Research article

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

María Belén Carboneras Contreras [a], José Villaseñor Camacho [a,*], Francisco Jesús Fernández-Morales [a], Pablo Cañizares Cañizares [b], Manuel Andrés Rodrigo Rodrigo [b]

[a] Chemical Engineering Department. Research Institute for Chemical and Environmental Technology (ITQUIMA), University of Castilla- La Mancha, 13071, Ciudad Real, Spain
[b] Chemical Engineering Department. Faculty of Chemical Sciences and Technology. University of Castilla- La Mancha, 13071, Ciudad Real, Spain

ARTICLE INFO

ABSTRACT

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

1. Introduction

Biological treatment is the most common technology used to treat polluted water effluents. The main reasons 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 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 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 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, 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 and Xu, 2012). There are two kinds of anodes depending on the Oxygen Evolution Reaction. On one hand, actives 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 physorbed 'active oxygen', may assist the nonselective oxidation of organics (Panizza and Cerisola, 2009; Moreira et al., 2017). Boron-Doped Diamond (BBD), 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 (Borràs 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 dm^3 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 dm^3 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 $MgSO_4 \cdot 7H_2O$, 0.132 NaCl, 0.130 $NaNO_3$, 0.025 KI and 0.249 $CaCO_3$. After 6 h 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 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 m^2 g^{-1} and 17,700 m^2 m^{-2}, areal weight 500 g m^{-2}, porosity 95% and roughness 30 μm. Geometric area of anodes were 78 cm^{-2} (BDD, MMO-Ir and MMO-Ru) and 100 cm^{-2} (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 BOD_5/COD ratios. BOD_5 (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 BOD_5 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.

Fig. 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 and 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). 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
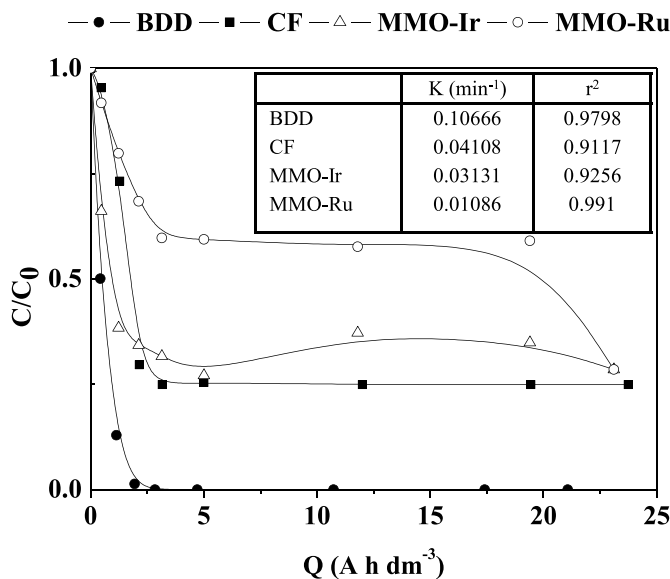

Fig. 1. Evolution of the atrazine relative concentration with the applied electrical charge when treating polluted SWE with different anodic materials.

efficiency higher than 90% under analogues conditions, applying a current density of 13.3 mA cm^{-2} using BDD and the initial atrazine concentration was 20 mg dm^{-3}.

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. Fig. 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 oxide 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 CO_2. 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 Fig. 2.

Fig. 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 (Fig. 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 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).

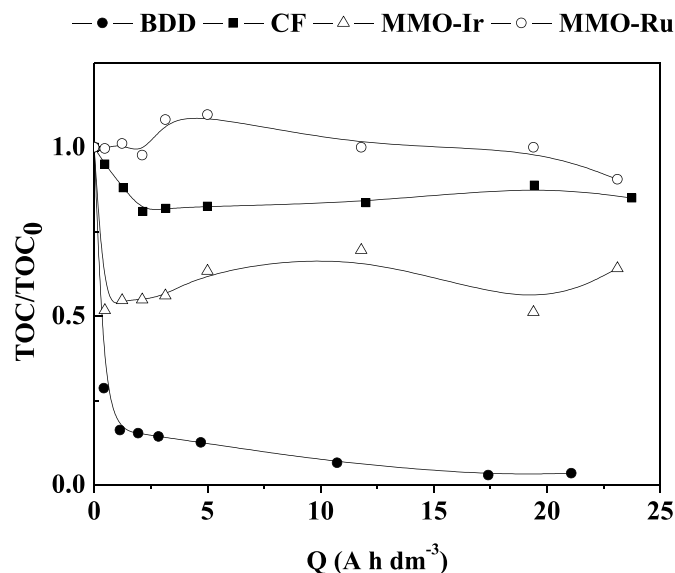TOC depletion is also related to the generation of sulphate when SDS is oxidized, because the sulphate group contained in the tail of SDS molecule is broken and generates sulphate (dos Santos et al., 2016). The generation of sulphate ions is plotted in Fig. 3.

The results shown in Fig. 3 agree to the ones in Fig. 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 Fig. 2), no clear differences have been observed between both MMO anodes regarding sulphate ions produced during electrolysis (Fig. 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 de accumulated and used to degrade organics (Sopaj et al., 2015).

The changes in pH are shown in Fig. 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.

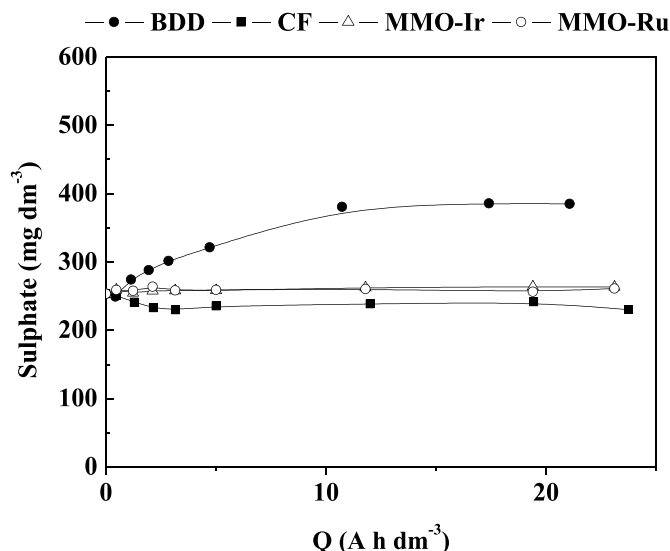Before finishing the discussion of the effect of the different anodes,

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

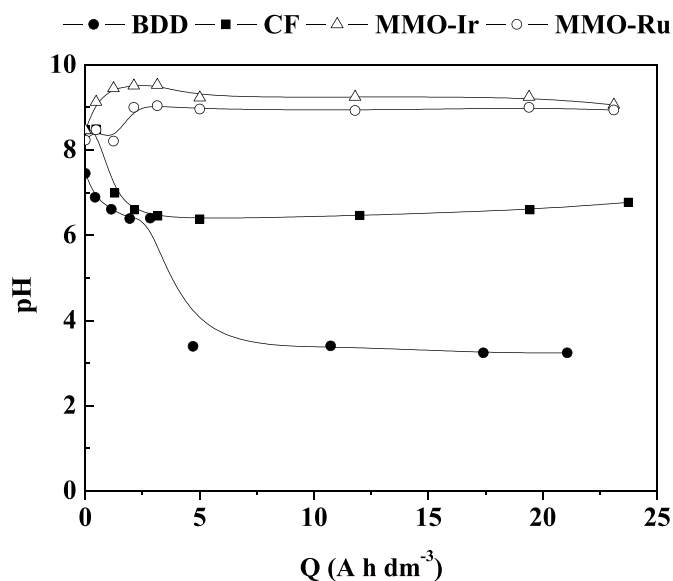Fig. 3. Sulphate ions produced during the electrolysis of polluted SWE.

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

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.

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 Fig. 5. It can be observed that the

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

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 (MMO-Ru) < 1.17 (BDD) < 1.19 (CF) < 1.56 (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 electro-oxidation could be present in the remaining organic composition.

After evaluating the toxicity of the effluents, the changes produced in biodegradability were expressed according to BOD$_5$/COD ratio. This parameter indicates that an effluent is biodegradable when its value is higher than 0.4 (Zaghdoudi et al., 2017). Fig. 6 shows that the ratio BOD$_5$/COD of the atrazine-polluted SWE without AO treatment is very low and thus it is a non-biodegradable effluent. Fig. 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 Fig. 6.

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 eco-toxicity of the water effluents. Regarding biodegradability, the ratio BOD$_5$/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
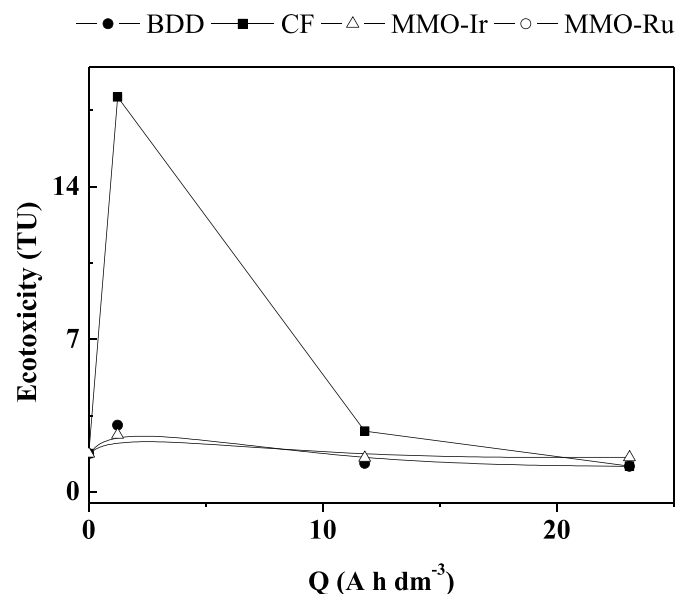

Fig. 5. Changes in the toxicity of the atrazine polluted SWE during the electrolyses with the different anodic materials.
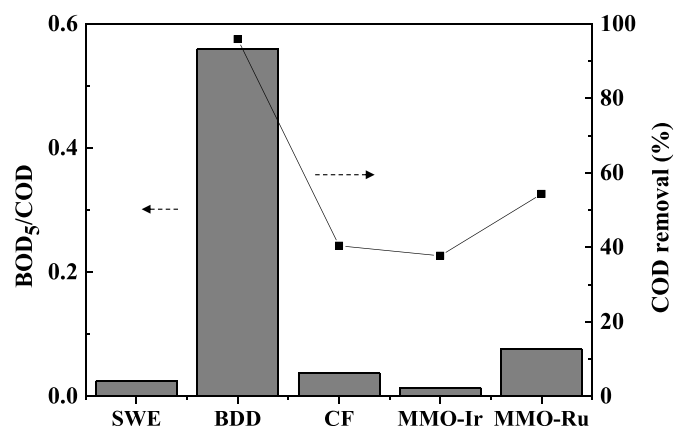
Fig. 6. Comparison of the biodegradability of SWE after applying 23 A h dm^{-3}.

additional efforts should be made to find the most adequate working conditions.

Author's contribution

M. B. Carboneras: Experimental work and global discussion. Dr. J. Villaseñor: Manuscript preparation Discussion of biological aspects. Dr. F.J. Fernández: Manuscript preparation Discussion of biological aspects. Dr. P. Cañizares: Discussion of electrochemical aspects. Dr. M.A. Rodrigo: Discussion of electrochemical aspects.

Declaration of competing interest

The authors disclose any actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations.

Acknowledgements

References

A.P.H.A.-A.W.W.A.-W.P.C.F., 1998. Standard Methods for the Examination of Water and Wastewater, twentieth ed. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.

Aydin, M.E., Aydin, S., Beduk, F., Ulvi, A., Bahadir, M., 2018. Accumulation of micropollutants in aqueous media and sediment, a risk sssessment for Konya Main Drainage Channel, Turkey. In: Areces, P. (Ed.), Advances in Safety Management and Human Factors. Springer, pp. 286–295, 2018.

Barba, S., Villaseñor, J., Cañizares, P., Rodrigo, M.A., 2019. Strategies for the electrobioremediation of oxyfluorfen polluted soils. Electrochim. Acta 297, 137–144.

Barrera-Díaz, C., Cañizares, P., Fernández, F., Natividad, R., Rodrigo, M., 2014. Electrochemical advanced oxidation processes: an overview of the current applications to actual industrial effluents. J. Mexican Chem. Soc. 58, 256–275.

Belluck, D.A., Benjamin, S.L., Dawson, T., 1991. Groundwater contamination by atrazine and its metabolites: risk assessment, policy, and legal implications. In: Somasundaram, L., Coats, J.R. (Eds.), Pesticide Transformation Products: Fate and Significance in the Environment, vol. 459. American Chemical Society, pp. 255–273.

Borràs, N., Oliver, R., Arias, C., Brillas, E., 2010. Degradation of atrazine by electrochemical advanced oxidation processes using a boron-doped diamond anode. J. Phys. Chem. A 114, 6613–6621.

Boye, B., Michaud, P.A., Marselli, B., Dieng, M.M., Brillas, E., Comninellis, C., 2002. Anodic oxidation of 4-chlorophenoxyacetic acid on synthetic boron-doped diamond electrodes. New Diam. Front. Carbon Technol. 12, 63–72.

Bravo-Yumi, N.P., Espinoza-Montero, P., Brillas, E., Peralta-Hernández, J.M., 2018. Electrochemical abatement of atrazine solutions using an undivided stirred tank cell with Pt or BDD anode. J. Mexican Chem. Soc. 62, 295–304.

Bu, L., Zhu, S., Zhou, S., 2018. Degradation of atrazine by electrochemically activated persulfate using BDD anode: role of radicals and influencing factors. Chemosphere 195, 236–244.

Carboneras, B., Villaseñor, J., Fernandez-Morales, F.J., 2017. Modelling aerobic biodegradation of atrazine and 2, 4-dichlorophenoxy acetic acid by mixed-cultures. Bioresour. Technol. 243, 1044–1050.

Carboneras, M.B., Cañizares, P., Rodrigo, M.A., Villaseñor, J., Fernandez-Morales, F.J., 2018. Improving biodegradability of soil washing effluents using anodic oxidation. Bioresour. Technol. 252, 1–6.

Carboneras, M.B., Rodrigo, M.A., Canizares, P., Villaseñor, J., Fernandez-Morales, F.J., 2019. Electro-irradiated technologies for clopyralid removal from soil washing effluents. Separ. Purif. Technol. 227, 115728.

Carboneras, M.B., Rodrigo, M.A., Canizares, P., Villasenor, J., Fernandez-Morales, F.J., 2020. Removal of oxyfluorfen from polluted effluents by combined bio-electro processes. Chemosphere 240, 124912.

Chan, C., Tao, S., Dawson, R., Wong, P., 2004. Treatment of atrazine by integrating photocatalytic and biological processes. Environ. Pollut. 131, 45–54.

Chawla, N., Sunita, S., Kamlesh, K., Kumar, R., 2013. Bioremediation: an emerging technology for remediation of pesticides. Res. J. Chem. Environ. 17, 88–105.

Cobb, S.J., Ayres, Z.J., Macpherson, J.V., 2018. Boron doped diamond: a designer electrode material for the twenty-first century. Annu. Rev. Anal. Chem. 11, 463–484.

Debasmita, N., Rajasimman, M., 2013. Optimization and kinetics studies on biodegradation of atrazine using mixed microorganisms. Alexandria Eng. J. 52, 499–505.

Dominguez, C.M., Oturan, N., Romero, A., Santos, A., Oturan, M.A., 2018. Removal of lindane wastes by advanced electrochemical oxidation. Chemosphere 202, 400–409.

dos Santos, E.V., Sáez, C., Martínez-Huitle, C.A., Cañizares, P., Rodrigo, M.A., 2015. Combined soil washing and CDEO for the removal of atrazine from soils. J. Hazard Mater. 300, 129–134.

dos Santos, E.V., Sáez, C., Martínez-Huitle, C.A., Cañizares, P., Rodrigo, M.A., 2016. Removal of oxyfluorfen from ex-situ soil washing fluids using electrolysis with diamond anodes. J. Environ. Manag. 171, 260–266.

Fontmorin, J.M., Siguié, J., Fourcade, F., Geneste, F., Floner, D., Soutrel, I., Amrane, A., 2014. Combined electrochemical treatment/biological process for the removal of a commercial herbicide solution. U46D®. Sep. Purif. Technol. 132, 704–711.

Ganzenko, O., Huguenot, D., Van Hullebusch, E.D., Esposito, G., Oturan, M.A., 2014. Electrochemical advanced oxidation and biological processes for wastewater treatment: a review of the combined approaches. Environ. Sci. Pollut. Res. 21, 8493–8524.

Garza-Campos, B.R., Guzmán-Mar, J.L., Reyes, L.H., Brillas, E., Hernández-Ramírez, A., Ruiz-Ruiz, E.J., 2014. Coupling of solar photoelectro-Fenton with a BDD anode and solar heterogeneous photocatalysis for the mineralization of the herbicide atrazine. Chemosphere 97, 26–33.

Grandclément, C., Seyssiecq, I., Piram, A., Wong-Wah-Chung, P., Vanot, G., Tiliacos, N., Roche, N., Doumenq, P., 2017. From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: a review. Water Res. 111, 297–317.

Mandelbaum, R., Wackett, L.P., Allan, D.L., 1993. Mineralization of the s-triazine ring of atrazine by stable bacterial mixed cultures. Appl. Environ. Microbiol. 59, 1695–1701.

Marselli, B., Garcia-Gomez, J., Michaud, P.A., Rodrigo, M., Comninellis, C., 2003. Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes. J. Electrochem. Soc. 150, D79–D83.

Martínez-Huitle, C.A., Brillas, E., 2009. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review. Appl. Catal. B Environ. 87, 105–145.

Moreira, F.C., Boaventura, R.A., Brillas, E., Vilar, V.J., 2017. Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters. Appl. Catal. B Environ. 202, 217–261.

Muñoz-Morales, M., Braojos, M., Sáez, C., Cañizares, P., Rodrigo, M.A., 2017. Remediation of soils polluted with lindane using surfactant-aided soil washing and electrochemical oxidation. J. Hazard Mater. 339, 232–238.

Oller, I., Malato, S., Sánchez-Pérez, J.A., 2011. Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. Sci. Total Environ. 409, 4141–4166.

Oturan, N., Brillas, E., Oturan, M.A., 2012. Unprecedented total mineralization of atrazine and cyanuric acid by anodic oxidation and electro-Fenton with a boron-doped diamond anode. Environ. Chem. Lett. 10, 165–170.

Panizza, M., Barbucci, A., Ricotti, R., Cerisola, G., 2007. Electrochemical degradation of methylene blue. Separ. Purif. Technol. 54, 382–387.

Panizza, M., Cerisola, G., 2009. Direct and mediated anodic oxidation of organic pollutants. Chem. Rev. 109, 6541–6569.

Rajkumar, D., Palanivelu, K., 2003. Electrochemical degradation of cresols for wastewater treatment. Ind. Eng. Chem. Res. 42, 1833–1839.

Ribeiro, A.R., Moreira, N.F., Puma, G.L., Silva, A.M., 2019. Impact of water matrix on the removal of micropollutants by advanced oxidation technologies. Chem. Eng. J. 363, 155–173.

Ridruejo, C., Salazar, C., Cabot, P.L., Centellas, F., Brillas, E., Sirés, I., 2017. Electrochemical oxidation of anesthetic tetracaine in aqueous medium. Influence of the anode and matrix composition. Chem. Eng. J. 326, 811–819.

Sanchis, S., Polo, A., Tobajas, M., Rodriguez, J., Mohedano, A., 2014. Coupling Fenton and biological oxidation for the removal of nitrochlorinated herbicides from water. Water Res. 49, 197–206.

Shestakova, M., Sillanpää, M., 2017. Electrode materials used for electrochemical oxidation of organic compounds in wastewater. Rev. Environ. Sci. Bio/Technol. 16, 223–238.

Sopaj, F., Rodrigo, M.A., Oturan, N., Podvorica, F.I., Pinson, J., Oturan, M.A., 2015. Influence of the anode materials on the electrochemical oxidation efficiency.

Application to oxidative degradation of the pharmaceutical amoxicillin. Chem. Eng. J. 262, 286–294.

Stackelberg, P.E., Gibs, J., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Lippincott, R.L., 2007. Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. Sci. Total Environ. 377, 255–272.

Vidali, M., 2001. Bioremediation. An overview. Pure Appl. Chem. 73, 1163–1172.

Wang, J.L., Xu, L.J., 2012. Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application. Crit. Rev. Environ. Sci. Technol. 42, 251–325.

Wang, P., Keller, A.A., 2008. Soil particle-size dependent partitioning behavior of pesticides within water–soil–cationic surfactant systems. Water Res. 42, 3781–3788.

Zaghdoudi, M., Fourcade, F., Soutrel, I., Floner, D., Amrane, A., Maghraoui-Meherzi, H., Geneste, F., 2017. Direct and indirect electrochemical reduction prior to a biological treatment for dimetridazole removal. J. Hazard Mater. 335, 10–17.

Zhu, K., Wang, X., Ma, X., Sun, Z., Hu, X., 2019. Comparative degradation of atrazine by anodic oxidation at graphite and platinum electrodes and insights into electrochemical behavior of graphite anode. Electrocatalysis 10, 35–44.

Zhu, X., Tong, M., Shi, S., Zhao, H., Ni, J., 2008. Essential explanation of the strong mineralization performance of boron-doped diamond electrodes. Environ. Sci. Technol. 42, 4914–4920.