.

Figure 7. Changes in the biodegradability during: A) single technologies, without ZVI addition; B) ZVI-dehalogenation pretreatment; C) ZVI-dehalogenation simultaneous with the AOP. Symbols: Electrolysis MMO ○; Electrolysis BDD ●; photolysis ●.

High values of this parameter indicate high biodegradability of the samples, because more oxygen must be consumed by the sludge to fully degrade it. Results shows that higher biodegradability is obtained with BDD-electrolysis, as it was expected because the higher removal of clopyralid and intermediates and, hence, the higher concentration of carboxylic acids, which are the final intermediates formed during the oxidation of aromatic compounds. The highest value was obtained with the simultaneous ZVI-dehalogenation (around 15 times higher the value of DBO$_{st}$ than TOC). Similar pattern is followed without ZVI and with a pretreatment with ZVI but with smaller ratios (1.6 –
Regarding to the use of MMO-electrolysis and photolysis, the ratios are less than 2 in all cases, however better results are obtained with MMO in the case of the use of ZVI particles before to the electrochemical process and, on the contrary, with photolysis better results are obtained using ZVI particles also in the photo-treatment.

**Conclusions**

From this work, the following conclusions are drawn:

- Photolysis and electrolysis with MMO or DDB anodes can treat wastes polluted with clopyralid. Results obtained by these technologies are significantly modified by dehalogenating the waste with ZVI, either previously to the treatment or simultaneously to the treatment. Biological characteristics of the effluents are modified importantly.
- Respirometry indicates that photolysis attains the highest increases in the metabolic activity of microorganisms and that this treatment is not importantly affected by the ZVI dehalogenation. Regarding the electrolysis, MMO lead to more biologically active systems than BDD. This respirometry indicates the activity of a consortium of microorganisms, with similar characteristic to those that has to treat waste if discharge to a municipal sewer.
- Toxicity determined by EC50 decreases when adding ZVI for all technologies tested. However, single electrolyses do not affect positively to the survival of the bioluminescence microorganisms. Formation of oxidants and specificity of the microorganisms can help to explain this different behavior as compared to respirometry.
- Ratio \( \text{DBO}_{5} / \text{TOC} \) increases more importantly for BDD-electrolysis than for the other technologies evaluated. The more important progress of the reaction up to the formation of carboxylic acids can help to explain this behavior.
Acknowledgements

Financial support from Agencia Estatal de Investigación through project CTM2016-76197-R (AEI/FEDER, UE) and the Spanish Government (Grant Nº FPU16/00067) are gratefully acknowledged.

References


