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Title: Biodegradability improvement and toxicity reduction of soil washing effluents polluted with atrazine by means of electrochemical pre-treatment: influence of the anode material.

Article Type: Research Article

Keywords: Atrazine; soil washing effluent; anodic oxidation; biodegradability; toxicity

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Biodegradability improvement and toxicity reduction of soil washing effluents polluted with atrazine by means of electrochemical pre-treatment: influence of the anode material.

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Keywords

Atrazine, soil washing effluent, anodic oxidation, biodegradability, toxicity

Conflict of Interest: The authors declare that they have no conflict of interest.

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Journal of Environmental Management
Editor

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Dear Editor:

Attached you will find the REVISED form of the manuscript JEMA-D-19-03753 “*Biodegradability improvement and toxicity reduction of soil washing effluents polluted with atrazine by means of electrochemical pre-treatment: influence of the anode material*”, by María Belén Carboneras, José Villaseñor, Francisco Jesús Fernández, Pablo Cañizares and Manuel A. Rodrigo (corresponding author: jose.villasenor@uclm.es), in order to be reviewed for a possible publication as research paper in *Journal of Environmental Management*.

The following items are included in the new submission:

1. The “**Responses to reviewers**”: One MS Word document containing the detailed answers to each concrete reviewer’s comments. Each answer indicates the position of the modifications in the highlighted revised manuscript.
2. The “**Highlighted revised manuscript**”, that is the revised manuscript MS Word file, using the track changes mode, where you can easily find the modifications made to the text.
3. The “**Revised manuscript**”

Yours sincerely

Dr. J. Villaseñor

Revision Notes: Response to Reviewers

This document shows detailed responses to the reviewer's comments. The responses indicate also the changes made in the revised manuscript. The changes are easily identifiable in the highlighted revised manuscript (revised manuscript changes marked document). The location of changes (page/line details in the responses) always refer to the highlighted revised manuscript MS Word file. Note that it is possible that the PDF generated by EES move lines.

Reviewers' comments:

Reviewer #1:

A large amount of papers have been available related to the anodic oxidation of various pollutants on different types of electrodes. The BDD has been accepted as the most effective and suitable electrode. Therefore, this manuscript does not give any new findings in this respect. Atrazine is selected as the model pollutant, but its accounts for only 1% of the organic amount in the tested solution. Thus, the efficiency of the process is virtually based on the surfactant but no atrazine. In addition, the language requires an improvement.

The present work is not focused on the treatment of atrazine but on the treatment of a soil washing effluent SWE containing atrazine. The main difference is that a low atrazine concentration is emulsified into a large amount of surfactant, but despite atrazine concentration is low, SWE presents toxicity and low biodegradability. Soil washing using surfactants is a widely used method for soil remediation. This is the main novelty point of the present work and it is an important difference as compared to other atrazine electrooxidation works found in the literature (see Bravo-Yumi et al., 2018; Zhu et al., 2019 cited in references list). This statement has been deeply explained at the end of introduction section (lines 139-143 revised manuscript) and also was stated in discussion (lines 267-268 in revised manuscript).

Additionally, English language has been revised in the whole manuscript (changes can be observed in the highlighted revised manuscript)

Some specific comments are listed as follows:

What are the degradation products of atrazine?

Degradation products of atrazine were not identified as there are many interferences caused by partial degradation of the high surfactant concentration in SWE. This information has been included in revised manuscript (lines 277-278 revised manuscript).

What is the main oxidant in the system? Reactive oxygen species or active chlorine?

According to the background in introduction section, the main oxidant species in the system depend on the anode nature. BDD anode is considered as non-active electrode, where the degradation of the organic molecules is carried out by hydroxyl radicals. Conversely, the other anodes (CF and MMO) are active-electrodes and hydroxyl radical can interact with the anode surface in spite of attacking the target pollutant. In the present work, active chlorine species should be considered because the medium contains chloride ions, however the concentration of NaCl is only 84 mg dm^{-3} , and it remains below the optimal concentration found in bibliography to take advantage about active chlorine oxidant species. In addition, in the case of BDD, the subsequent formation of chlorite, chlorate and perchlorate ions is expected to occur, according to Equations 1 to 4.

This explanation has been included in discussion section, lines 306-315 in revised manuscript.

L 243 For carbon felt with large porosity and surface area, what is the contribution of adsorption?

The present work belongs to a research program about partial electrooxidation of different organochlorines (atrazine, lindane, clopyralid, oxyfluorfen) using carbon felt (CF)

and other anode materials. Because of the possible contribution of pollutant adsorption on CF surface, previous adsorption tests are always performed (see *Carboneras et al., Bioresource Technology* 252, 2018, 1-6) although in the present work it was not detailed in section “materials and methods” in the original manuscript. Our previous adsorption tests proved that atrazine adsorption on CF was negligible during experiments in this work. This information has been now detailed in revised manuscript (lines 219 - 224 revised manuscript)

L250 I don't agree with this statement. Biodegradability of the products is not determined by the mineralization efficiency, and partial mineralization is usually necessary to generate products with good biodegradability.

The statement in L250 has been modified according to the reviewer's comment (lines 356-358 revised manuscript).

L263-264 low mineralization efficiency does not ensure good biodegradability of products. So, it may not be "a good result".

The reviewer's comment is true but note that the sentence is “in principle is a good result”, that is, we look for the compromise between (1) no strong mineralization and (2) increase in biodegradability. Thus, low mineralization is a “good result” but only if biodegradability increases. The results of the present work show that it is difficult to reach this point. The sentence has been modified according to this explanation (lines 372-373 revised manuscript).

L348 While more than 90% TOC removal is obtained on the BDD electrode, why the effluent displays so high toxicity?

According to the reviewer's comments above, it is assumed that at least partial mineralization is necessary to improve biodegradability.

However, authors do not consider that there is a direct relationship between these two parameters. Despite high mineralization is obtained with BDD, toxic products (not identified) from electrooxidation could be present in the remaining organic composition. This information has been included in the revised manuscript (lines 482-484).

Reviewer #2:

The manuscript JEMA-D-19-03753, Biodegradability improvement and toxicity reduction of soil washing effluents polluted with atrazine by means of electrochemical pretreatment: influence of the anode material, present an interesting study about the possibility of combined sequential treatment in order to reduce the cost and improve the efficiency.

Some additional information or improvements should be done:

- The references along the text appear sometimes by chronologic order and other times by alphabetic order ...

Instructions for authors indicate “Groups of references can be listed either first alphabetically, then chronologically, or vice versa”.

The option chronologically has been selected and changes have been made where necessary in revised manuscript.

- In section 2.2 – The volume of effluent used in the assays should be referred and also the geometric area of electrodes (anodes and cathode)

The experimental details (volume of effluent and area of electrodes) have been included in section 2.2 in the revised manuscript.

- In line 157 – “ $35.3\text{ m}^2\text{ g}^{-1}$ and $17,700\text{ m}^2\text{ m}^{-2}$, areal weight 500 g m^{-2} ,” should be $35.3\text{ m}^2\text{ g}^{-1}$ and $17,700\text{ m}^2\text{ m}^{-2}$, areal weight 500 g m^{-2}

The line has been changed (Line 209 revised manuscript)

- In lines 285-286 – “This increment is more important working with MMO-Ir, as can be shown in TOC depletion figure.” Please explain! An referred to fig 2.

The sentence is not correct. It has been rewritten:

“Despite MMO-Ir causes higher TOC removal than MMO-Ru (as shown in figure 2), no clear differences have been observed between both MMO anodes regarding sulphate ions produced during electrolysis (figure 3).”

It has been included in revised manuscript (lines 404-408).

- In lines 292-293 – “They are transformed into oxygen, which help to explain the lower efficiency observed”. Please, improve this explanation!

The sentence has been changed:

“They are transformed into oxygen, which help to explain the lower efficiency observed since active electrodes have low O₂ overpotentials. It means that hydroxyl radicals are quickly converted into oxygen, in contrast to BDD electrode, where these radicals could be accumulated and used to degrade organics.” (Revised manuscript lines 414-418).

- In lines 308-309 – “keeps near to neutral values” with pH above 9?

The sentence has been changed (line 436).

SURFACTANT AIDED WASHING OF ATRAZINE POLLUTED SOIL

Atrazine polluted
effluent (SWE)

ELECTROCHEMICAL PRE-TREATMENT

Check different
anode materials:
BDD, CF, MMO

Atrazine removal and changes in toxicity and biodegradability

Highlights

Anode material influences electrooxidation of atrazine in soil washing effluents

BDD completely removes atrazine but also produces strong mineralization of surfactant

Rest of anodes reached approximately 75% atrazine removal and partial mineralization

Toxicity slightly decreased in all cases

Biodegradability improved only when using BDD but mineralization should be reduced

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Abstract

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changes in toxicity and biodegradability, were monitored during electrochemical experiments, showing important differences in their evolution during the treatment. It was observed that BDD was the most powerful anodic material to completely degrade atrazine. The other materials achieve an atrazine degradation rate about 75%. Regarding mineralization of the organics in SWE, BDD overtakes clearly the rest of anodes tested. CF obtains good atrazine removal ~~results while no excess~~ but low mineralization results. All the anodes tested slightly reduced the ecotoxicity of the water effluents. ~~Regarding~~ About the biodegradability, only the effluent ~~obtained after the pre-treatment~~ pre-treated with BDD ~~presented a high biodegradability at the conditions used in the present work~~ would be suitable for the application of a post-biological step, although mineralization is too strong. In this sense, it must be highlighted the mineralization obtained during the BDD pre-treatment was very strong. These results globally indicate that it is necessary to find a compromise between reaching efficient atrazine removal and biodegradability improvement, while also simultaneously avoiding strong mineralization. Additional efforts should be made to find the most adequate working conditions.

Keywords

Atrazine, soil washing effluent, anodic oxidation, biodegradability, toxicity

Highlights

Anode material influences electrooxidation of atrazine in soil washing effluents

BDD completely removes atrazine but also produces strong mineralization of surfactant

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Biodegradability improved only when using ~~BDD~~BDD, but mineralization should be reduced

Conflict of Interest: The authors declare that they have no conflict of interest.

1. Introduction

Biological treatment is the most common technology used to treat polluted water effluents. The main reasons ~~which support this statement~~ are the following: it is a cost effective and eco-friendly technology, it has a high public acceptance, sometimes it is able to carry out the complete destruction of target pollutants, and it can often be carried out on site and ~~can prove less expensive~~ at lower costs than other technologies (Vidali, 2001; Chawla et al., 2013). Nevertheless, it is not specifically designed to eliminate recalcitrant compounds such as pesticides, ~~which can pass through wastewater biological treatment processes~~ which are hardly biodegradable (Grandclément et al., 2017). For this reason, pesticides and other organic recalcitrant compounds can be usually found in aquatic environment (Aydin et al., 2018) ~~and also~~ and in drinking-water supplies (Stackelberg et al., 2007).

Atrazine has been one of the most used herbicides around the world from his appearance in 1950 because of its suitable properties. This pesticide is used to control annual grasses and broad-leaved weeds in selected vegetable and cereal crops, vines, fruit orchards, citrus grove, sugar cane, grassland and forestry (Chan et al., 2004). The widely use of atrazine has caused that it can be found in soil, aquatic environment and groundwater (Mandelbaum et al., 1993). Atrazine concentrations about 13 mg kg⁻¹ in heavily contaminated sites have been reported (Belluck et al, 1991), which is 20 times

more frequent than other pesticides in groundwater. Atrazine has been shown as a very stable molecule which presents a relative resistance to microbial attack. A previous study done in our research group showed that atrazine was not able to be biodegraded after a period of 90 days of incubation with activated sludge from a conventional wastewater treatment plant (Carboneras et al., 2017).

~~Because of that~~~~In this regard~~, new remediation alternatives have been suggested to pretreat effluents ~~polluted~~ with non-biodegradable ~~compounds~~ ~~pollutants~~ before applying a biological treatment. Electrochemical Advanced Oxidation Processes (EAOPs) have gained increasing attention as a promising technology to remove recalcitrant molecules (Moreira et al., 2017). Anodic Oxidation (AO) is one of the most used EAOP, where pollutants could be oxidized directly at the anode surface by electron transfer or indirectly oxidized thanks to the action of hydroxyl radicals and other oxidative species such as chlorine species or persulphates (Moreira et al., 2017).

An important variable which should be considered when using AO is the ~~kind of~~ ~~anode~~ ~~anodic~~ material used to perform the electrochemical pretreatment. The ~~anode~~ ~~ic~~ ~~material~~ influences the effectiveness of oxidation, degradation pathways, and reactions mechanisms ([Zhu et al., 2008](#); Wang et al., 2012; ~~Zhu et al., 2008~~). There are two kinds of anodes depending on the Oxygen Evolution Reaction. On one hand, active anodes, with low O₂-overpotentials, where higher oxidation states are available on the electrode surface and adsorbed hydroxyl radicals may interact with the anode. Mixed Metals Oxides and carbon anodes belong to this group. On the other hand, non-active anodes (with high O₂-overpotentials) where hydroxyl radicals, called physisorbed 'active oxygen', may assist the nonselective oxidation of organics ([Panizza and Cerisola, 2009](#); Moreira et al., 2017; ~~Panizza and Cerisola, 2009~~). Boron-Doped Diamond (BDD),

which takes part in the second group, is presented as a potential material to degrade organics thanks to its extraordinary properties (Cobb et al., 2018).

AO is a powerful technology to treat recalcitrant wastewater, however the main drawback relate to AO is the energy consumption (Shestakova and Sillanpää, 2017).

Hence, some authors have reported the combination of EAOP with biological treatments with the aim of taking advantage of the upsides of both technologies (Oller et al., 2011; Fontmorin et al., 2014; Ganzenko et al., 2014). Coupling EAOP with biological treatment can be combined in 2 ways. If the electrochemical pre-treatment is applied in the first step, the objective will be the partial oxidation of the biologically persistent organic fraction to produce biodegradable reaction intermediates (Carboneras et al., 2018). The opposite way is to apply the EAOP as a post-treatment: first, the mostly biodegradable compounds will be oxidized by microbial attack, and then, the post EAOP step will degrade the recalcitrant compounds (Carboneras et al., 2020). As expected, some authors have achieved good removal efficiencies in the electrochemical

degradation of atrazine using BDD ([Borrás et al., 2010](#); [Oturán et al., 2012](#); ~~[Bu et al., 2018](#)~~; [Bravo-Yumi et al., 2018](#); ~~[Bu et al., 2018](#)~~ ~~[Oturán et al., 2012](#)~~; ~~[Borrás et al., 2010](#)~~).

However, the degradation of this herbicide has not been studied using another ~~kind of~~ anode ~~ic-~~ materials. Moreover, the composition of the matrix, ~~in this case a polluted soil, effluent directly~~ affects ~~directly~~ to the removal efficiency ~~of the pollutant~~ (Ribeiro et al., 2019) ~~and the present work considers the case of atrazine contained in polluted soil washing effluents.~~

In this context, the aim of the present work is to study the partial anodic oxidation of atrazine-polluted soil washing effluents, in order to reduce its toxicity and improve its biodegradability. Thus, such partial oxidation step could be considered as a pre-treatment for a subsequent biological treatment. ~~In order to reach this objective, the At~~

~~first~~, atrazine was extracted from a polluted soil by means of a surfactant-aided soil-washing process. Then, four different anodic materials were checked in partial electro-oxidation ~~pre-treatment~~ batch experiments. The changes in toxicity or biodegradability of soil washing atrazine-polluted effluents were subsequently ~~checked~~ determined by using biological and toxicity standard tests. It is important to note that the present work is not focused on the treatment of atrazine but on the treatment of SWE containing a high amount of surfactant and a low amount of atrazine which is an important difference as compared to other atrazine electrooxidation studies. To the author's knowledge, no previous works regarding the combination of electrooxidation and biodegradation of atrazine-polluted soil washing effluents using different anod~~ice~~ materials have been reported to date.

2. Materials and methods

2.1. Soil and soil washing process

The soil used in this work is a real clay soil obtained from a quarry located in Toledo (Spain). The main properties of this soil can be checked elsewhere (Barba et al., 2019). The soil was polluted with pure atrazine (99.1%) supplied by Sigma Aldrich. Atrazine

(100 mg) was dissolved in 0.1 dm³ of hexane and then 1 kg of soil was polluted with this solution. To favor the evaporation of hexane, the clay soil was aerated for 1 day.

Because of the low solubility of atrazine, the addition of a surfactant ~~was~~ required ~~for to~~ carry out the soil washing procedure. ~~Thise~~ kinds of washing processes ~~are~~ known as Surfactant-Aided Soil Washing (SASW) (Wang and Keller, 2008). The surfactant used was Sodium Dodecyl Sulphate (SDS) and it was supplied by Panreac. The SASW process was carried out in a stirred tank, operated in batch conditions. The polluted soil was mixed with 0.8 dm³ of soil washing fluid (SWF) and 0.5 g of SDS. The SWF consists of a synthetic groundwater. According to the literature (Carboneras et al., 2019), ~~t~~he composition of ~~this~~ groundwater used in this work, expressed in mg dm⁻³, ~~was~~ the following: 0.667 MgSO₄· 7H₂O, 0.13~~4~~² NaCl, 0.130 NaNO₃, 0.025 KI and 0.249 CaCO₃. After 6 hours of mixing, the soil was settled for 12 additional hours to separate the soil from the aqueous phase. The optimization of the SASW process was develop in a previous study (dos Santos et al., 2015). The atrazine concentration obtained in the polluted effluent was about 40 mg dm⁻³.

2.2. Electrochemical reactor and experimental procedure

Electrooxidation batch experiments were carried out in ~~ana~~ bench-scale electrochemical flow cell detailed elsewhere (Carboneras et al., 2018). The polluted effluent was introduced into a reservoir tank (5.0 L) and it was passed through the electrochemical cell and recirculated by means of a peristaltic pump (flow rate of 15 mL s⁻¹). The temperature was kept constant (22°C) using a recirculating water bath. The electrical current was applied using a DC Power Supply (FA-376 PROMAX).

Regarding electrode materials, 4 different anodes were used: p-Si Boron Doped Diamond (BDD) manufactured by Adamant (Switzerland), Ruthenium based Mixed Metal Oxides (Ru-MMO) and Iridium based Mixed Metal Oxides (Ir-MMO)

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manufactured by Tiaano (India) and Carbon Felt (CF) Sigracell[®] GFA6EA manufactured by ElectroChem Inc. (USA). CF presented an specific surface area of 35.3 m² g⁻¹ and 17,700 m² m⁻², areal weight 500 g m⁻², porosity 95% and roughness 30 µm. ~~In all cases, the cathode was an AISI 316 steel electrode.~~ Geometric area of anodes were 78 cm² (BDD, MMO-Ir and MMO-Ru) and 100 cm² (CF). In all cases, the cathode was an AISI 316 steel electrode, and cathode geometric area was identical to anode area in each case.

The experiments were carried out under galvanostatic ~~mode-conditions~~ (15 mA cm⁻²) and liquid samples were taken at different times. The selection of this current density was based on previous experiments carried out with similar pesticides (Bravo-Yumi et al., 2018; Carboneras et al., 2018). A higher current density would generate a higher voltage, leading to detrimental effects for the stability of the carbonaceous anode (Ridruejo et al., 2017).

Before experiments, and because of the porosity of the CF electrode, the potential adsorption of atrazine over the electrode surface was determined. To do that, pieces of CF electrodes were submerged in soil washing effluents containing different atrazine concentrations ranging from 25 to 200 ppm during three days (Carboneras et al., 2018). From the obtained results, it can be concluded that atrazine was not absorbed on the CF electrode.

2.3. Analytical techniques

Atrazine concentration in liquid samples was determined by spectrophotometry. The spectrophotometer used was a Pharma Spec 1700 Shimazu[®]. The wavelength to detect atrazine corresponds to 229 nm. This technique has been reported to show good results for pesticide determination (Debasmita and Rajasimman; 2013; Carboneras et al., 2017;

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197 | [Debasmita and Rajasimman, 2013](#)). Total Organic Carbon (TOC) concentration was
198 | monitored using a Multi N/C 3100 Analytic Jena analyzer. The inorganic ions
199 | concentration in the water samples were determined by ionic chromatography in a
200 | Metrohm 930 Compact IC Flex device. The species monitored by this methodology
201 | were fluoride, chloride, chlorate, perchlorate, nitrate, sulphate, sodium, potassium,
202 | calcium, phosphate, ammonium and magnesium.

203 | Biodegradability was measured by BOD₅/COD ratios. BOD₅ (Biological Oxygen
204 | Demand) measures the oxygen mass that is consumed by microorganisms in the course
205 | of 5 days to oxidatively degrade the organic substances present in water, and it was
206 | determined by using standard BOD₅ tests by triplicate using Standard Methods
207 | (A.P.H.A., 1998). The test and the required BOD nutrient solution were provided by
208 | Merck. COD (Chemical Oxygen Demand) was also measured by Standard Methods.
209 | The required tests for COD determination were supplied by Merck (Germany) in the
210 | range of 25-1500 mg dm⁻³ COD.

211 | The determination of toxicity of water samples was carried out by using the 1243-500
212 | BioToxTM Kit. The inhibition of the luminescence is determined by combining
213 | different dilutions of the test sample with luminescent bacteria. The bacteria used are
214 | *Aliivibrio fischeri*. The sample toxicity was evaluated as toxicity units (TU), calculated
215 | as 100/IC₅₀, where IC₅₀ represents the percent dilution of the initial solution causing
216 | 50% reduction of the luminescence (Sanchis et al., 2014). The luminometer employed
217 | was a Junior LB 9509 portable tube luminometer from Berthold.

3. Results and discussion

3.1. Electrolysis of soil washing effluents

The atrazine recovery efficiency of the SAWS corresponded to 40%. This percentage is similar to the obtained in previous studies working with atrazine and other non-polar pesticides (dos Santos et al., 2015; Muñoz-Morales et al., 2017). Because of the high amount of surfactant needed, it is important to consider that only about 1% of the organic amount dissolved in the polluted SWE was atrazine, while the rest corresponds to SDS. This is an important difference as compared to other atrazine electrooxidation works found in the literature (Bravo-Yumi et al., 2018; Zhu et al., 2019), because the atrazine degradation rates, the organic degradation or mineralization efficiencies, and changes in the biodegradability and toxicity can be influenced by the presence of such a high amount of surfactant.

Figure 1 presents the results of atrazine degradation (relative decrease: C/C_0) using the four anodes as a function of the electrical charge between 0 to 20 A h dm⁻³ at a current density of 15 mA cm⁻². BDD achieved the total degradation of atrazine after applying 3 A h dm⁻³ of electrical charge. In contrast, atrazine concentration was only reduced by

75% and 72% with CF and MMO anodes respectively after applying more than 20 A h dm⁻³. Degradation products of atrazine were not identified as there are many interferences caused by partial degradation of the high surfactant concentration in SWE. The oxidation ability of the anodes in the groundwater medium increased in the order MMO-Ru < MMO-Ir < CF < BDD. This trend agrees with the expected oxidative superiority of non-active BDD anodes over the other three active anodes (Boye et al., 2002; Marselli et al., 2003; Panizza and Cerisola, 2009; Ridruejo et al., 2017; Boye et al., 2002; Marselli et al., 2003). The good performance of BDD over atrazine removal has been previously reported in some research works (Borràs et al., 2010; dos Santos et al., 2015; Bravo-Yumi et al., 2018; Bu et al., 2018; Bravo-Yumi et al., 2018; dos Santos et al., 2015; Borràs et al., 2010). Garza-Campos et al. (2014) reported an atrazine degradation efficiency higher than 90% under analogous conditions, applying a current density of 13.3 mA cm⁻² using BDD and the initial atrazine concentration was 20 mg dm⁻³.

Figure 1. Concentration decay of atrazine over the electrical applied charged for the electrochemical oxidation of polluted SWE. Evolution of the atrazine relative

concentration with the applied electrical charge when treating polluted SWE with different anodic materials, ~~apparent rate constant and square of correlation coefficient.~~

According to the background in introduction section, the main oxidant species in the system depend on the anode nature. BDD anode is considered as non-active electrode, where the degradation of the organic molecules is carried out by hydroxyl radicals. Conversely, the other anodes (CF and MMO) are active-electrodes and hydroxyl radical can interact with the anode surface in spite of attacking the target pollutant. In the present work, active chlorine species should be considered because the medium contains chloride ions, however the concentration of NaCl is only 84 mg dm^{-3} , and it remains below the optimal concentration found in bibliography to take advantage about active chlorine oxidant species. In addition, in the case of BDD, the subsequent formation of chlorite, chlorate and perchlorate ions is expected to occur.

The initial stage of atrazine depletion, from 0 to 5 A h dm^{-3} of electrical applied charge can be adjusted to a first-order kinetic model. Figure 1 also summarizes the apparent rate constants and the square of correlation coefficient of the linear fittings. Kinetics analyses corroborate the statement of the superior ability of BDD to degrade organic matter.

It is known that the active anode MMO-Ru has good performances in chloride medium, because it allows the production of active chlorine species that can attack rapidly the aromatic structures, and they are good catalysts for chlorine evolution (Panizza and Cerisola, 2009). Groundwater medium in the present work contains a concentration of chloride ions about 84 mg dm^{-3} and therefore, in principle it was expected that MMO-Ru could act as a good anode material for atrazine removal. ~~Meanwhile~~However, the

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behaviour of MMO-Ru in atrazine degradation was not good as expected. ~~Once-A~~
reason that could justify the unexpected operation of this anode is that such chloride
concentration, as previously indicated, is not high enough. Rajkumar and Palanivelu
(2003) optimized a NaCl concentration about 2.5 g dm^{-3} to degrade cresol using MMO-
Ru anodes. On the other hand, Panizza et al. (2007) reported an optimal chloride
concentration of 1.2 g dm^{-3} to degrade methylene blue through anodic oxidation with
MMO-Ru anode. As indicated, the chloride concentration in the synthetic groundwater
in the present work was only 84 mg dm^{-3} , this value is below to the optimum NaCl
concentrations observed in bibliography.

Regarding carbon felt electrode, it offered similar behaviour to MMO-Ir. Generally, the
use of ~~carbon-based~~carbon-based material as anode generates low degradation
efficiencies because they can also be electrochemically incinerated (transformed into
carbon dioxide) during the electrochemical process when using the high voltages
required to oxide organic pollutants (Sopaj et al., 2015). Additionally, it~~It~~ should be
considered the ~~large-great~~ porosity of the carbon felt. Due to this fact, the electrode
surface is much larger than that of the other electrodes, which helps ~~and this may help~~
to explain the better performance in atrazine degradation ~~of this electrode in the current~~
~~density studied over MMO anodes~~when carbon felt electrodes are used instead of the
MMO anodes.

At this point, it is known that the atrazine molecule is degraded during the electrolysis
but, both atrazine and surfactant could be converted into intermediate compounds or
they could be ~~finally-completely~~ mineralized to CO_2 . ~~Mineralization is not a desired~~
~~result in the present work, but it is difficult to avoid~~, Partial mineralization is usually
necessary to generate products with good biodegradability, but strong mineralization is
not a desired result in the present work. Note that strong mineralization would produce

high operation cost as it would reduce the fraction of organic pollution to be oxidized by a subsequent biological step. The mineralization rate of the solution is directly related to the degradation of the surfactant, SDS. It is important to remark that the SWE has an important amount of TOC due to the use of SDS during the SW process. For this reason, TOC is a significant parameter to consider. Relative TOC depletions (TOC/TOC_0) appear in Figure 2.

Figure 2 shows that the BDD anode is the most powerful material that mineralizes most of the organic matter in solution, it means that BDD was powerful enough not only to remove atrazine (Figure 1), but also to mineralize a large amount of its by-products and the surfactant. On the contrary, MMO-Ru was the most inefficient anode to transform the intermediates into CO_2 . This is not surprising based on the very slow degradation rate observed for atrazine. Regarding the other two materials, MMO-Ir caused an important TOC removal, reaching a 50% of TOC ~~decay~~removal. Finally, CF only achieved a 20% of mineralization, ~~which in principle is a good result as atrazine is removed while TOC is not strongly reduced, which in principle may be a good result (atrazine is removed while TOC is not strongly reduced) if subsequent tests would show a biodegradability increase.~~ The mineralization results obtained with active anodes ~~are in agreement~~agree to the expected because ~~these kind of materials~~these kinds of materials allow the partial organic degradation, along the formation of many refractory species as final products (Moreira et al., 2017). The greater mineralization achieved with BDD could then be accounted for two factors: the low formation of active chloride species, with subsequent accumulation of a lower amount of chloroderivatives, and the larger ability of BDD to mineralize the intermediates formed (Ridruejo et al., 2017).

Figure 2. TOC removal over the electrical applied charged for the electrochemical oxidation of polluted SWE.

TOC depletion is also related to the generation of sulphate when SDS is oxidized, because the sulphate group contained in the tail of SDS molecule is broken and generates sulphate (dos Santos et al., 2016). The generation of sulphate ions is plotted in Figure 3.

The results shown in Figure 3 agree to the ones in Figure 2 (TOC depletion). The highest sulphate concentration is achieved working with BDD anode, which corroborates the good ability of BDD to eliminate TOC. In the experiment carried out with CF, the concentration of sulphate remains constant during electrolysis, indicating again that this anodic material does not degrade the surfactant. Using MMO anodes cause a slight increase of the sulphate ion concentration. ~~This increment is more important working with MMO-Ir, as can be shown in TOC depletion figure.~~ Despite MMO-Ir causes higher TOC removal than MMO-Ru (as shown in Figure 2), no clear differences have been observed between both MMO anodes regarding sulphate ions produced during electrolysis (Figure 3).- Using BDD anodes, hydroxyl radicals are

available to be combined with sulphate, forming sulphate radical and mono and diperoxosulphate, a powerful oxidant, which may extend the oxidation from the nearness of the electrode surface to the bulk (Barrera-Díaz et al., 2014). On the other hand, with MMO and CF anodes, these radicals are produced but are consumed in other processes (reversible oxidation of the electrode components) before they can oxidize sulphate anions to sulphate radicals. ~~They are transformed into oxygen, which help to explain the lower efficiency observed~~ They are transformed into oxygen, which help to explain the lower efficiency observed since active electrodes have low O_2 overpotentials. It means that hydroxyl radicals are quickly converted into oxygen, in contrast to BDD electrode, where these radicals could be accumulated and used to degrade organics (Sopaj et al., 2015).

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Figure 3. Sulphate ions produced during the electrolysis of polluted SWE.

The changes in pH are shown in Figure 4. In the experiment completed with BDD, the value of pH dropped significantly to a final value close to 3. This behaviour is due to the fact that atrazine can generate many acidic compounds of low molecular weight, which

decreases the pH (Martínez-Huitle and Brillas, 2009). This drop in the pH during electrolysis of atrazine with BDD has been previously detected (Bravo-Yumi et al., 2018). Moreover, the depletion in pH can be also associated to the release of H^+ to the liquid medium during the mineralization or the progressive oxidation of chloride ions which generates H^+ (Dominguez et al., 2018).

On the other hand, CF produces also a decrease in the pH. This decrease is not so high as the produced with BDD, and thus it would allow a subsequent biological treatment.

MMO anodes do not ~~generate a depletion in~~ decreased the pH, but just a slight increase. ~~keeping the -and the~~ pH ~~keeps~~ near to ~~neutral value~~ 9.0s. Regarding electrical conductivity, not important changes were appreciated during the different electrolyses, and the values (not shown) were kept constants over electrical charge with the four anodes checked.

Figure 4. pH values during anodic oxidation of polluted SWE.

Before finishing the discussion of the effect of the different anodes, the changes in the concentrations of inorganic ions were studied. Table 1 shows the ion concentrations for the initial SWE and after electrolyses using the four anodes tested.

Table 1. Inorganic ions concentrations before and after electrolysis with different anodic materials.

	SWE	BDD (end)	CF (end)	MMO-Ir (end)	MMO-Ru (end)
NO_3^- (mg dm ⁻³)	134.71	152.60	109.06	150.96	151.48
Cl^- (mg dm ⁻³)	83.98	1.52	46.78	11.38	19.15
ClO_3^- (mg dm ⁻³)	-	220.23	14.88	124.11	120.99
ClO_4^- (mg dm ⁻³)	-	179.63	2.53	0	0

The NO_3^- concentration increases in the case of using BDD and MMO anodes. This trend is indicative of the presence of much lower amounts of N-derivate in the final solutions using these three anodes. It could be due to the preferential destruction of the by-products by active chlorine. On the contrary, the electrolysis carried out with CF tried out a decrease in NO_3^- concentration (Ridruejo et al., 2017). Moreover, deamination of the atrazine molecule leads to the release of NO_3^- (Borràs et al., 2010). The nitrogen of atrazine is converted progressively into NO_3^- , as well as NH_4^+ to a much lesser extent, but only in the case of BDD, in a concentration of 3.21 mg dm⁻³. Similar concentrations of NO_3^- and NH_4^+ were detected by Borràs et al. (2010) in the degradation of 30 mg dm⁻³ of atrazine using BDD.

The dechlorination process of atrazine is not detected by IC due to that this process competes with the chlorine evolution. Cl^- ion is unstable and disappears from the solution in all electrolyses. Table 1 shows that initial Cl^- was more rapidly removed using BDD than using MMO and CF anodes. The larger destruction of Cl^- with BDD

can be ascribed to the quicker consecutive oxidation of active chlorine to ClO_3^- and ClO_4^- (Ridruejo et al., 2017).

3.2. Changes in the biodegradability and toxicity

Changes in the toxicity and biodegradability of the SWE during the electrolytic treatments were evaluated with the four electrodes. The changes in toxicity are shown in Figure 5. It can be observed that the toxicity trend in the case of using CF anode increased at low electrical charges, which could be related to the formation of more toxic by-products. This behaviour was also previously observed ~~previously~~ in a similar research work carried out using clopyralid as pollutant (Carboneras et al., 2018). Toxicity did not undergo a final significant change compared to the initial value with all the anodes tested. The initial value of ecotoxicity expressed in TU is 1.76, and the ecotoxicity values after electrolysis are: 0.52 (MMO-Ru) < 1.17 (BDD) < 1.19 (CF) < 1.56 (MMO-Ir). Note that ecotoxicity of SWE without atrazine, used as references value, was (that is, a reference value) is negligible (0 TU). Despite high mineralization is obtained with BDD, toxic products (not identified) from electrooxidation could be present in the remaining organic composition.

Figure 5. Changes in the toxicity of the atrazine polluted SWE during the electrolyses with the different anodic materials.

After evaluating the toxicity of the effluents, the changes produced in biodegradability were expressed according to BOD₅/COD ratio. This parameter indicates that an effluent is biodegradable when its value is higher than 0.4~~shows if an effluent can be considered biodegradable when its value is upper 0.4~~ (Zaghdoudi et al., 2017). Figure 6 shows that the ratio BOD₅/COD of the atrazine-polluted SWE without AO treatment is very low and thus it is a non-biodegradable effluent. Figure 6 also shows that biodegradability is only clearly improved by AO pre-treatment of SWE when using BDD as anode material. As previously commented, BDD is also the anode which achieves the best degradation of atrazine, although BDD also achieves the highest efficiency in mineralization and COD removal (the initial value of COD is 1290 mg dm⁻³) and it can explain the best performance of BDD. The COD percentage removal at the end of the process is also expressed in Figure 6.

Figure 6. Comparison of the biodegradability of SWE after applying 23 A h dm⁻³.

4. Conclusions

It can be concluded that BDD is the most powerful anodic material to completely degrade atrazine. The other materials achieve an atrazine degradation rate about 75%. Regarding mineralization of the surfactant contained in SWE and sulphate formation, BDD clearly overtakes ~~clearly~~ the rest of anodes tested. CF obtain good atrazine removal results while no excess mineralization. All the anodes tested slightly reduced the ecotoxicity of the water effluents. Regarding biodegradability, the ratio BOD₅/COD shows that only the effluent pre-treated with BDD at the conditions used in the present work would be suitable for the application of a post-biological step, although mineralization is too strong. These results globally indicate that the compromise between reaching efficient atrazine removal and biodegradability improvement, while simultaneously avoiding strong mineralization, is not easy to obtain, and thus additional efforts should be made to find the most adequate working conditions.

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1 **Biodegradability improvement and toxicity reduction of soil**
2 **washing effluents polluted with atrazine by means of**
3 **electrochemical pre-treatment: influence of the anode**
4 **material.**

5

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13

14 **Abstract**

15 This work focuses on the partial anodic electro-oxidation of atrazine-polluted soil
16 washing effluents (SWE) in order to reduce its toxicity and to improve its
17 biodegradability. Concretely it has been evaluated the influence of the anodic material
18 used. It is hypothesized that such partial oxidation step could be considered as a pre-
19 treatment for a subsequent biological treatment. At first, atrazine was extracted from a
20 polluted soil by means of a surfactant-aided soil-washing process. Then, four different
21 anodic materials were studied in partial electro-oxidation pre-treatment batch
22 experiments at different electric charges applied: Boron Doped Diamond (BDD),
23 Carbon Felt (CF), and Mixed Metal Oxides Anodes with Iridium and Ruthenium.
24 Atrazine, TOC, surfactant and sulphate species concentrations, as well as changes in

toxicity and biodegradability, were monitored during electrochemical experiments, showing important differences in their evolution during the treatment. It was observed that BDD was the most powerful anodic material to completely degrade atrazine. The other materials achieve an atrazine degradation rate about 75%. Regarding mineralization of the organics in SWE, BDD overtakes clearly the rest of anodes tested. CF obtains good atrazine removal but low mineralization results. All the anodes tested slightly reduced the ecotoxicity of the water effluents. About the biodegradability, only the effluent obtained after the pre-treatment with BDD presented a high biodegradability. In this sense, it must be highlighted the mineralization obtained during the BDD pre-treatment was very strong. These results globally indicate that it is necessary to find a compromise between reaching efficient atrazine removal and biodegradability improvement, while also simultaneously avoiding strong mineralization. Additional efforts should be made to find the most adequate working conditions.

Keywords

Atrazine, soil washing effluent, anodic oxidation, biodegradability, toxicity

Highlights

Anode material influences electrooxidation of atrazine in soil washing effluents
BDD completely removes atrazine but also produces strong mineralization of surfactant
Rest of anodes reached approximately 75% atrazine removal and partial mineralization
Toxicity slightly decreased in all cases
Biodegradability improved only when using BDD, but mineralization should be reduced

50

51 **Conflict of Interest:** The authors declare that they have no conflict of interest.

52 **1. Introduction**

53 Biological treatment is the most common technology used to treat polluted water
54 effluents. The main reasons are the following: it is a cost effective and eco-friendly
55 technology, it has a high public acceptance, sometimes it is able to carry out the
56 complete destruction of target pollutants, and it can often be carried out on site and at
57 lower costs than other technologies (Vidali, 2001; Chawla et al., 2013). Nevertheless, it
58 is not specifically designed to eliminate recalcitrant compounds such as pesticides,
59 which are hardly biodegradable (Grandclément et al., 2017). For this reason, pesticides
60 and other organic recalcitrant compounds can be usually found in aquatic environment
61 (Aydin et al., 2018) and in drinking-water supplies (Stackelberg et al., 2007).

62 Atrazine has been one of the most used herbicides around the world from his
63 appearance in 1950 because of its suitable properties. This pesticide is used to control
64 annual grasses and broad-leaved weeds in selected vegetable and cereal crops, vines,
65 fruit orchards, citrus grove, sugar cane, grassland and forestry (Chan et al., 2004). The
66 widely use of atrazine has caused that it can be found in soil, aquatic environment and
67 groundwater (Mandelbaum et al., 1993). Atrazine concentrations about 13 mg kg⁻¹ in
68 heavily contaminated sites have been reported (Belluck et al, 1991), which is 20 times
69 more frequent than other pesticides in groundwater. Atrazine has been shown as a very
70 stable molecule which presents a relative resistance to microbial attack. A previous
71 study done in our research group showed that atrazine was not able to be biodegraded
72 after a period of 90 days of incubation with activated sludge from a conventional
73 wastewater treatment plant (Carboneras et al., 2017).

Because of that, new remediation alternatives have been suggested to pretreat effluents with non-biodegradable pollutants before applying a biological treatment. Electrochemical Advanced Oxidation Processes (EAOPs) have gained increasing attention as a promising technology to remove recalcitrant molecules (Moreira et al., 2017). Anodic Oxidation (AO) is one of the most used EAOP, where pollutants could be oxidized directly at the anode surface by electron transfer or indirectly oxidized thanks to the action of hydroxyl radicals and other oxidative species such as chlorine species or persulphates (Moreira et al., 2017).

An important variable which should be considered when using AO is the anodic material used to perform the electrochemical pretreatment. The anodic material influences the effectiveness of oxidation, degradation pathways, and reactions mechanisms (Zhu et al., 2008; Wang et al., 2012). There are two kinds of anodes depending on the Oxygen Evolution Reaction. On one hand, active anodes, with low O_2 -overpotentials, where higher oxidation states are available on the electrode surface and adsorbed hydroxyl radicals may interact with the anode. Mixed Metals Oxides and carbon anodes belong to this group. On the other hand, non-active anodes (with high O_2 -overpotentials) where hydroxyl radicals, called physisorbed 'active oxygen', may assist the nonselective oxidation of organics (Panizza and Cerisola, 2009; Moreira et al., 2017). Boron-Doped Diamond (BDD), which takes part in the second group, is presented as a potential material to degrade organics thanks to its extraordinary properties (Cobb et al., 2018).

AO is a powerful technology to treat recalcitrant wastewater, however the main drawback related to AO is the energy consumption (Shestakova and Sillanpää, 2017). Hence, some authors have reported the combination of EAOP with biological treatments with the aim of taking advantage of the upsides of both technologies (Oller et

al., 2011; Fontmorin et al., 2014; Ganzenko et al., 2014). Coupling EAOP with biological treatment can be combined in 2 ways. If the electrochemical pre-treatment is applied in the first step, the objective will be the partial oxidation of the biologically persistent organic fraction to produce biodegradable reaction intermediates (Carboneras et al., 2018). The opposite way is to apply the EAOP as a post-treatment: first, the mostly biodegradable compounds will be oxidized by microbial attack, and then, the post EAOP step will degrade the recalcitrant compounds (Carboneras et al., 2020). As expected, some authors have achieved good removal efficiencies in the electrochemical degradation of atrazine using BDD (Borrás et al., 2010; Oturan et al., 2012; Bravo-Yumi et al., 2018; Bu et al., 2018). However, the degradation of this herbicide has not been studied using another anodic materials. Moreover, the composition of the matrix, in this case a polluted soil, directly affects to the removal efficiency of the pollutant (Ribeiro et al., 2019).

In this context, the aim of the present work is to study the partial anodic oxidation of atrazine-polluted soil washing effluents, in order to reduce its toxicity and improve its biodegradability. Thus, such partial oxidation step could be considered as a pre-treatment for a subsequent biological treatment. In order to reach this objective, the atrazine was extracted from a polluted soil by means of a surfactant-aided soil-washing process. Then, four different anodic materials were checked in partial electro-oxidation batch experiments. The changes in toxicity or biodegradability of soil washing atrazine-polluted effluents were subsequently determined by using biological and toxicity standard tests. It is important to note that the present work is not focused on the treatment of atrazine but on the treatment of SWE containing a high amount of surfactant and a low amount of atrazine which is an important difference as compared to other atrazine electrooxidation studies. To the author's knowledge, no previous works

regarding the combination of electrooxidation and biodegradation of atrazine-polluted soil washing effluents using different anodic materials have been reported to date.

2. Materials and methods

2.1. Soil and soil washing process

The soil used in this work is a real clay soil obtained from a quarry located in Toledo (Spain). The main properties of this soil can be checked elsewhere (Barba et al., 2019). The soil was polluted with pure atrazine (99.1%) supplied by Sigma Aldrich. Atrazine (100 mg) was dissolved in 0.1 dm³ of hexane and then 1 kg of soil was polluted with this solution. To favor the evaporation of hexane, the clay soil was aerated for 1 day. Because of the low solubility of atrazine, the addition of a surfactant was required to carry out the soil washing procedure. This kind of washing process is known as Surfactant-Aided Soil Washing (SASW) (Wang and Keller, 2008). The surfactant used was Sodium Dodecyl Sulphate (SDS) and it was supplied by Panreac. The SASW process was carried out in a stirred tank, operated in batch conditions. The polluted soil was mixed with 0.8 dm³ of soil washing fluid (SWF) and 0.5 g of SDS. The SWF consists of a synthetic groundwater. According to the literature (Carboneras et al., 2019), the composition of the groundwater used in this work, expressed in mg dm⁻³, was the following: 0.667 MgSO₄ · 7H₂O, 0.132 NaCl, 0.130 NaNO₃, 0.025 KI and 0.249 CaCO₃. After 6 hours of mixing, the soil was settled for 12 additional hours to separate the soil from the aqueous phase. The optimization of the SASW process was developed in a previous study (dos Santos et al., 2015). The atrazine concentration obtained in the polluted effluent was about 40 mg dm⁻³.

2.2. Electrochemical reactor and experimental procedure

Electrooxidation batch experiments were carried out in a bench-scale electrochemical flow cell detailed elsewhere (Carboneras et al., 2018). The polluted effluent was introduced into a reservoir tank (5.0 L) and it was passed through the electrochemical cell and recirculated by means of a peristaltic pump (flow rate of 15 mL s⁻¹). The temperature was kept constant (22°C) using a recirculating water bath. The electrical current was applied using a DC Power Supply (FA-376 PROMAX).

Regarding electrode materials, 4 different anodes were used: p-Si Boron Doped Diamond (BDD) manufactured by Adamant (Switzerland), Ruthenium based Mixed Metal Oxides (Ru-MMO) and Iridium based Mixed Metal Oxides (Ir-MMO) manufactured by Tiaano (India) and Carbon Felt (CF) Sigracell[®] GFA6EA manufactured by ElectroChem Inc. (USA). CF presented an specific surface area of 35.3 m² g⁻¹ and 17,700 m² m⁻², areal weight 500 g m⁻², porosity 95% and roughness 30 µm. Geometric area of anodes were 78 cm² (BDD, MMO-Ir and MMO-Ru) and 100 cm² (CF). In all cases, the cathode was an AISI 316 steel electrode, and cathode geometric area was identical to anode area in each case.

The experiments were carried out under galvanostatic conditions (15 mA cm⁻²) and liquid samples were taken at different times. The selection of this current density was based on previous experiments carried out with similar pesticides (Bravo-Yumi et al., 2018; Carboneras et al., 2018). A higher current density would generate a higher voltage, leading to detrimental effects for the stability of the carbonaceous anode (Ridruejo et al., 2017).

Before experiments, and because of the porosity of the CF electrode, the potential adsorption of atrazine over the electrode surface was determined. To do that, pieces of CF electrodes were submerged in soil washing effluents containing different atrazine

concentrations ranging from 25 to 200 ppm during three days (Carboneras et al., 2018). From the obtained results, it can be concluded that atrazine was not absorbed on the CF electrode.

2.3. Analytical techniques

Atrazine concentration in liquid samples was determined by spectrophotometry. The spectrophotometer used was a Pharma Spec 1700 Shimadzu[®]. The wavelength to detect atrazine corresponds to 229 nm. This technique has been reported to show good results for pesticide determination (Debasmita and Rajasimman; 2013; Carboneras et al., 2017). Total Organic Carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytic Jena analyzer. The inorganic ions concentration in the water samples were determined by ionic chromatography in a Metrohm 930 Compact IC Flex device. The species monitored by this methodology were fluoride, chloride, chlorate, perchlorate, nitrate, sulphate, sodium, potassium, calcium, phosphate, ammonium and magnesium.

Biodegradability was measured by BOD₅/COD ratios. BOD₅ (Biological Oxygen Demand) measures the oxygen mass that is consumed by microorganisms in the course of 5 days to oxidatively degrade the organic substances present in water, and it was determined by using standard BOD₅ tests by triplicate using Standard Methods (A.P.H.A., 1998). The test and the required BOD nutrient solution were provided by Merck. COD (Chemical Oxygen Demand) was also measured by Standard Methods. The required tests for COD determination were supplied by Merck (Germany) in the range of 25-1500 mg dm⁻³ COD.

The determination of toxicity of water samples was carried out by using the 1243-500 BioToxTM Kit. The inhibition of the luminescence is determined by combining different dilutions of the test sample with luminescent bacteria. The bacteria used are

Aliivibrio fischeri. The sample toxicity was evaluated as toxicity units (TU), calculated as $100/IC_{50}$, where IC_{50} represents the percent dilution of the initial solution causing 50% reduction of the luminescence (Sanchis et al., 2014). The luminometer employed was a Junior LB 9509 portable tube luminometer from Berthold.

3. Results and discussion

3.1. Electrolysis of soil washing effluents

The atrazine recovery efficiency of the SAWS corresponded to 40%. This percentage is similar to the obtained in previous studies working with atrazine and other non-polar pesticides (dos Santos et al., 2015; Muñoz-Morales et al., 2017). Because of the high amount of surfactant needed, it is important to consider that only about 1% of the organic amount dissolved in the polluted SWE was atrazine, while the rest corresponds to SDS. This is an important difference as compared to other atrazine electrooxidation works found in the literature (Bravo-Yumi et al., 2018; Zhu et al., 2019), because the atrazine degradation rates, the organic degradation or mineralization efficiencies, and changes in the biodegradability and toxicity can be influenced by the presence of such a high amount of surfactant.

Figure 1 presents the results of atrazine degradation (relative decrease: C/C_0) using the four anodes as a function of the electrical charge between 0 to 20 A h dm^{-3} at a current density of 15 mA cm^{-2} . BDD achieved the total degradation of atrazine after applying 3 A h dm^{-3} of electrical charge. In contrast, atrazine concentration was only reduced by 75% and 72% with CF and MMO anodes respectively after applying more than 20 A h dm^{-3} . Degradation products of atrazine were not identified as there are many

interferences caused by partial degradation of the high surfactant concentration in SWE. The oxidation ability of the anodes in the groundwater medium increased in the order $\text{MMO-Ru} < \text{MMO-Ir} < \text{CF} < \text{BDD}$. This trend agrees with the expected oxidative superiority of non-active BDD anodes over the other three active anodes (Boye et al., 2002; Marselli et al., 2003; Panizza and Cerisola, 2009; Ridruejo et al., 2017). The good performance of BDD over atrazine removal has been previously reported in some research works (Borràs et al., 2010; dos Santos et al., 2015; Bravo-Yumi et al., 2018; Bu et al., 2018). Garza-Campos et al. (2014) reported an atrazine degradation efficiency higher than 90% under analogous conditions, applying a current density of 13.3 mA cm^{-2} using BDD and the initial atrazine concentration was 20 mg dm^{-3} .

Figure 1. Evolution of the atrazine relative concentration with the applied electrical charge when treating polluted SWE with different anodic materials.

According to the background in introduction section, the main oxidant species in the system depend on the anode nature. BDD anode is considered as non-active electrode, where the degradation of the organic molecules is carried out by hydroxyl radicals.

Conversely, the other anodes (CF and MMO) are active-electrodes and hydroxyl radical can interact with the anode surface in spite of attacking the target pollutant. In the present work, active chlorine species should be considered because the medium contains chloride ions, however the concentration of NaCl is only 84 mg dm^{-3} , and it remains below the optimal concentration found in bibliography to take advantage about active chlorine oxidant species. In addition, in the case of BDD, the subsequent formation of chlorite, chlorate and perchlorate ions is expected to occur.

The initial stage of atrazine depletion, from 0 to 5 A h dm^{-3} of electrical applied charge can be adjusted to a first-order kinetic model. Figure 1 also summarizes the apparent rate constants and the square of correlation coefficient of the linear fittings. Kinetics analyses corroborate the statement of the superior ability of BDD to degrade organic matter.

It is known that the active anode MMO-Ru has good performances in chloride medium, because it allows the production of active chlorine species that can attack rapidly the aromatic structures, and they are good catalysts for chlorine evolution (Panizza and Cerisola, 2009). Groundwater medium in the present work contains a concentration of chloride ions about 84 mg dm^{-3} and therefore, in principle it was expected that MMO-Ru could act as a good anode material for atrazine removal. However, the behaviour of MMO-Ru in atrazine degradation was not good as expected. A reason that could justify the unexpected operation of this anode is that such chloride concentration, as previously indicated, is not high enough. Rajkumar and Palanivelu (2003) optimized a NaCl concentration about 2.5 g dm^{-3} to degrade cresol using MMO-Ru anodes. On the other hand, Panizza et al. (2007) reported an optimal chloride concentration of 1.2 g dm^{-3} to degrade methylene blue through anodic oxidation with MMO-Ru anode. As indicated, the chloride concentration in the synthetic groundwater in the present work was only 84

mg dm⁻³, this value is below to the optimum NaCl concentrations observed in bibliography.

Regarding carbon felt electrode, it offered similar behaviour to MMO-Ir. Generally, the use of carbon-based material as anode generates low degradation efficiencies because they can also be electrochemically incinerated (transformed into carbon dioxide) during the electrochemical process when using the high voltages required to oxidize organic pollutants (Sopaj et al., 2015). Additionally, it should be considered the great porosity of the carbon felt. Due to this fact, the electrode surface is much larger than that of the other electrodes, which helps to explain the better performance in atrazine degradation when carbon felt electrodes are used instead of the MMO anodes.

At this point, it is known that the atrazine molecule is degraded during the electrolysis but, both atrazine and surfactant could be converted into intermediate compounds or they could be completely mineralized to CO₂. Partial mineralization is usually necessary to generate products with good biodegradability, but strong mineralization is not a desired result in the present work. Note that strong mineralization would produce high operation cost as it would reduce the fraction of organic pollution to be oxidized by a subsequent biological step. The mineralization rate of the solution is directly related to the degradation of the surfactant, SDS. It is important to remark that the SWE has an important amount of TOC due to the use of SDS during the SW process. For this reason, TOC is a significant parameter to consider. Relative TOC depletions (TOC/TOC₀) appear in Figure 2.

Figure 2 shows that the BDD anode is the most powerful material that mineralizes most of the organic matter in solution, it means that BDD was powerful enough not only to remove atrazine (Figure 1), but also to mineralize a large amount of its by-products and the surfactant. On the contrary, MMO-Ru was the most inefficient anode to transform

the intermediates into CO₂. This is not surprising based on the very slow degradation rate observed for atrazine. Regarding the other two materials, MMO-Ir caused an important TOC removal, reaching a 50% of TOC removal. Finally, CF only achieved a 20% of mineralization, which in principle may be a good result (atrazine is removed while TOC is not strongly reduced) if subsequent tests would show a biodegradability increase. The mineralization results obtained with active anodes agree to the expected because these kinds of materials allow the partial organic degradation, along the formation of many refractory species as final products (Moreira et al., 2017). The greater mineralization achieved with BDD could then be accounted for two factors: the low formation of active chloride species, with subsequent accumulation of a lower amount of chloroderivatives, and the larger ability of BDD to mineralize the intermediates formed (Ridruejo et al., 2017).

Figure 2. TOC removal over the electrical applied charged for the electrochemical oxidation of polluted SWE.

TOC depletion is also related to the generation of sulphate when SDS is oxidized, because the sulphate group contained in the tail of SDS molecule is broken and

generates sulphate (dos Santos et al., 2016). The generation of sulphate ions is plotted in Figure 3.

The results shown in Figure 3 agree to the ones in Figure 2 (TOC depletion). The highest sulphate concentration is achieved working with BDD anode, which corroborates the good ability of BDD to eliminate TOC. In the experiment carried out with CF, the concentration of sulphate remains constant during electrolysis, indicating again that this anodic material does not degrade the surfactant. Using MMO anodes cause a slight increase of the sulphate ion concentration. Despite MMO-Ir causes higher TOC removal than MMO-Ru (as shown in Figure 2), no clear differences have been observed between both MMO anodes regarding sulphate ions produced during electrolysis (Figure 3). Using BDD anodes, hydroxyl radicals are available to be combined with sulphate, forming sulphate radical and mono and diperoxosulphate, a powerful oxidant, which may extend the oxidation from the nearness of the electrode surface to the bulk (Barrera-Díaz et al., 2014). On the other hand, with MMO and CF anodes, these radicals are produced but are consumed in other processes (reversible oxidation of the electrode components) before they can oxidize sulphate anions to sulphate radicals. They are transformed into oxygen, which help to explain the lower efficiency observed since active electrodes have low O_2 overpotentials. It means that hydroxyl radicals are quickly converted into oxygen, in contrast to BDD electrode, where these radicals could be accumulated and used to degrade organics (Sopaj et al., 2015).

Figure 3. Sulphate ions produced during the electrolysis of polluted SWE.

The changes in pH are shown in Figure 4. In the experiment completed with BDD, the value of pH dropped significantly to a final value close to 3. This behaviour is due to the fact that atrazine can generate many acidic compounds of low molecular weight, which decreases the pH (Martínez-Huitle and Brillas, 2009). This drop in the pH during electrolysis of atrazine with BDD has been previously detected (Bravo-Yumi et al., 2018). Moreover, the depletion in pH can be also associated to the release of H^+ to the liquid medium during the mineralization or the progressive oxidation of chloride ions which generates H^+ (Dominguez et al., 2018).

On the other hand, CF produces also a decrease in the pH. This decrease is not so high as the produced with BDD, and thus it would allow a subsequent biological treatment. MMO anodes do not decreased the pH, but just a slight increase, keeping the pH near to 9.0. Regarding electrical conductivity, not important changes were appreciated during the different electrolyses, and the values (not shown) were kept constants over electrical charge with the four anodes checked.

Figure 4. pH values during anodic oxidation of polluted SWE.

Before finishing the discussion of the effect of the different anodes, the changes in the concentrations of inorganic ions were studied. Table 1 shows the ion concentrations for the initial SWE and after electrolyses using the four anodes tested.

Table 1. Inorganic ions concentrations before and after electrolysis with different anodic materials.

	SWE	BDD (end)	CF (end)	MMO-Ir (end)	MMO-Ru (end)
NO_3^- (mg dm ⁻³)	134.71	152.60	109.06	150.96	151.48
Cl^- (mg dm ⁻³)	83.98	1.52	46.78	11.38	19.15
ClO_3^- (mg dm ⁻³)	-	220.23	14.88	124.11	120.99
ClO_4^- (mg dm ⁻³)	-	179.63	2.53	0	0

The NO_3^- concentration increases in the case of using BDD and MMO anodes. This trend is indicative of the presence of much lower amounts of N-derivate in the final solutions using these three anodes. It could be due to the preferential destruction of the by-products by active chlorine. On the contrary, the electrolysis carried out with CF

tried out a decrease in NO_3^- concentration (Ridruejo et al., 2017). Moreover, deamination of the atrazine molecule leads to the release of NO_3^- (Borràs et al., 2010). The nitrogen of atrazine is converted progressively into NO_3^- , as well as NH_4^+ to a much lesser extent, but only in the case of BDD, in a concentration of 3.21 mg dm^{-3} . Similar concentrations of NO_3^- and NH_4^+ were detected by Borràs et al. (2010) in the degradation of 30 mg dm^{-3} of atrazine using BDD. The dechlorination process of atrazine is not detected by IC due to that this process competes with the chlorine evolution. Cl^- ion is unstable and disappears from the solution in all electrolyses. Table 1 shows that initial Cl^- was more rapidly removed using BDD than using MMO and CF anodes. The larger destruction of Cl^- with BDD can be ascribed to the quicker consecutive oxidation of active chlorine to ClO_3^- and ClO_4^- (Ridruejo et al., 2017).

3.2. Changes in the biodegradability and toxicity

Changes in the toxicity and biodegradability of the SWE during the electrolytic treatments were evaluated with the four electrodes. The changes in toxicity are shown in Figure 5. It can be observed that the toxicity trend in the case of using CF anode increased at low electrical charges, which could be related to the formation of more toxic by-products. This behaviour was also previously observed in a similar research work carried out using clopyralid as pollutant (Carboneras et al., 2018). Toxicity did not undergo a final significant change compared to the initial value with all the anodes tested. The initial value of ecotoxicity expressed in TU is 1.76, and the ecotoxicity values after electrolysis are: $0.52 \text{ (MMO-Ru)} < 1.17 \text{ (BDD)} < 1.19 \text{ (CF)} < 1.56 \text{ (MMO-Ir)}$. Note that ecotoxicity of SWE without atrazine, used as references value, was negligible (0 TU). Despite high mineralization is obtained with BDD, toxic products

(not identified) from electrooxidation could be present in the remaining organic composition.

Figure 5. Changes in the toxicity of the atrazine polluted SWE during the electrolyses with the different anodic materials.

After evaluating the toxicity of the effluents, the changes produced in biodegradability were expressed according to BOD₅/COD ratio. This parameter indicates that an effluent is biodegradable when its value is higher than 0.4 (Zaghdoudi et al., 2017). Figure 6 shows that the ratio BOD₅/COD of the atrazine-polluted SWE without AO treatment is very low and thus it is a non-biodegradable effluent. Figure 6 also shows that biodegradability is only clearly improved by AO pre-treatment of SWE when using BDD as anode material. As previously commented, BDD is also the anode which achieves the best degradation of atrazine, although BDD also achieves the highest efficiency in mineralization and COD removal (the initial value of COD is 1290 mg dm⁻³) and it can explain the best performance of BDD. The COD percentage removal at the end of the process is also expressed in Figure 6.

Figure 6. Comparison of the biodegradability of SWE after applying 23 A h dm⁻³.

4. Conclusions

It can be concluded that BDD is the most powerful anodic material to completely degrade atrazine. The other materials achieve an atrazine degradation rate about 75%. Regarding mineralization of the surfactant contained in SWE and sulphate formation, BDD clearly overtakes the rest of anodes tested. CF obtain good atrazine removal results while no excess mineralization. All the anodes tested slightly reduced the ecotoxicity of the water effluents. Regarding biodegradability, the ratio BOD₅/COD shows that only the effluent pre-treated with BDD at the conditions used in the present work would be suitable for the application of a post-biological step, although mineralization is too strong. These results globally indicate that the compromise between reaching efficient atrazine removal and biodegradability improvement, while simultaneously avoiding strong mineralization, is not easy to obtain, and thus additional efforts should be made to find the most adequate working conditions.

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Biodegradability improvement and toxicity reduction of soil washing effluents polluted with atrazine by means of electrochemical pre-treatment: influence of the anode material.

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Author's contribution:

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Dr. F.J. Fernández: Manuscript preparation Discussion of biological aspects.

Dr. P. Cañizares: Discussion of electrochemical aspects

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