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Short communication

Removal of oxyfluorfen from *ex-situ* soil washing fluids using electrolysis with diamond anodes

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ABSTRACT

In this research, firstly, the treatment of soil spiked with oxyfluorfen was studied using a surfactant-aided soil-washing (SASW) process. After that, the electrochemical treatment of the washing liquid using boron doped diamond (BDD) anodes was performed. Results clearly demonstrate that SASW is a very efficient approach in the treatment of soil, removing the pesticide completely by using dosages below 5 g of sodium dodecyl sulfate (SDS) per Kg of soil. After that, complete mineralization of organic matter (oxyfluorfen, SDS and by-products) was attained (100% of total organic carbon and chemical oxygen demand removals) when the washing liquids were electrolyzed using BDD anodes, but the removal rate depends on the size of the particles in solution. Electrolysis of soil washing fluids occurs via the reduction in size of micelles until their complete depletion. Lower concentrations of intermediates are produced (sulfate, chlorine, 4-(trifluoromethyl)-phenol and ortho-nitrophenol) during BDD-electrolyses. Finally, it is important to indicate that, sulfate (coming from SDS) and chlorine (coming from oxyfluorfen) ions play an important role during the electrochemical organic matter removal.

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1. Introduction

Oxyfluorfen is a diphenyl-ether herbicide used for broad spectrum pre- and post-emergent control of annual broadleaf and grassy weeds in a variety of tree fruit, nut, vine, and field crops. The largest agricultural markets are wine grapes and almonds. There are also non-agricultural, ornamental and forestry uses of it. Oxyfluorfen is also used for weed control in landscapes, patios, driveways, and similar areas in residential sites. This compound (see, Fig. 1 in supplementary material) has a low water solubility (0.116 mg dm⁻³ at 20 °C), low vapor pressure (0.026 mPa at 25 °C), high K_{OC} (log K_{OC} = 3.46–4.13) and high K_{OW} (log K_{OW} = 4.86) (Mantzios et al., 2014).

Oxyfluorfen has the potential to affect terrestrial plants and aquatic ecological systems at all levels; it is toxic to plants, invertebrates and fishes. Birds and mammals may also experience subchronic and chronic effects from oxyfluorfen use (Alister et al., 2009; Das et al., 2003; Sondhia and Dixit, 2010; Hall et al., 2012).

For this reason, it is very important the decontamination, against accidental discharges of hazardous species, with efficient technologies that remediate the soil rapidly, avoiding the diffuse pollution. One of these technologies is Surfactant-Aided Soil Washing (SASW); it has been successfully studied and applied for the remediation of soils polluted with pesticides and polycyclic aromatic hydrocarbons (PAHs) (Saez et al., 2010; Lopez-Vizcaino et al., 2012a, 2012b; Rodrigo et al., 2014; Santos et al., 2015; Trellu et al., 2016). This approach involves the washing of soils with an aqueous surfactant solution (Trellu et al., 2016); with the aim of enhancing the water solubility of the organic compounds by forming oil/water (O/W) emulsions with micro-drops of pollutant compounds (Rodrigo et al., 2014; Trellu et al., 2016).

However, this type of effluent is difficult to be treated by conventional wastewater treatment methods due to the refractory properties of the persistent organic pollutants and surfactants dissolved (Trellu et al., 2016). For this reason, many works have focused on the development of efficient technologies to treat these effluents, including advanced oxidation processes (AOPs), such as photodegradation (Fdil et al., 2003; Martinez et al., 2009; Diagne et al., 2009), electro-Fenton (Kaichouh et al., 2008; Balci et al., 2009 Oturan et al., 2012; Trellu et al., 2016) and electrochemical

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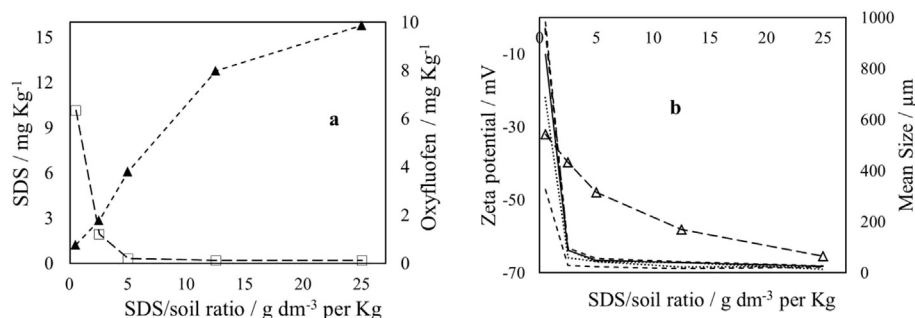


Fig. 1. Evaluation of soil polluted with oxyfluorfen after washing process with different SDS concentrations, as a function of SDS/soil ratio: (a) (▲) remaining SDS and (□) oxyfluorfen concentrations in the soil; (b) (Δ) Zeta potential and size limits including (---) 50% of the particles; size limits including 80% of the particles (....).

oxidation (EO) (Polcaro et al., 2004, 2005; Panizza et al., 2008; Sires et al., 2008; Santos et al., 2014; Trellu et al., 2016; Martínez-Huitle et al., 2015).

Nowadays, the most relevant technology for the treatment of O/W emulsions is EO using diamond electrodes, which has become a reference in the recent years for the depletion of persistent organic pollutants contained in wastewaters (Panizza et al., 2005; Malpass et al., 2006; Weiss et al., 2007; Louhichi et al., 2008; Sirés et al., 2014; Madsen et al., 2015; Martínez-Huitle et al., 2015). In fact, this type of electrolysis has received a great attention, thanks to the attractive characteristics of diamond anodes. Their high efficiency is associated to the production of many types of oxidant species, ranging from hydroxyl radicals ($\bullet\text{OH}$) formed by water electrolysis (Marselli et al., 2003) to $\text{S}_2\text{O}_8^{2-}$, Cl_2 , ClO_2^- or $\text{C}_2\text{O}_6^{2-}$ produced from the electrolyte salts (Rodrigo et al., 2010; Velazquez-Pena et al., 2013; García-Morales et al., 2013; Sirés et al., 2014; Brillas and Martínez-Huitle, 2015; Araújo et al., 2015). Treatment with this technology of complex wastewater, such as soil washing fluids polluted with pesticides, is a topic of a great interest nowadays, because it involves the study of the removal of highly toxic micro-emulsions (Trellu et al., 2016; Santos et al., 2015). Due to heterogeneity, treatment of emulsions becomes a challenge, as compared to the typical studies focused on the treatment of wastewater polluted with soluble organics. Taking into account this background, the objective of this study was to investigate, under laboratory conditions, the remediation of soils polluted with oxyfluorfen by combined approaches. First, the soil polluted with oxyfluorfen was washed by using SDS solution (Mousset et al., 2014; Trellu et al., 2016), and after that, the washing fluid obtained in the SASW process was treated electrochemically by using boron doped diamond (BDD) anodes. The effect of the ratio surfactant/soil is also going to be assessed to determine its influence in the soil washing efficiency and in the characteristics of the washing waste.

2. Materials and methods

2.1. Chemical

Oxyfluorfen (99.8% purity), benzene, acetonitrile, ethyl acetate and hexane (solvents with HPLC-grade) were obtained from Sigma–Aldrich (Spain). Sodium dodecyl sulfate (SDS) and sodium hydrogen carbonate (NaHCO_3) were obtained from Panreac. Deionized water (Millipore Milli-Q system) was used to prepare all solutions.

2.2. Analytical techniques

The oxyfluorfen concentration in the liquid phase was

determined using a liquid–liquid (L–L) extraction process. This process was carried out in separator flasks of 100 cm³ using ethyl acetate/hexane as extraction solvent (ratio oxyfluorfen solution/solvent = 0.52 v/v). All samples extracted from electrolyzed solution were filtered with 0.25 μm nylon Whatman filters before analysis. The concentrations of the compounds were quantified by HPLC (Agilent 1100 series) using analytical column Phenomenex Gemini 5 μm C18 with as mobile phase, a mixture of acetonitrile/water (70:30 (v/v)) at 0.3 cm³ min⁻¹. The detection wavelength of 220 nm was selected and the temperature of the oven was maintained at 25 °C. Aliquots of 20 μL were injected. The total organic carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. Chemical oxygen demand (COD) was also used as a parameter to follow the elimination of oxyfluorfen and surfactants during electrolysis using a HACH DR2000 analyzer. Zeta potential was also determined using a Zetasizer Nano ZS (Malvern, UK). Measurements of pH were carried out with an InoLab WTW pH-meter. The particle size was monitored during EO with a Master sizer hydro 2000SM (Malvern). The colorimetric method used to determine the concentration of the SDS surfactant was reported by Jurado et al. (2006). The anions present in the target wastewater were characterized using ion chromatography – a Shimadzu LC-20A system (Souza et al., 2014). Robustness of the results was evaluated by three independent analyses.

2.3. Preparation of spiked soil

Spiked soil approach is the most frequently contamination method used in the lab-scale studies (Saichek and Reddy, 2005; Villaverde et al., 2005; Yang et al., 2006; Navarro et al., 2008; Paria, 2008; Villa et al., 2010; Atteia et al., 2013; Rosas et al., 2013; Mousset et al., 2014; Lau et al., 2014; Trellu et al., 2016), for this reason, a model soil was chosen and it was polluted with oxyfluorfen. The model soil used in this work was kaolinite. A known amount of oxyfluorfen was dissolved in acetonitrile to contaminate the soil, mixing this oxyfluorfen/acetonitrile solution with kaolinite. The spiked clay was aerated for 1 day to favor the evaporation of the solvent used. This way, the oxyfluorfen was homogeneously distributed on the clay surface. The concentration of oxyfluorfen present in the soil at the beginning of the experiments was fixed around 100 mg kg⁻¹.

2.4. Soil washing procedure

Ex situ soil washing (Trellu et al., 2016) with surfactant solution was carried out in a stirred tank operated in discontinuous mode. The tank volume was 1000 cm³. Low-permeability soil (1000 g) polluted with oxyfluorfen and 800 cm³ of solubilizing agent (containing deionized water, 500 mg dm⁻³ of NaHCO_3 , and different

concentrations of SDS surfactant ranging from 100 to 5000 mg dm⁻³) were mixed in the reactor for 6 h at a stirring rate of 120 rpm. Then, the same tank operated as a settler (for 24 h) was used to separate the soil from the effluent. These effluents consisted of complex aqueous mixtures of oxyfluorfen, surfactant and sodium hydrogen carbonate, with emulsified micro drops and soluble species, which become the influent of the electrolytic treatment.

2.5. Electrochemical oxidation of the soil washing effluents

EO experiments were carried out in a table-scale plant by using an electrochemical flow cell with a single-compartment cell, as described in previous works (Saez et al., 2010; Santos et al., 2015; Araújo et al., 2015). BDD and steel electrodes were used as anode and cathode, respectively. Characteristic of BDD are as follows: sp³/sp² ratio of 225; boron content about 500 ppm and width of the diamond layer of 2.68 μm. For the electrochemical flow cell, inlet and outlet were provided for effluent circulation through the reactor; the SASW effluent was stored in a thermo-regulated glass tank (1000 cm³) and circulated through the cell using a peristaltic pump at a flow rate of 200 dm³ h⁻¹. The electrical current was applied using a DC Power Supply (FA-376 PROMAX). Temperature was kept constant by means of a water bath.

3. Results and discussions

3.1. SASW process

The SW process by using surfactant is an *ex situ* process that improves the removal of contaminants sorbed to soil (Trellu et al., 2016). The SW process enhances the contact between extracting agents and soil pollutants, thereby allowing better transference of the pesticide from the soil matrix into a simpler and easier liquid phase to be treated (Atteia et al., 2013; Rosas et al., 2013; Mousset et al., 2014; Lau et al., 2014; Trellu et al., 2016). For pesticides with a low solubility, the washing fluid dosed should contain surfactants, being SDS one of the most commonly used, because of the typically high efficiencies attained and its low hazardousness (Saez et al., 2010; Lopez-Vizcaino et al., 2011, 2012a, 2012b; Atteia et al., 2013; Trellu et al., 2016). Then, samples of the polluted soil (0.2 Kg) were treated by SASW process using different SDS concentrations (from 100 to 5000 mg dm⁻³) (Lau et al., 2014; Trellu et al., 2016). After that, the remaining concentrations of oxyfluorfen and SDS were determined in order to establish the decontamination level by SASW process. Fig. 1 shows the oxyfluorfen and SDS concentrations in the soil, as a function of SDS/soil ratio, after the washing treatment of the spiked soil studied. As expected, the higher the amount of SDS used, the lower the oxyfluorfen and the higher is the SDS remaining concentrations in the soil (Atteia et al., 2013; Trellu et al., 2016). For SDS/soil ratios above 5 g kg⁻¹, surplus oxyfluorfen is negligible in the soil and under the detection limits of the HPLC (0.25 mg dm⁻³). From a practical point of view, higher doses are not useful neither cost-effective (Trellu et al., 2016), as it increases unnecessarily the surfactant content of the soil, provoking other kind of pollution.

Comparing the resulting effluents (see Fig. 1); it can be observed that the mean size of the micelles depends on the ratio SDS/soil applied in the soil washing process. The higher the amount of SDS, the lower the mean micelle size and the more negative the resulting particle (according to the z-potential measurement) (Santos et al., 2015). Size of micelles tends to a constant value for high values of the SDS/soil ratio (Fig. 1). Conversely, charge is not stabilized, but it continues decreasing for higher doses. This behavior indicates that the characteristics of the washing fluids depend strongly on the dose of surfactant (Mousset et al., 2014;

Trellu et al., 2016), and it could be a determining parameter for the successive treatment approach for the depollution of effluent generated (see Fig. 8. reported by Trellu et al. (2016)).

Comparing these figures with other studies (Saichek and Reddy, 2005; Villaverde et al., 2005; Yang et al., 2006; Navarro et al., 2008; Paria, 2008; Villa et al., 2010; Lopez-Vizcaino et al., 2012a, 2012b; Rosas et al., 2013; Mousset et al., 2014; Lau et al., 2014), some similarities can be found (dose of surfactant, complexity of effluent obtained, surfactant/soil ratio, efficiency of soil depollution). Meanwhile, more important similarities regarding the size and charge of particles can be found with previous study with atrazine (Santos et al., 2015), where lower size of micelles and more negative charge when an increase of SDS/soil ratio is achieved. It can be also stated that main changes observed during the SASW process are the total depletion of pesticide attained (in the case of atrazine (Santos et al., 2015), surplus concentration was about 1 mg kg⁻¹ at very large SDS dosages) and the differences in the main characteristics of the washing fluid (mean size and total charge that depend on the nature of the pesticide washed from soil). Thus, with a SDS/soil ratio of 25 g kg⁻¹, the washing fluid for atrazine leads to an average micelles size of 178.22 μm and a charge of -51 mV, while for oxyfluorfen, 28.3 μm and -65.4 mV were achieved, respectively. It is important to remark that, these are new insights regarding the washing fluids, no have been investigated yet.

Obviously, in spite of having the same two species (the oxyfluorfen pesticide and the SDS surfactant), the washing fluids are completely different wastes. For this reason, the EO with diamond anodes was chosen as treatment approach for removing organic matter and these compounds should behave in a diverse way.

3.2. Electrolysis of soil washing effluents

Bulk electrolyses were performed with different effluents generated (700 cm³) by SASW process by applying 300 A m⁻² of current density (j). Fig. 2 compares the changes in the size and charge of particles during these electrolysis tests. As it can be observed, during the electrochemical treatment, mean size of micelles decreases rapidly and after 10 Ah dm⁻³, these are below the detection limit of the particle size analyzer. Decreased rate of the size particle seems to follow an exponential decay, with the exception of the washing fluid obtained at the lowest SDS/soil ratio (0.5 mg SDS Kg⁻¹ of soil). Likewise, it is important to point out the time course of the micelles charged because they do not follow the same trend (decreasing or increasing) but these tend to an intermediate z-potential value of about -50 mV. This kind of variation was also observed in our previous work about the treatment of atrazine soil washing fluids (Santos et al., 2015), but in this case the final z-potential was slightly lower (-35 mV). In this frame, we can infer that this value should be related to the structure of the smallest micro-drops produced in the waste during the electrochemical treatment (Santos et al., 2015; Trellu et al., 2016). Hence, the lower polarity of the oxyfluorfen (when compared to atrazine) indicates the higher amount of SDS required to stabilize a constant emulsified microdrop.

Changes in the average size of the particles reflect on the value of the turbidity, as it is shown in Fig. 3. This parameter decreases with the electrical charge passed (Q) during the electrolysis time. In comparing the initial values, it can be stated that it has a clear trend, completely opposite to that discussed for the size of the particles. Higher turbidities are obtained for the washing fluids with higher SDS/soil ratios because in these soils the ratio of small particles is much higher when compared to the washing fluids with lower SDS/soil ratio. Then, the turbidity is a measurement related to the colloids contained in the fluid (Saez et al., 2010; Mousset et al., 2014; Trellu et al., 2016).

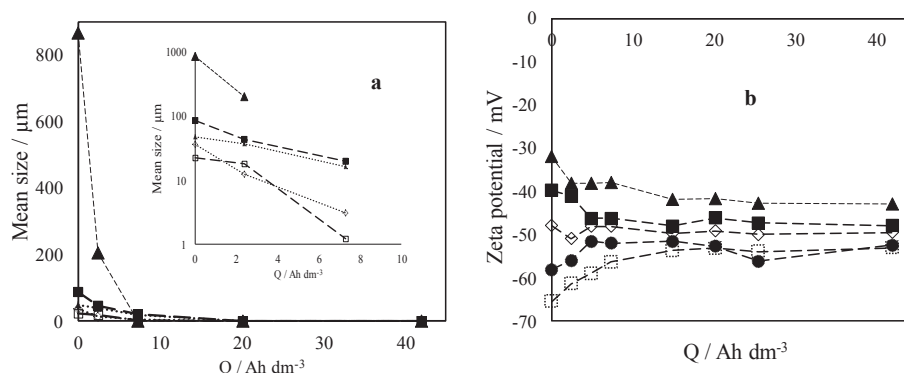


Fig. 2. Changes in the particle size (a) and z-potential (b), as a function of electrical charge passed (Q), during the electrolysis with diamond electrode (constant $j = 300 \text{ A m}^{-2}$) of soil-washing effluents obtained with different SDS/soil dosages: (▲) 0.5 g kg^{-1} , (■) 2.5 g kg^{-1} , (◇) 5.0 g kg^{-1} , (●) 12.5 g kg^{-1} and (□) 25 g kg^{-1} .

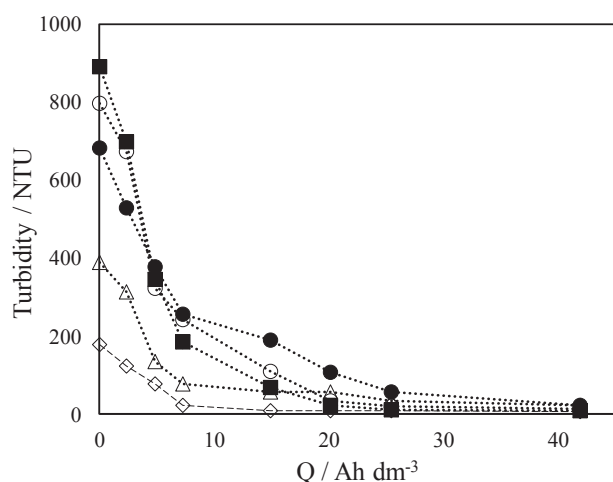
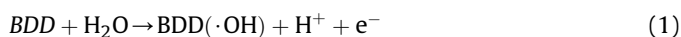


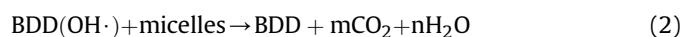
Fig. 3. Changes in the turbidity during the electrolytic treatment (constant $j = 300 \text{ A m}^{-2}$) of SASW effluents obtained during the soil washing with different SDS/soil dosages, as a function of electrical charge passed (Q): (◇) 0.5 g kg^{-1} , (Δ) 2.5 g kg^{-1} , (●) 5.0 g kg^{-1} , (○) 12.5 g kg^{-1} and (■) 25.0 g kg^{-1} .

Nevertheless, a very important point is that turbidity is not increased during the treatment as a consequence of the depletion of large drops (which according to Fig. 2 are depleted at 10 Ah dm^{-3}). In opposition, it keeps in an almost constant value (plateau zone) from 10 to 20 Ah dm^{-3} and this fact can be indicative of the oxidation of the microscopic drops (those quantified by turbidity) during the treatment. This effect is in agreement with the figures reported by Saez et al. (2010) and Santos et al. (2015).

The two main species contained in the raw washing fluid were monitored during the tests and results are shown in Fig. 4. Taking into account the large differences, results are plotted in semi logarithmic scale. As it can be observed, the SDS surfactant is depleted faster than oxyfluorfen pesticide, especially when effluents with lower SDS were treated (0.5 and 2.5 g kg^{-1}). This behavior clearly indicates that the micelles are attacked on their surface layer by mediated oxidants (hydroxyl radicals) produced during electrolysis at BDD surface from electrolysis of water (Martinez-Huitle et al., 2015; Trellu et al., 2016):



After that, as already commented, hydroxyl radicals participate in the fragmentation of micelles in solution (Santos et al., 2015; Trellu et al., 2016):



Additionally, as can be observed in Fig. 4, the rate of the depletion of SDS is almost constant (same slope in the semi-logarithmic plot) while the rate in the depletion of oxyfluorfen increases with the amount of SDS contained in the washing fluid.

At this point, it is worth taking into consideration that, the oxidation of SDS leads to the production of sulfate (Panizza et al., 2005, 2013; Santos et al., 2015), see Fig. 5. Total concentration of sulfate released in solution is not directly related to the concentration of SDS added to the soil; actually, it is related to the sulfate contained in the washing fluid (according to Fig. 1, the retention of SDS in the soil increases for large dosages of this surfactant). Nevertheless, the higher the dosed used in the soil washing process; the higher is the resulting sulfate released (Santos et al., 2015). In this frame, the sulfate released in solution can play a determining role during electrochemical treatment. As it is well studied in the literature, sulfate ions can be further oxidized to peroxosulfate during electrolysis (Serrano et al., 2002; Weiss et al., 2007; Araújo et al., 2015; Martinez-Huitle et al., 2015; Trellu et al., 2016):



Then, mediated oxidation process by hydroxyl radicals and persulfate can be considered responsible to eliminate the organic matter in solution (Araújo et al., 2015; Cañizares et al., 2009; Sires et al., 2008). This fact can explain the more efficient degradation of oxyfluorfen in the washing fluids, which reflects on a higher slope (kinetic constant). Likewise, the smaller size of the particles in the highly surfactant loaded washing fluid may promote the faster release of sulfate (Fig. 5) (Santos et al., 2015), producing persulfate and consequently, attacking the pesticide (Serrano et al., 2002; Sires et al., 2008).

Obviously, the oxidation of the washing fluid leads to the formation of intermediates. Table 1 in supplementary material reports the total of chromatographic area (related to the concentration) of intermediates detected in each one of the experiments. Meanwhile, Fig. 2 in supplementary material shows the TOC and COD decays, which was totalized in a single parameter to the removal of pollutants. Two intermediates were identified by HPLC (with retention times at 3.7 and 9.0 min) and the total chromatographic areas are very low and not depending on the total TOC or COD. These intermediates are related to the oxyfluorfen (whose concentration is almost kept constant in the five raw washing fluids) and not to SDS (whose concentration depends on the ratio SDS/soil used in the soil washing). By comparing with standards, 4-(trifluoromethyl)-phenol and ortho-nitrophenol were identified as intermediates of

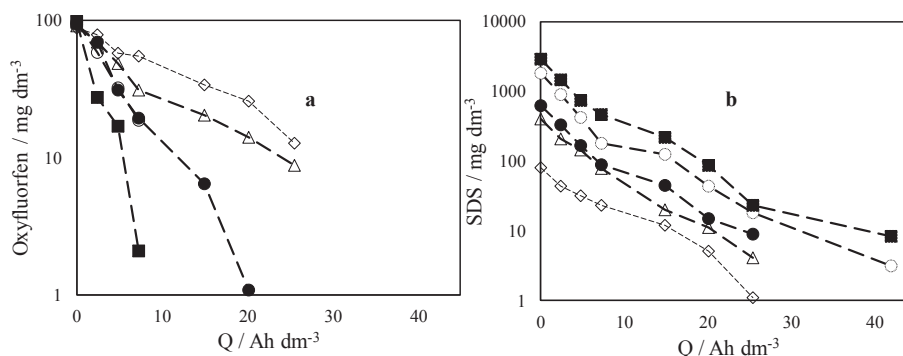


Fig. 4. Changes in the concentration of (a) oxyfluorfen and (b) SDS profiles during the electrolytic treatment ($j = 300 \text{ A m}^{-2}$) of SASW effluents obtained during the soil washing with different SDS/soil dosages. (◇) 0.5 g kg^{-1} , (Δ) 2.5 g kg^{-1} , (●) 5.0 g kg^{-1} , (○) 12.5 g kg^{-1} and (■) 25.0 g kg^{-1} .

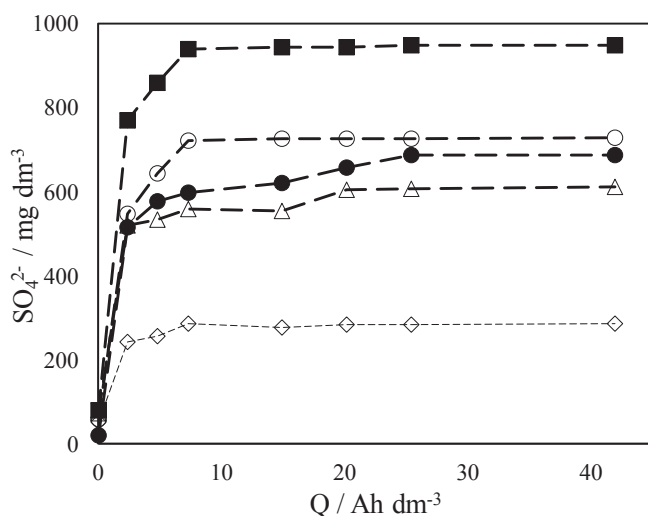


Fig. 5. Sulfate ions produced during the electrolysis ($j = 300 \text{ A m}^{-2}$) of SASW effluents obtained during the soil washing with different SDS/soil dosages. (◇) 0.5 g kg^{-1} , (Δ) 2.5 g kg^{-1} , (●) 5.0 g kg^{-1} , (○) 12.5 g kg^{-1} and (■) 25.0 g kg^{-1} .

oxyfluorfen degradation at BDD anodes (Mantzos et al., 2014; Alister et al., 2009; Das et al., 2003; Sondhia and Dixit, 2010). No intermediates coming from SDS were detected. This behavior indicates that intermediates formed during the process are very rapidly oxidized and that the most important processes occur on the surface of the micelles.

On the other hand, in comparing the TOC and COD changes, higher values of both parameters obtained with increasing SDS/soil ratio in the soil washing are easily explained in terms of the higher initial concentration of surfactant. Anyhow, the process' efficiency clearly depends on the concentration (mass transport controlled process), the total electric charge required for the complete mineralization is nearly the same for the five washing fluids tested (around 25 Ah dm^{-3}).

Finally the release of chlorine during oxidation of the oxyfluorfen is also an important point. Chlorine is contained in the chemical structure of the pesticide, and it is mainly transformed to hypochlorite during electrolysis (Fig. 3 in supplementary material) (Cañizares et al., 2009). This observation was not expected because typically the final product in the oxidation with diamond electrodes of chloride is not chlorine/hypochlorite but perchlorates, in particular, at the range of current densities applied (Bergmann et al., 2008, 2014; Cano et al., 2011, 2012). However, during the treatment of the five washing fluids studied, occurrence of chlorates and perchlorates was very low and these species do not

behave as final products but as intermediates. Another remarkable point is that, the final concentration of chlorinated species in the liquid is not the same; in spite that all the washing fluids had almost the same initial concentration of oxyfluorfen. Stripping of gaseous chlorine and the complex chemistry of persulfates and oxidized chlorine species can help understand this anomalous behavior.

Recently, the role of some species such as H_2O_2 in preventing the formation of perchlorates has been pointed out (Cotillas et al., 2015; Llanos et al., 2015). It can be produced from the decomposition of persulfate, so occurrence of persulfates at higher concentration can be preventing the oxidation of chloride to perchlorate and chlorate. Anyhow, at the light of the present knowledge we can only hypothesized this fact and more work has to be done in order to confirm this behavior.

4. Conclusions

From this work, the following conclusions can be drawn:

- SASW with SDS solutions is an efficient technology for the removal of oxyfluorfen from spiked soils when dosages below 5.0 g kg^{-1} are used. Higher surfactant dosages can provoke soil contamination.
- Characteristics of the effluents obtained by SASW process depend largely on the SDS/soil dosage. Despite the same chemical compounds are present, effluents are and behave in a completely different way due to their different type of microdrops.
- Electrolysis with diamond electrode is an efficient technology for treating effluents generated by SASW process, mineralizing completely pesticide and SDS (100% of TOC and COD removal) by applying 300 A m^{-2} for different SDS/soil dosages (ranging from 0.5 to 25.0 g kg^{-1}) and consequently, favoring a decrease in size of drops in solution.
- Rate of removal of SDS is faster than that of oxyfluorfen. It is due to the release of sulfate in solution from SDS molecules when these are degraded by hydroxyl radicals during the electrolysis. Sulfate is transformed to persulfate, favoring the enhancement in the process efficiency by mediated electrolysis. Chlorine coming from oxyfluorfen is also released and it is mainly transformed into hypochlorite, achieving higher concentrations when lower SDS/soil dosages are used to extract oxyfluorfen from soil.
- Opposite to other advanced oxidation processes, production of intermediates is almost negligible in this process. Only 4-(tri-fluoromethyl)-phenol and ortho-nitrophenol were detected by HPLC as the main byproducts from the oxidation of oxyfluorfen.

No intermediates coming from SDS were detected in spite of the high concentrations of SDS in several of the effluents, indicating that intermediates formed during the process are rapidly oxidized.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2016.01.027>.

Conflicts of interest

The authors confirm that this article's content has no conflict of interest. Also, we declare that all authors have participated in the elaboration of this manuscript.

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