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Selection of anodic material for the combined electrochemical-biological treatment of lindane polluted soil washing effluents

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Highlights

- Faster electrolytic oxidation of lindane than of the surfactant contained in the SWE
- Important differences between the performance of the four electrodes tested
- Biodegradability and toxicity of the treated wastes is better for CF and BDD
- Biodegradability of mixed wastes (effluent electrolysis+conventional) is better for CF and BDD

Abstract

This paper focuses on the removal of lindane from soil washing effluents (SWEs) using combined electrochemical -biological processes. In particular, it has been evaluated the influence of the anodic material used in the electrolysis of the SWE on the biodegradability and toxicity of the effluents. Four anode materials were tested: Boron Doped Diamond (BDD), Carbon Felt (CF), and Mixed Metal Oxides Anodes with iridium and ruthenium (MMO-Ir and MMO-Ru). These materials were tested at different current densities and electric current charges applied. Lindane, TOC, sulphate, and chlorine species concentrations were monitored during electrochemical experiments, showing important differences in their evolution during the treatment. In spite of reaching a good removal of lindane with all the materials tested, results showed that Boron Doped Diamond working at 15 mA cm^{-2} achieved the best biodegradability results in the electrolyzed effluents, because the ratio BOD_5/COD increased from 0.2 to 0.5, followed by Carbon Felt anode. Regarding toxicity, Carbon Felt decreased toxicity by 80%. Opposite to what it was expected, MMO anodes did not achieve biodegradability improvement and they only showed reduction in toxicity at high electrical charges.

Keywords

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

1. Introduction

Lindane or γ -Hexachlorocyclohexane is an organochlorine pesticide that has been used for many years in agricultural, veterinary and human applications. Currently, lindane has been banned in many European countries, United States and Canada. However, it is already in use other countries. In addition, even in countries in which the use of lindane is now forbidden, there are significant environmental problems related to previous episodes of application or manufacturing of this pesticide [1].

Inefficient manufacturing of this product can generate a great amount of hazardous wastes [2]. In fact, the hexachlorocyclohexane (HCH) isomers produced during the lindane synthesis (α -HCH, β -HCH, and γ -HCH) were added to the list of the Stockholm convention on persistent organic pollutants (POPs) in 2009 [3-6]. The isomer γ -HCH has been shown as a potential pollutant for environment and living beings. It has a rather long lifetime, that facilitates its transport at long distances and its accumulation in the food chain [7, 8]. Additionally, lindane brings about an extensive range of adverse health effects in humans (fertility problems, skin irritation, dizziness, headaches, diarrhoea, nausea, vomiting, convulsions, and even death) and in animals [3, 9, 10].

Sabiñañigo is a small town located in the north of Spain, which has been very seriously affected because of the industrial manufacturing of lindane, mainly in the seventies and eighties of the last century. Thus, great amounts of solid and liquid lindane-polluted wastes were poured into two landfills from 1975 to 1992 [4, 11]. Despite the fact that tonnes of lindane and its isomers have been properly removed, it has been assessed that approximately 100 tons of HCH still remain in the abandoned manufacturing place [4,

11]. These wastes have caused the contamination of soil and groundwater, what has become one of the most important incidents of soil contamination in Spain [12].

One of the most effective techniques for organics-polluted soil remediation is surfactant-aided soil-washing (SASW). This treatment consists of transferring the organic contaminant from soil into a liquid stream [13, 14]. Due to the presence of non-soluble pollutants, it is necessary the addition of surfactants in order to enhance their solubility into the soil washing fluid. After the solid-liquid extraction, the polluted effluent contains a high organic load and a complex mixture of organics consisting of dissolved organic pollutants, surfactants and micelles, and also inorganic salts dissolved in the soil washing fluid (SWF) [14]. Regarding lindane pollution, SASW technology has been reported by Muñoz Morales et al. (2017). The organic-polluted wastewater obtained from SASW process needs to be further treated.

Different technologies have been already studied for treatment of different types of lindane-polluted effluents including SWF. Thus, Usman and coworkers [15] studied the application of chemical oxidation to eliminate HCH from soil and water. An ozonation process combined with iron nanoparticles was also evaluated to eliminate this compound [16]. Electrochemical Advanced Oxidation processes (EAOPs) have been also proposed as a good set of technologies to attain the elimination of lindane from polluted effluents [3, 7, 17] and, particularly, the lindane removal by electrolysis has shown rather good results working with different anodes, especially Boron Doped Diamond (BDD) anodes [7, 18].

Regarding biological treatment of lindane, some authors proposed the use of specific bacteria, mixed bacterial cultures and different fungi species isolated from diverse geographic polluted locations to attain it [19-23]. However, lindane has been shown as a toxic molecule in many reported works. In addition, the possibility of using sludge from

domestic wastewater treatment plants to remove lindane has not been found in literature, despite lindane spills sometimes could easily reach domestic sewers and domestic wastewater treatment plants and the occurrence of microorganisms capable to degrade this pollutant may be expected.

Despite the good performance of AO as compared to biodegradation regarding efficiency, there is an important drawback of this technology: the very important energy consumption. For this reason, the coupling of partial oxidation by EAOP with biological treatments is considered as a promising combination to treat water effluents, maximizing the removal efficiency and minimizing operational costs [24]. EAOP could be applied as a pre-treatment, generating more biodegradable reaction species from the initial complex chemical molecule. Alternatively, EAOP may be applied as a post-treatment, for the complete mineralization of the recalcitrant contaminants that could remain after a biological treatment as microorganisms were not able to eliminate [25]. However, this later combination needs for at least a partially biodegradable effluent.

In this context, the key point of the present work is to study the partial anodic oxidation of a lindane-polluted soil washing effluent, in order to improve its biodegradability and reduce its toxicity. Thus, such partial oxidation process could be considered as a pre-treatment for a subsequent biological treatment. At first, lindane was extracted from a polluted soil by means of a surfactant-aided soil-washing step. Then, four different anodic materials were checked in partial electro-oxidation pre-treatment batch experiments. The changes in biodegradability or toxicity of soil washing lindane-polluted effluents were subsequently checked by using biological and toxicity standard tests. To the author's knowledge, no previous works regarding the combination of electrooxidation and biodegradation of lindane-polluted soil washing effluents using different anode materials have been reported to date.

2. Materials and methods

2.1. Soil and soil washing fluid

The chemicals Lindane ($C_6H_6Cl_6$, 97%, Sigma Aldrich), Sodium Dodecyl Sulphate (SDS) and Hexane were used. A clay soil, whose characteristics can be found elsewhere [26] was used in the lindane-polluted soil washing process. To spike soil 1 g of lindane was dissolved in 0.1 dm^{-3} of hexane (Sigma Aldrich) and this solution was spiked over 1.0 kg of clay soil. The spiked soil was then aerated for 1 day to promote hexane evaporation. After that, the soil was mixed with 5 dm^{-3} of soil Soil-Washing Fluid (SWF) consisting of a SDS solution in water (5000 mg dm^{-3}). Finally, the Soil-Washing Effluent (SWE) is obtained in order to perform the electrochemical experiments. The SWE simulated synthetic polluted groundwater that ensured enough electrical conductivity to develop the electrochemical process without the addition of electrolyte. The inorganic composition of the SWF was the following: 0.66 g L^{-1} of $MgSO_4 \cdot 7H_2O$, 0.1318 g L^{-1} of NaCl, 0.02555 g L^{-1} of KI, 0.2497 g L^{-1} of $CaCO_3$ and 0.1302 g L^{-1} of $NaNO_3$. Additional information about the soil washing process is described elsewhere [27].

2.2. Electrooxidation experiments

Electrooxidation batch experiments were carried out in an bench-scale electrochemical flow cell detailed elsewhere [27]. Four different anodic materials were checked in order to study the influence of the anode material over the oxidation of the SWE organics: p-Si Boron Doped Diamond (BDD) manufactured by Adamant (Switzerland); Ruthenium based Mixed Metal Oxides (MMO-Ru) and Iridium based Mixed Metal Oxides (MMO-Ir) manufactured by Tiaano (India); and porous Carbon Felt (CF) Sigracell® GFA6EA manufactured by ElectroChem Inc. (USA). CF characteristics were: specific surface

area $35.3 \text{ m}^2 \text{ g}^{-1}$ and $17.700 \text{ m}^2 \text{ m}^{-2}$; areal weight 500 g m^{-2} , porosity 95% and roughness $30 \text{ }\mu\text{m}$. An AISI 316 steel cathode was used in all experiments. The experiments were carried out under galvanostatic conditions. Two different current densities were checked with each anode: the current densities to perform the experiments with BDD were 15 and 30 mA cm^{-2} ; 10 and 15 mA cm^{-2} were used in CF experiments; and 30 and 50 mA cm^{-2} were used with DSA anodes. The difference among current densities are owing to the properties on each anode to degrade complex organic compounds as well as their resistance to support high current densities in the case of CF electrode [28].

2.3. Sampling and analytical techniques

Liquid samples were taken at different times. Lindane concentration in samples was measured by a previous liquid extraction step followed by Gas Chromatography. Ethyl acetate was used as extraction solvent (ratio lindane solution/solvent v/v). The percentage of lindane recovery after the extraction process was 100%. Then, samples were analysed by Gas Chromatography-Electron Capture Detector (GC ECD) (Thermo Fisher Scientific) using a TG-5MS capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ mm}$) and ^{63}Ni micro-electron capture detector, a split/splitless injector and ChromCrd Software. The quantification limit of the GC ECD was 0.02 mg dm^{-3} and the injector temperature was 260°C . Helium was used as the carrier gas with a flow rate of 1.0 mL min^{-1} . The concentration of Total Organic Carbon (TOC) was measured using a Multi C/C 3100 Analytik Jena. Chloride and sulphate ions and oxidized chlorine species were determined by ionic chromatography in a Metrohm 930 Compact IC Flex device.

Biodegradability and toxicity of electrochemically treated SWE samples were measured as follows. In order to determine toxicity, *Vibrio fischeri* tests were performed by means of a BioTox™ Kit supplied by Aboatox. The toxic effect was calculated from the

average value of the luminescence decay of bacteria *Vibrio fischeri*, after periods of 15 and 30 minutes of incubation at 15°C. The luminescence was measured with a luminometer (Junior LB 9509 of Berthold Technologies). Toxicity was evaluated as IC_{50} defined as the percent dilution of the initial solution causing 50% reduction of the luminescence. Results were expressed in toxicity units (TU), calculated from IC_{50} values ($TU = 100/IC_{50}$) [29]. In order to determine biodegradability, standard BOD_5 tests by triplicate were performed to electrolysed SWE samples. Aerobic biodegradability was then calculated as BOD_5/COD ratio, where BOD (Biological Oxygen Demand) and COD (Chemical Oxygen Demand) were measured according to standard methods [30].

The possible inhibition effect of electrolysed SWE discharges over a conventional aerobic biological wastewater treatment process was also checked. It was performed by two methods: First, it was measured BOD_5/COD ratio in a wastewater to be treated by conventional aerobic sludge which received low discharges of such electrolysed SWE samples (4 mL SWE discharge over a total 20 mL volume of wastewater). Second, changes in the maximum specific aerobic sludge respiration rates after the SWE discharges were determined (Sanchis et al., 2014) employing a Strathox respirometer by Strathkelvin instruments. The respirometer measures the maximum oxygen consumption rate by bacteria over a period of 30 minutes. The sludge required to perform such inhibition tests was collected from a conventional wastewater treatment plant. The activated sludge was aerated overnight in order to ensure the full consumption of the organic substrate contained in the sludge sample and therefore to keep the sludge to endogenous conditions. A blank reference test was performed to isolate the oxygen consumption rate caused by endogenous respiration of the inoculum added.

3. Results and discussion

3.1. Electrochemical pre-treatment with different anode materials

Taking into account that lindane is not a soluble molecule, the SASW process was considered as a suitable technology to extract it from soil, as it has been previously evidenced in several research works carried out during the last decade focused on other pollutants [14, 31, 32] and also in a recent study focused on lindane [7]. Following the methodology of that work, the recovery of lindane from soil in the best conditions was about 40%, which corresponded to $70 \text{ mg}\cdot\text{dm}^{-3}$ of lindane in the SWE. Once the SWE was obtained, it was treated as wastewater. It is important to take in mind that only 1.5% of the organic amount dissolved in SWE was lindane and the rest of organic matter was SDS. This is an important difference as compared to other lindane electrooxidation works found in the literature, because the lindane 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 shows the changes in the concentration of lindane and TOC during the AO tests performed at 30 and 15 mA cm^{-2} using BDD. The figure also shows the concentrations of SO_4^{2-} and Cl^- vs the electric charge applied (Q).

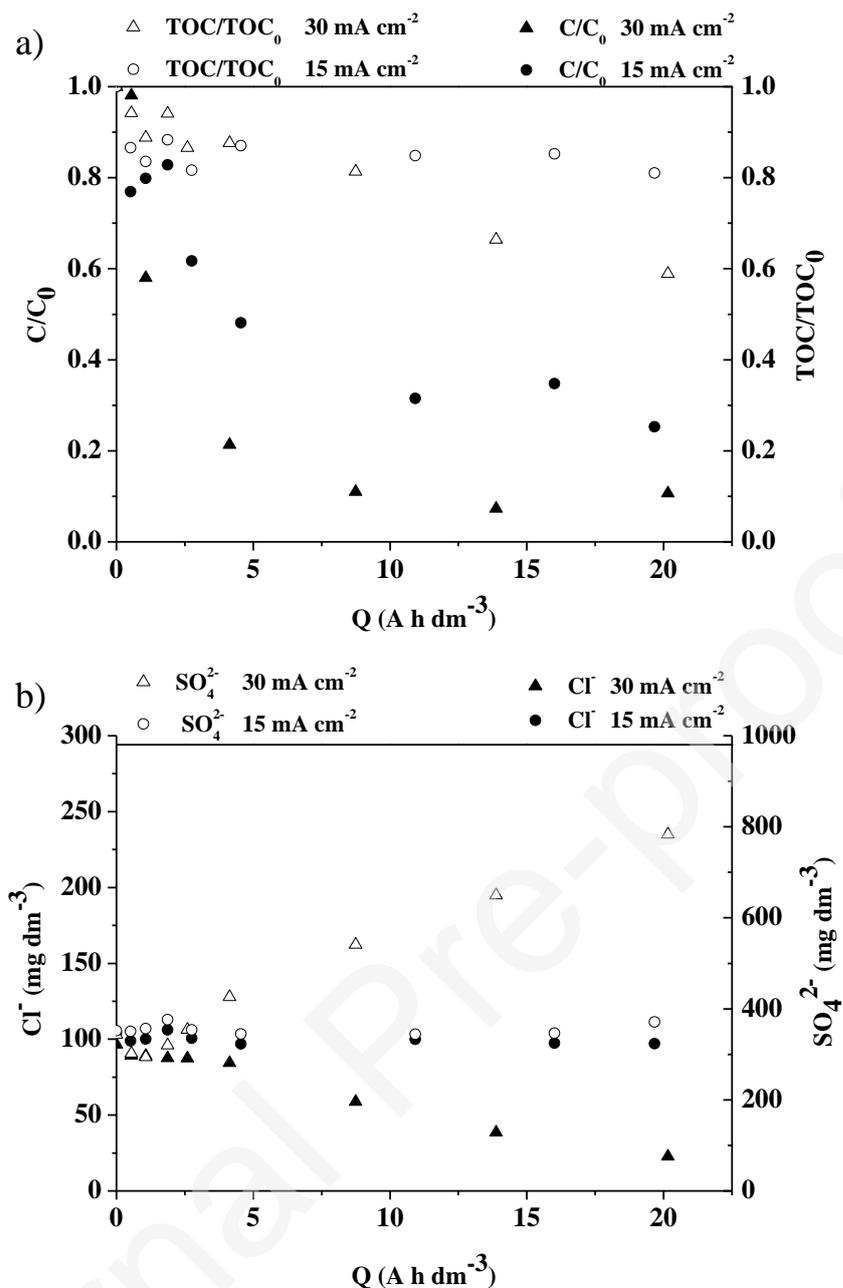


Figure 1. Influence of electrical charge applied and current density on (a) lindane concentration (full points) and total organic carbon concentration (empty points) and (b), sulphate (empty points) and chloride (full points) during the galvanostatic electrolysis with BDD at 30 mA cm⁻² (\triangle \blacktriangle) and 15 mA cm⁻² (\circ \bullet).

Lindane is oxidized during both electrolyses. The higher the current density applied, the higher is degradation rate and the more efficient is the degradation of lindane observed. This observation has to be explained in terms of the fact that larger current densities

promote the formation of hard oxidants in the bulk [3, 33, 34]. Thus, depending on the species electrolyzed, in the literature it can be seen that the change in the current density can be the same or even opposite, because when plotting the concentration of pollutant vs the current charge, what it is really represented is not the rate but the efficiency of the process and when the primary oxidation mechanism is the oxidation in the nearness of the surface of the electrode (either direct or mediated by hydroxyl radicals), mass transfer limitations appear, explaining the decrease of efficiency at larger current charges applied. In this case, this limitation is not found, suggesting that the primary mechanism is the oxidation of the pollutant in the bulk by electrogenerated oxidants. Regarding TOC, a nearly negligible decrease is observed when using 15 mA cm^{-2} , while a faster decrease is observed at 30 mA cm^{-2} . It means that despite lindane is oxidized under 15 mA cm^{-2} , SDS oxidation is almost nil. On the contrary, this oxidation develops at 30 mA cm^{-2} , which means that different oxidation mechanisms can be activated simply by increasing this parameter.

The sulphate ions generation shown in part b of the figure confirms the above mentioned results. Sulphate is produced from the oxidation of SDS, simply by breaking the sulphonate group contained in the tail of this molecule. This is very important, not only because it states different mechanisms, but also because sulphate released may be related to the final production of a very efficient oxidant, the peroxosulphate (equation 1), which it is expected to perform an important effect in mediated oxidation processes [14, 35, 36] and supports the explanation given for the different behaviour observed at 15 and 30 mA cm^{-2} .



The variation of chloride concentration is also shown in this Figure. Chloride concentration evolution is important because active chlorine species are powerful

oxidants, which can influence on the process via well-known ‘mediated oxidation’ [3, 33, 37]. It is important to take in mind that chloride concentration includes chloride ions present in SWE and also the possible chloride formation because of lindane oxidation and reduction reactions (including in this later group the hydro-dehalogenation processes that can develop on the cathode). Thus, chlorine concentration should increase with the applied charge (dechlorination). However, this ion can also be consumed because it can be directly oxidized on the anode surface to chlorine (Cl_2) via Eq. (2). This behaviour has been only observed in the present work at 30 mA cm^{-2} . The electrogenerated chlorine would diffuse away from the anode and it would be quickly hydrolyzed to hypochlorous acid (HClO) and chloride by disproportionation through Eq. (3) and Eq. (4).



In addition, in the case of BDD, the subsequent formation of chlorite, chlorate and perchlorate ions is expected to occur, according to Eq. (5), (6), (7) and (8). In the present work, chlorate and perchlorate ions were only formed working under 30 mA cm^{-2} .

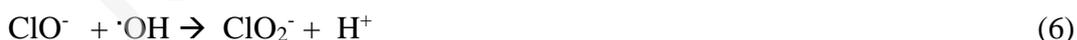


Figure 2 shows the results obtained using carbon felt (CF) as anodic material during the electrolyses, where it can be seen important differences when comparing results to those obtained with BDD.

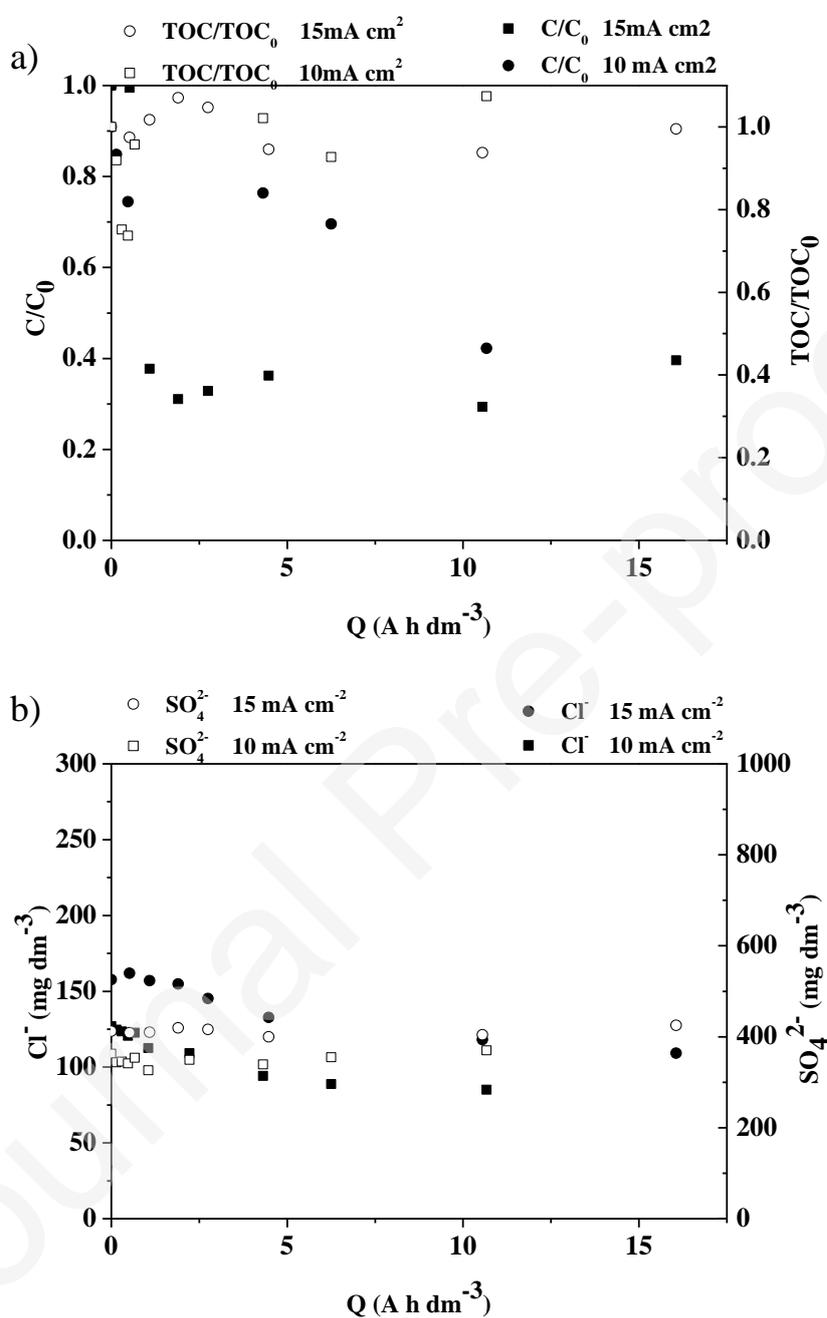


Figure 2. Influence of electrical charge applied and current density on (a) lindane concentration (full points) and total organic carbon concentration (empty points) and

(b), sulphate (empty points) and chloride (full points) during the galvanostatic electrolysis with CF at 15 mA cm⁻² (○●) and 10 mA cm⁻² (□■).

In this case, the applied current densities (15 and 10 mA cm⁻²) were lower than those used with Boron Doped Diamond anode, because of the corrosion (degradation by cold electrochemical combustion) undergone by the surface on the CF electrode during electrolysis [28]. Moreover, previous electrolysis carried out in this range allow to obtain successful results regarding organochlorinated compounds degradation without the corrosion of the CF electrode [27].

As previously observed, the lindane degradation is faster when working at higher current densities, while the relative TOC values are kept almost constant over the electrolyses, indicating that no mineralization of the organic matter contained in SWE occurred. The nil formation of sulphate also supports this nil change in the TOC concentration. No formation of sulphate involves no degradation of surfactant, and this is the reason that explains both trends, as SDS is the main responsible for the high TOC concentration. Finally, chloride concentration decreases, which could be explained again by the reactions previously described (equations 2, 3 and 4), although such decrease is not as important as the one observed using BDD under 30 mA cm⁻². The formation of chlorate was the lowest in all the experiments carried out and no perchlorate formation was detected (results not shown).

Figures 3 and 4 show the results obtained using MMO-Ir and MMO-Ru respectively. The current density applied in these experiments is higher (30 and 50 mA cm⁻²) than the applied with the other anodes, because they were expected to be robuster than the CF and, initially, they were expected to be less efficient than the BDD, allowing only the partial oxidation of the raw pollutants [28].

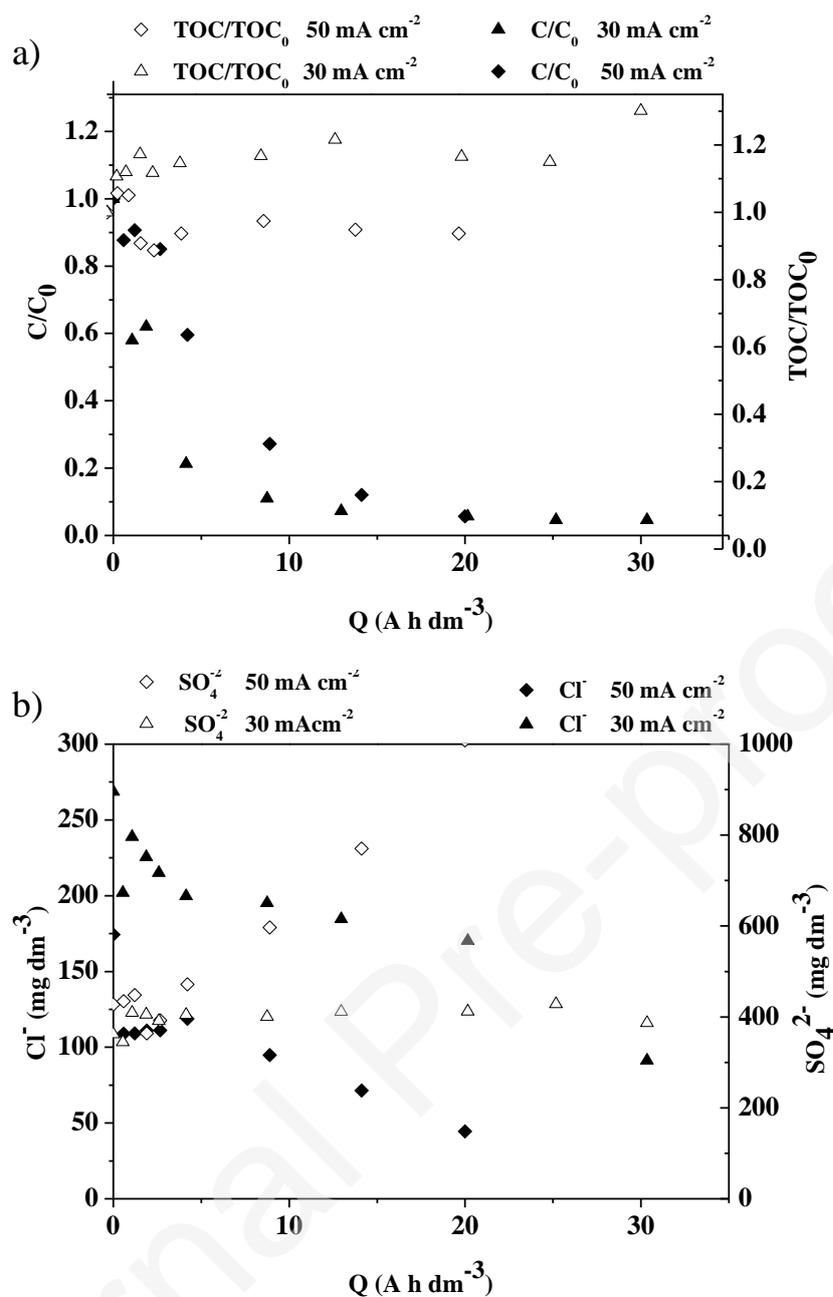


Figure 3. Influence of electrical charge applied and current density on (a) lindane concentration (full points) and total organic carbon concentration (empty points) and (b), sulphate (empty points) and chloride (full points) during the galvanostatic electrolysis with MMO-Ir at $50\ mA\ cm^{-2}$ (\diamond \blacklozenge) and $30\ mA\ cm^{-2}$ (\triangle \blacktriangle).

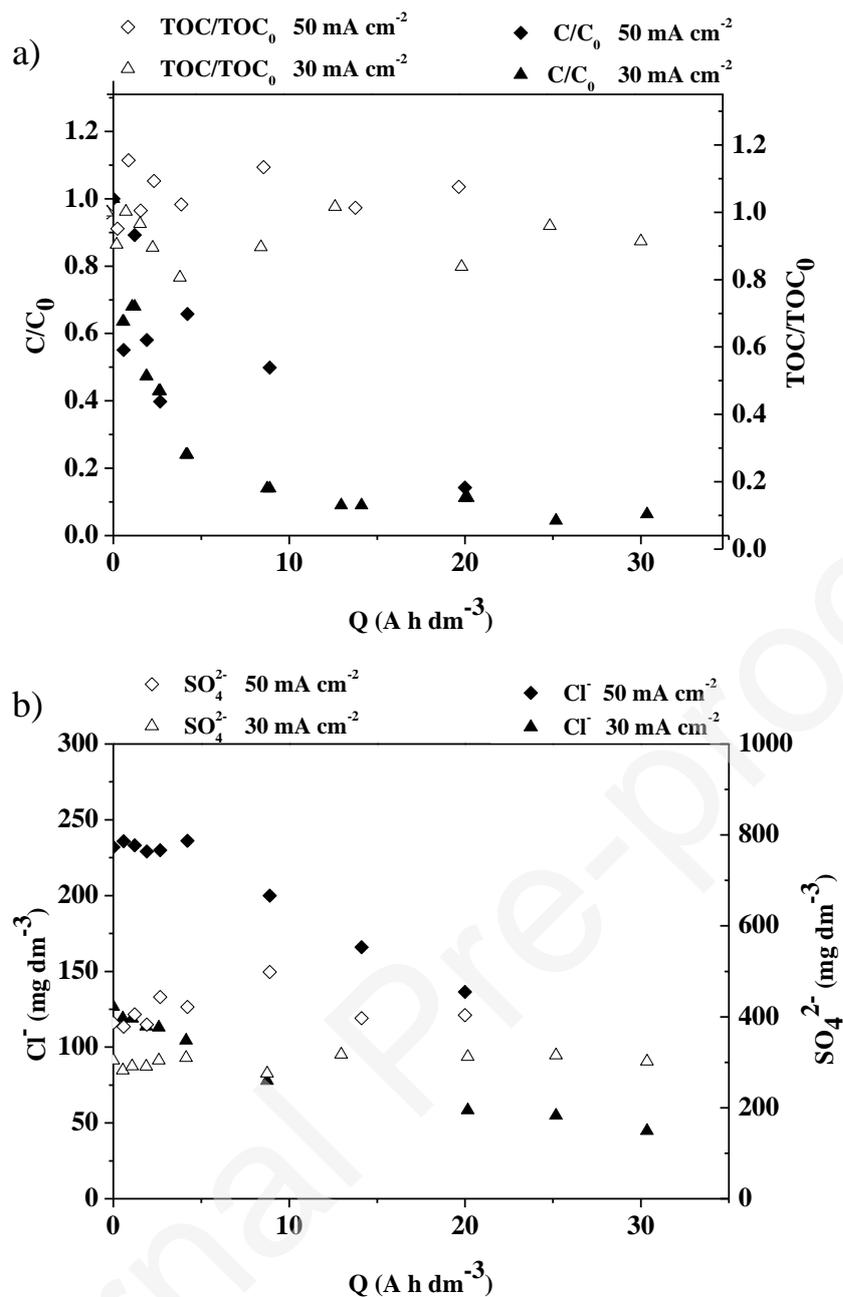


Figure 4. Influence of electrical charge applied and current density on (a) lindane concentration (full points) and total organic carbon concentration (empty points) and (b), sulphate (empty points) and chloride (full points) during the galvanostatic electrolysis with MMO-Ru at $30\ mA\ cm^{-2}$ (\diamond \blacklozenge) and $50\ mA\ cm^{-2}$ (\triangle \blacktriangle).

As seen, lindane is efficiently degraded with the two MMO anodes. However, TOC and sulphate concentrations kept constant during electrolysis with the MMO-Ru, meaning that not mineralization of SDS was carried out. It also means that lindane is transformed into organic intermediates but not mineralized. At 50 mA cm^{-2} , during the electrolysis with MMO-Ir a small sulphate formation is detected and a short depletion in TOC rate is observed, suggesting harsher oxidation conditions. However, it is not as important as the mineralization reached by BDD, even at lower current densities. Anyway, it could be related with the highest chlorate concentration detected that involves the generation of oxidant species as mentioned above.

3.2 Changes in the toxicity and biodegradability

Changes in the toxicity and biodegradability of the SWE, during the electrolytic treatments were evaluated with the four electrodes at selected conditions: BDD and CF electrodes working at 15 mA cm^{-2} , and MMO-Ir and MMO-Ru electrodes, working at 30 mA cm^{-2} . These current density values were selected taking into account the changes observed in the previous section in both, the lindane and TOC concentrations.

First, it was followed the changes in the toxicity (expressed in toxicity units, TU) during the electrolyses (Figure 5). As seen, as a general trend, toxicity decreases with the applied electrical charge in all cases. However, in the case of carbon felt anode, toxicity increases at low electrical charges. This behaviour was also observed in a previous investigation carried out with clopyralid, another organochlorinated pollutant [27], and this change was related to the formation of intermediates with higher toxicity of the parent molecules. Working with the rest of anodic materials, the higher the applied electrical charge is, the better the toxicity results are. The toxicity of the soil washing effluent without lindane (that is, a reference test using only SDS) is not shown, because toxicity was found to be negligible.

Toxicity indicates that the electrochemical treatment has a positive influence on the later application of a biological step. However, it is also important to check if the organics are being transformed during the treatment into compounds with a higher easiness of being metabolized by microorganisms. For this reason, biodegradability (calculated as by ratio BOD_5/COD) was evaluated. Final value of this parameter after passing an electric charge of $18 \text{ A}\cdot\text{h}\cdot\text{dm}^{-3}$ in the four electrolyses are shown in Figure 6. The discontinuous horizontal lines show the biodegradability of the raw SWE and that of the SWE without lindane (a reference test, only containing SDS). The presence of lindane decreases significantly the biodegradability of the effluent and the SWE with lindane almost reaches a ratio BOD_5/COD about 0.2, which can be explained because SDS is a rather biodegradable surfactant and its concentration in the SWE is high (5 g L^{-1}). It can be observed that biodegradability increased when using CF and especially BDD, where a ratio of approximately 0.5 is reached, which predicts a more successful biological post-treatment. However, results obtained after the electrolyses with both MMO electrodes are much worse indicating that intermediates formed, although less toxic, are less biodegradable than the initial composition of the raw SWE. This is important because in those case the depletion of the raw lindane was obtained and it suggests that opposite to what it could be thought, MMO electrodes are not as suitable as other electrodes for combined electrochemical-biological processes.

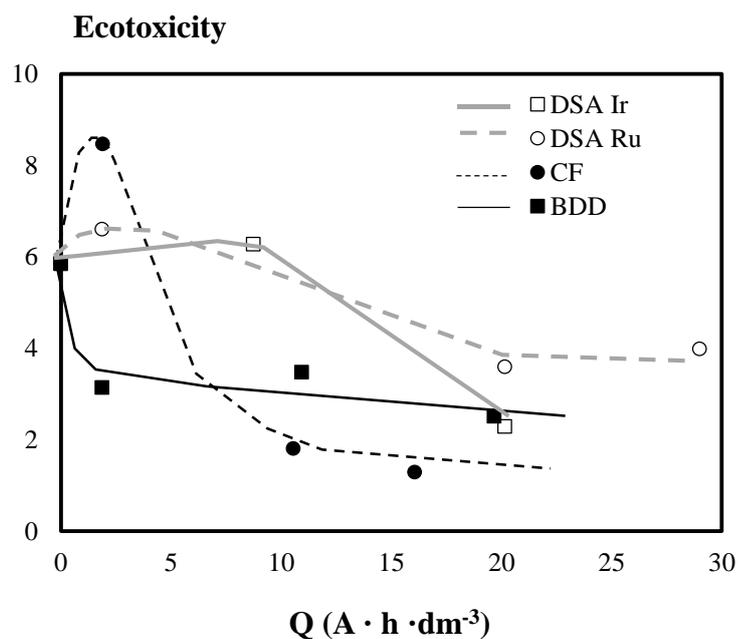


Figure 5. Changes in the toxicity of the SWE during the electrolyses with the different anodic materials.

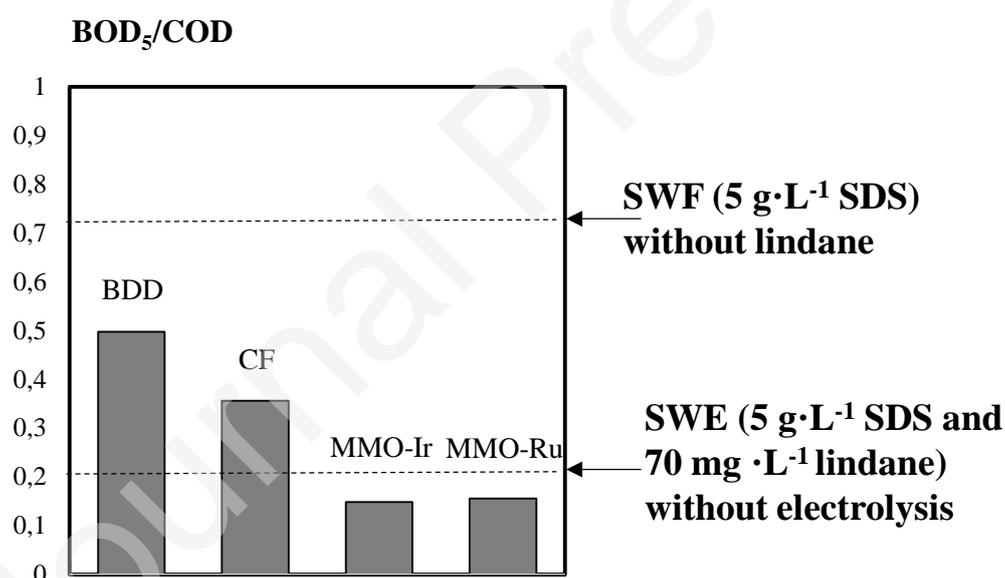


Figure 6. Comparison of the biodegradability of SWE after applying 18 $A \cdot h \cdot dm^{-3}$.

Both, toxicity and biodegradability shown in Figures 5 and 6, are indicative of the results that can be obtained in the direct biological post-treatment of the effluent of the

electrochemical process, that is, with a biological wastewater treatment which only treat these wastes (case of an industrial facility). However, the most typical situation is the discharge of this effluent into the sewer. In this case, the effluent will be merged with other substrates and it is important to determine if the same conclusions can be drawn in this case regarding the biodegradability.

Figure 7 shows how the ratio BOD_5/COD (of the wastewater to be treated by conventional aerobic sludge which received low discharges of such electrolysed SWE samples) decreases when SWE is added. However, this decrease is less important when the SWE is treated using BDD and specially CF electrodes, for which the same biodegradability can be reached at large current charge passed than that of the wastewater without SWE discharge. These results are also confirmed by the transient responses in Figure 8 in which the easily biodegradable fraction of the organic content is shown. Thus, changes in the maximum specific aerobic sludge respiration rates after the SWE discharges gives the same information than the changes in the biodegradability parameter, confirming the importance of the pre-treatment of SWE with CF or BDD in order to discharge SWE to sewers and do not affect to the operation of the biological treatment of municipal WWTP.

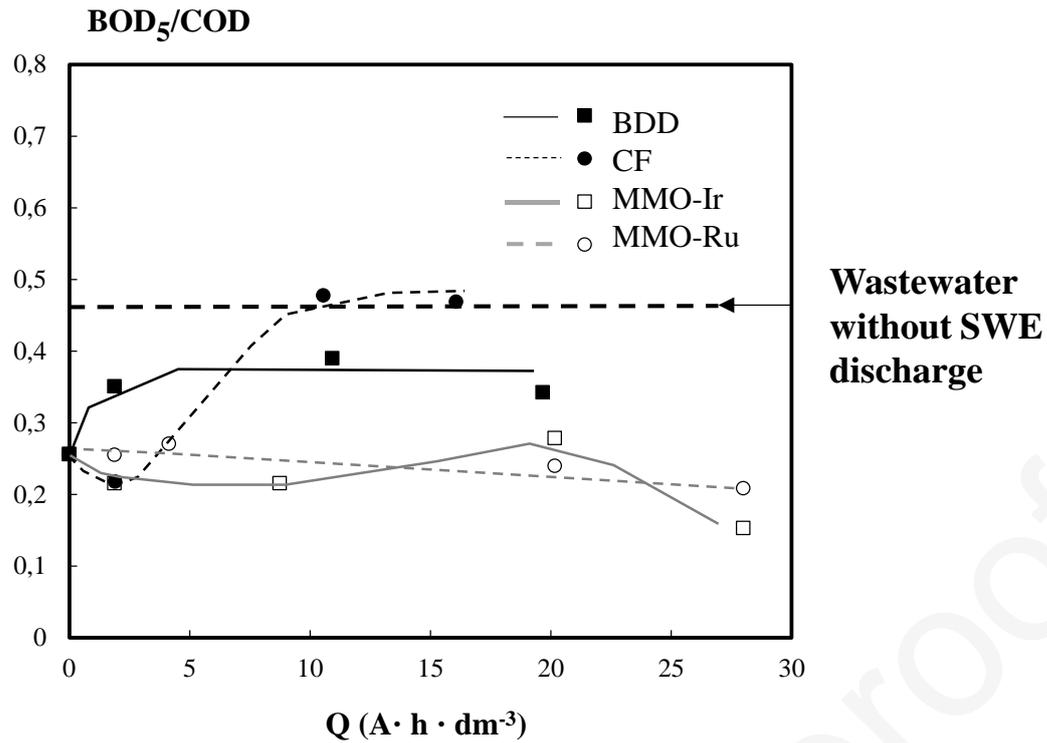


Figure 7. Evolution of the ratio BOD₅/COD during the aerobic treatment trough activated sludge after discharge of different AO pre-treated SWE.

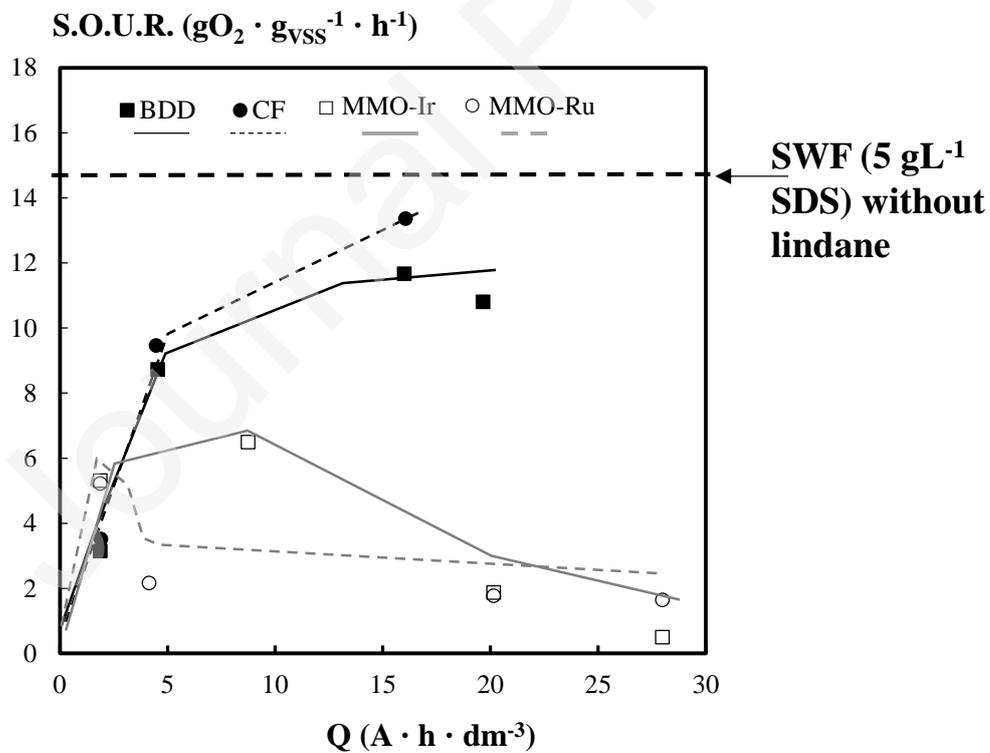


Figure 8. Changes in the Specific Oxygen Uptake Rate the aerobic treatment trough activated sludge after discharge of different AO pre-treated SWE.

Regarding the pre-treatment with MMO electrodes, results show that the MMO pre-treated effluents are not as suitable as the other effluents for being merged with other wastewater and being fed to a biological treatment. These results support the previous observations carried out during the direct treatment of the effluents.

4. Conclusions

From this work, the following conclusions can be drawn:

1. Important differences in the evolution of lindane, TOC, sulphate, and chlorine species during the electrochemical treatment. Lindane is degraded by the four electrodes tested but the degradation of the surfactant depends on the electrode. This degradation of the surfactant is seen not only with the decrease in the TOC but with the increase in the sulfate concentration.
2. For the direct biological treatment of the effluents of the electrolysis of SWE, BDD and CF show better performance for the reduction of toxicity and increase in the biodegradability than the two MMO anodes tested.
3. For the discharge of the effluents of the electrolysis of SWE into larger flows of water, BDD and CF show better performance for the increase in the biodegradability of the merged wastes than the two MMO anodes tested.

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