



Treating soil-washing fluids polluted with oxyfluorfen by sono-electrolysis with diamond anodes



E. Vieira dos Santos^a, C. Sáez^c, P. Cañizares^c, C.A. Martínez-Huitle^b, M.A. Rodrigo^{c,*}

^a School of Science and Technology, Federal University of Rio Grande do Norte, 59078-970 Natal, Brazil

^b Institute of Chemistry, Federal University of Rio Grande do Norte, 59078-970 Natal, Brazil

^c Department of Chemical Engineering, Enrique Costa Novella Building, Campus Universitario s/n, 13071 Ciudad Real, Spain

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ABSTRACT

This work is focused on the treatment by sono-electrolysis of the liquid effluents produced during the Surfactant-Aided Soil-Washing (SASW) of soils spiked with herbicide oxyfluorfen. Results show that this combined technology is very efficient and attains the complete mineralization of the waste, regardless of the surfactant/soil ratio applied in the SASW process (which is the main parameter of the soil remediation process and leads to very different wastes). Both the surfactant and the herbicide are completely degraded, even when single electrolysis is used; and only two intermediates are detected by HPLC in very low concentrations. Conversely, the efficiency of single sonolysis approach, for the oxidation of pollutant, is very low and just small changes in the herbicides and surfactant concentrations are observed during the tests carried out. Sono-electrolysis with diamond electrodes achieved higher degradation rates than those obtained by single sonolysis and/or single electrolysis with diamond anodes. A key role of sulfate is developed, when it is released after the electrochemical degradation of surfactant. The efficient catalytic effect observed which can be explained by the anodic formation of persulfate and the later, a sono-activation is attained to produce highly efficient sulfate radicals. The effect of irradiating US is more importantly observed in the pesticide than in the surfactant, in agreement with the well-known behavior of these radicals which are known to oxidize more efficiently aromatic compounds than aliphatic species.

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1. Introduction

Combination of electrochemical processes and ultrasound irradiation, so-called sono-electrochemical processes, are emerging as very interesting integrated technologies with clear advantages over conventional technology for various applications, such as deposition, analysis, and chemical synthesis. In the recent years, there is an increasing interest in its application to environmental remediation, in particular in the treatment of wastewater, trying to combine the effectivity of two processes based on completely different mechanisms, looking for synergy. Unfortunately, the current state of knowledge is far away from full scale application and most of the studies about the degradation of pollutants are mostly carried out at a laboratory scale, utilizing the simplest reactor configuration, consisting of an electrolytic vessel and ultrasonic horns dipped in it [1]. Results obtained have shown that sono-electrolysis is significantly useful for treating wastes with biologically-toxic or non-degradable materials, such as aromatics, pesticides, petroleum

constituents, and volatile organic compounds [1,2]. In those studies, ultrasound irradiation demonstrated to produce changes in the reaction media that enhance mass transfer and produce changes in the chemical composition of the electrolyte. These changes are related to the cavitation phenomenon [3,4]. This process can produce new radical species and derivatives based on the very high local pressure and temperature reached during the implosive collapse of bubbles, formed when the system is irradiated with ultrasound [3–6].

Frequency of US irradiation is the key parameter to promote an improvement in the mass transfer and/or a change in the reactivity. Formation of the desired and well-known hydroxyl radicals is only attained under irradiation of high-frequency US (Eq. (1)), although this fact does not mean that US irradiation at lower frequencies could not be involved in the production of other radical oxidants.



On the other hand, during electrolysis of wastewater, many different oxidants are produced in the electrolyte [7–9]. The formation of oxidants depends on process conditions and overall on

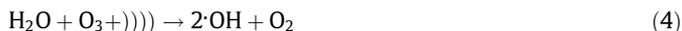
* Corresponding author.

E-mail address: manuel.rodrigo@uclm.es (M.A. Rodrigo).

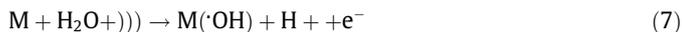
the anode material used. With anodes consisting of conductive-diamond coatings, it is demonstrated the efficient production of hydroxyl radicals (Eq. (2)) [10], which is known to be the key in the formation of other oxidants, in particular in the production of peroxocompounds.



Hence, electrolysis can produce many oxidants, such as chlorine, peroxosulfate, peroxocarbonate and peroxophosphate. One of these oxidants are powerful in terms of reduction potential but they need to be activated and transformed into more aggressive species. This is the case of peroxocompounds. Activation of oxidants, that is, the formation of highly reactive species from poorly reactive oxidants [11,12], can be attained by combination of oxidants or by UV light or ultrasounds irradiation [11,13–16]. Among them, the irradiation of US is becoming a very promising technology and the goal of the combination is to promote the formation of powerful radicals during the treatment such as the indicated in Eqs. (3)–(6), known to be produced also by irradiating UV light [17–19].



Thus, combination of electrolysis and sonolysis is expected to show other advantages as compared to the single processes. In addition to this clear advantage of the combination of technologies, production of hydroxyl radicals by the two single processes is not as efficient as their combined technology [10] (Eq. (7)), where the production of homogeneous and heterogeneous hydroxyl radicals is favored by US and electrochemical approaches, respectively [1,2].



Another important point regarding sono-electrolysis is that direct electrolysis can be benefit of the cavitation effects caused by US irradiation, improving the production of oxidants (and hence to improvements in the mediated electrolysis). A very interesting process is the microjet phenomena, where the diffusion-layer thickness of the electrolysis system is decreased to less than 1 μm , and activation of the electrode surfaces leads to the enhancement of mass transfer and a tenfold increase in electrolytic current [1,2,11,13]. It is already known that organic compounds interact with the surface of electrodes (through adsorption processes), leading to electrode fouling and subsequent losses in degradation efficiencies [14–16,20,21]. However, the direct application of ultrasound to an electrode surface enhances its performance by cleaning it and hence increasing considerably the degradation of organics.

In recent years, the use of sono-electrolysis has been successfully applied for degrading of pesticides, such as 2,4-Dichlorophenoxyacetic acid (2,4-D) [15,22], 2,4-Dichlorophenol (2,4-DCP) [22], Chloroacetic acid [23] and Diuron [24]. Yasman et al. reported the detoxification of the 2,4-D herbicide and its derivative 2,4-DCP using a combination of US irradiation, electrolysis with nickel electrodes and Fenton oxidation [22], demonstrating that combination of technologies was a very efficient process, even more than expected according to the addition of effects of the single processes. Likewise, Esclapez et al. evaluated the sono-electrolysis in the removal of trichloroacetic acid (TCAA). By single electrolysis, a poor performance was achieved, but the degradation of the main by-products of TCAA abatement was significantly

enhanced by high US frequency [23]. In another case, the degradation and mineralization of diuron was analyzed using sono-electrolysis and a synergistic effect was also achieved by the combination of the sono and electrochemical technologies [24]. In this context, the application of sono-electrolysis for degrading pesticides is clearly still under development and is potentially a promising alternative to treat this type of wastewater [25]. In this work, it is going to be studied the degradation of herbicide oxyfluorfen with sono-electrolysis with diamond anodes. Waste with oxyfluorfen becomes a very interesting model-wastewater because of the low solubility of oxyfluorfen [26–28], which made that this type of waste contains not only soluble molecules of pesticide but also a high concentration of micelles consisting of herbicide-surfactant and, of course, surplus free surfactant. To the authors' knowledge, to date, no reports have been published for describing the oxidation of oxyfluorfen using sono-electrolysis with diamond electrodes. Therefore, the main objective of the present research is to examine the effects of ultrasound irradiation on the electrolysis of oxyfluorfen, and this is going to be attained by studying the influence of different operating parameters of this wastewater treatment technology on the degradation of soil-washing waste obtained after applying this Surfactant-Aided Soil Washing (SASW) [29–31] to soil spiked with 20 mg/kg of oxyfluorfen with five different (in terms of concentration) surfactant solutions (surfactant used is SDS, sodium dodecyl sulfate). The resulting soil-washing fluid is a complex wastewater characterized by the presence of soluble pollutants and micelles of pesticide and surfactant. An important point is that no additional salts were added to improve the treatment performance but just the salts contained in the raw soil-washing fluid. Results of sono-electrolysis are to be compared with those obtained by single sonolysis and electrolysis.

2. Materials and methods

2.1. Chemicals

Oxyfluorfen (2-chloro-1-(3-ethoxy-4-nitrophenonyl)-4-(trifluoromethyl)), 99.8% purity benzene, HPLC-grade acetonitrile, ethyl acetate and hexane were obtained from Sigma-Aldrich (Spain). Sodium dodecyl sulfate (SDS) (used as solubilizing agent) and sodium hydrogen carbonate (NaHCO_3) were obtained from Pan-reac. Deionized water (Millipore Milli-Q system) was used to prepare all solutions.

2.2. Analytical techniques

To determine oxyfluorfen concentration in the liquid phase, an L–L extraction process was used before the analytical analysis. This process was carried out in separator flasks of 100 cm^3 using ethyl acetate/hexane as extraction solvent (ratio oxyfluorfen solution/solvent = 0.52 v/v). After that, 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. The detection wavelength of 220 nm was used and the temperature oven was kept at 25 $^\circ\text{C}$. 20 μL aliquots were injected, using as mobile phase, a mixture of acetonitrile/water (70:30 (v/v)) at 0.3 $\text{cm}^3 \text{min}^{-1}$. The total organic carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. The oxyfluorfen and surfactant removal were monitored through the COD content during electrolysis using a HACH DR2000 analyzer. Zeta potential was also measured for the clarified liquid 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 electrochemical oxidation with

a Mastersizerhydro 2000SM (Malvern) [29]. The colorimetric method used to determine the concentration of the SDS surfactant has been elsewhere [32]. The anions present in the target wastewater were characterized using ion chromatography by means of a Shimadzu LC-20A system.

2.3. Preparation of spiked soil

The soil was spiked with a target concentration of oxyfluorfen (mass of contaminant/mass of dry soil = 100 mg kg⁻¹). The oxyfluorfen quantity required to yield the target concentration was measured and completely dissolved in acetonitrile. The oxyfluorfen/acetonitrile solution was mixed with an adequate amount of soil (kaolinite, selected as clay-soil model). Thus, the soil-acetonitrile-oxyfluorfen mixture was stirred and blended homogeneously. Afterwards, the spiked clay was aerated for 1 day to favor evaporation of the acetonitrile. To check the initial concentration of oxyfluorfen and its homogeneous distribution in the soil, five samples of polluted soil were taken and oxyfluorfen concentration was quantified. The standard deviation of this determination is lower than 5%.

2.4. Preparation of the soil washing fluid

Soil washing with surfactant fluid solution was carried out in a stirred tank operated in discontinuous mode. The tank volume was 1000 cm³. Low-permeability soil, after polluted with 100 mg of oxyfluorfen per kg of soil and mixed with 800 cm³ of solubilizing agent (containing deionized water, 500 mg dm⁻³ of NaHCO₃, and different concentrations of sodium dodecyl sulfate (SDS) surfactant) was mixed in the reactor for 6 h at a stirring rate of 120 rpm. According to previous dynamic soil-washing tests, oxyfluorfen removal percentage increases sharply during the first hour and then a constant value is reached. At this point, the system has reached stationary conditions and further washing times are not able to increase the removal percentage. Taking into account these results, a washing time of 6.0 h was selected. SDS concentration ranging from 100 to 5000 mg dm⁻³ at each one of the tests performed. SDS concentration lower than 100 mg dm⁻³ are not recommended. The same tank used for mixing, then acted as a settler (during 24 h) 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. Sonolysis and sono-electrolysis

Two different degradation techniques were employed as follows: sonolysis and sono-electrolysis. Additionally, electrolysis essays have been also carried out in a bench-scale plant with a single-compartment electrochemical flow cell. This type of electrochemical cell is the most common for the treatment of industrial wastewater because of the large surface/volume ratio, which helps to attain an optimum performance of the electrochemical processes. Irradiated experiments were carried out in the electrolysis set up and using the same fluid-dynamic conditions. To do this, it was equipped with an ultrasound source (UP200S ultrasound horn, Hielscher Ultrasonics GmbH, equipped with a titanium glass horn of 40 mm diameter, length 100 mm, emitting 24 kHz and maximum ultrasonic power 200 W). The ultrasound generator irradiates energy into an auxiliary tank. Fig. 1 shows the experimental system used. The acoustic power dissipated was calculated in a separate experiment according to a procedure described elsewhere [33] and a value of 46 W was obtained. BDD and steel electrodes were used as anode and cathode, respectively. Characteristic of

BDD are as follows: sp³/sp² ratio: 225; boron content: 500 ppm; width of the diamond layer: 2.68 μm. For the electrochemical flow cell, inlet and outlet were provided for effluent circulation through the reactor (Fig. 1b); the SASW effluent was stored in a thermostated glass tank (1000 cm³) and circulated through the cell using a peristaltic pump at a flow rate of 200 dm³ h⁻¹. This connection helps to obtain mixing (by pumping), a proper regulation of temperature (very important due to the ohmic losses of electrochemical processes), a place for the gas stripping and, in case of combination of technologies (with chemical processes, sonolysis or photolysis), a place for the non-electrochemical reactions to be developed. It is a very simple to scale -up system and hence for all these reasons, it has been our choice for this type of treatment.

All electrodes were circular (100 mm diameter) with a geometric area of 70 cm². The inter-electrode gap was approximately 9 mm. The electrical current was applied using a DC Power Supply (FA-376 PROMAX). Temperature was kept constant by means of a water bath.

The current density employed was 30 mA cm⁻². The cell voltage did not vary during electrolysis, indicating that the conductive diamond layers did not undergo appreciable deterioration or passivation phenomena. Prior to use in galvanostatic electrolysis assays, the electrode was polarized for 10 min in a 0.035 M Na₂SO₄ solution at 15 mA cm⁻² to remove any impurities from its surface. In single sonolysis essays, the power supply was disconnected.

3. Results and discussions

The raw waste used in this work was obtained after a SASW process consisting of (1) mixing oxyfluorfen spiked soil (100 mg kg⁻¹) with a 500 mg dm⁻³ SDS solution at a washing fluid volume/soil weight ratio of 2.5, (2) maintaining stirring for 6 h to favor the transfer of the oxyfluorfen to the washing fluid and (3) splitting the washing fluid from soil by sedimentation. SASW effluents consists of emulsions of micelles with the pesticide and surfactant, low concentrations of pesticide (if as happens with oxyfluorfen pesticide, solubility is low) and varying concentrations of free surfactant (not linked with micelles) that depend on the dose used in the soil washing processes. Due to its complexity, besides COD and TOC, it was monitored the changes in the particle size, zeta potential and turbidity of the effluent during the electrolysis and sono-electrolysis tests. In this point, it is important to remind that zeta potential is a measure of the magnitude of the charge repulsion/attraction between particles, and is one of the fundamental parameters known to affect stability. Its measurement brings detailed insight into the causes of dispersion, aggregation or flocculation.

Figs. 2 and 3 compare the changes on the particles size and z-potential (Fig. 2a), TOC and COD decays (Fig. 2b), oxyfluorfen and SDS decays (Fig. 3a) and turbidity and sulfate concentration (Fig. 3b) as a function of electrical charge passed for sono-electrolysis and electrolysis of soil-washing fluids polluted with oxyfluorfen.

Results clearly indicate that electrolysis is an efficient technology for treating of this kind of wastewater; achieving a significant reduction of particle size (Fig. 2a) and a complete mineralization of the organic matter dissolved in the effluent (Fig. 2b). Meanwhile, US irradiation slightly improves the removal rate of oxyfluorfen (Fig. 2b) but no additional changes are observed in the main parameters monitored (see Fig. 3), suggesting similar mechanisms in the oxidation of organics.

As it can be observed, in both cases the particle size decreases rapidly during the initial stages of the electrolysis, and this trend is consistent with the changes until negative values obtained in the z-potential, indicating that the oxyfluorfen/surfactant micelles

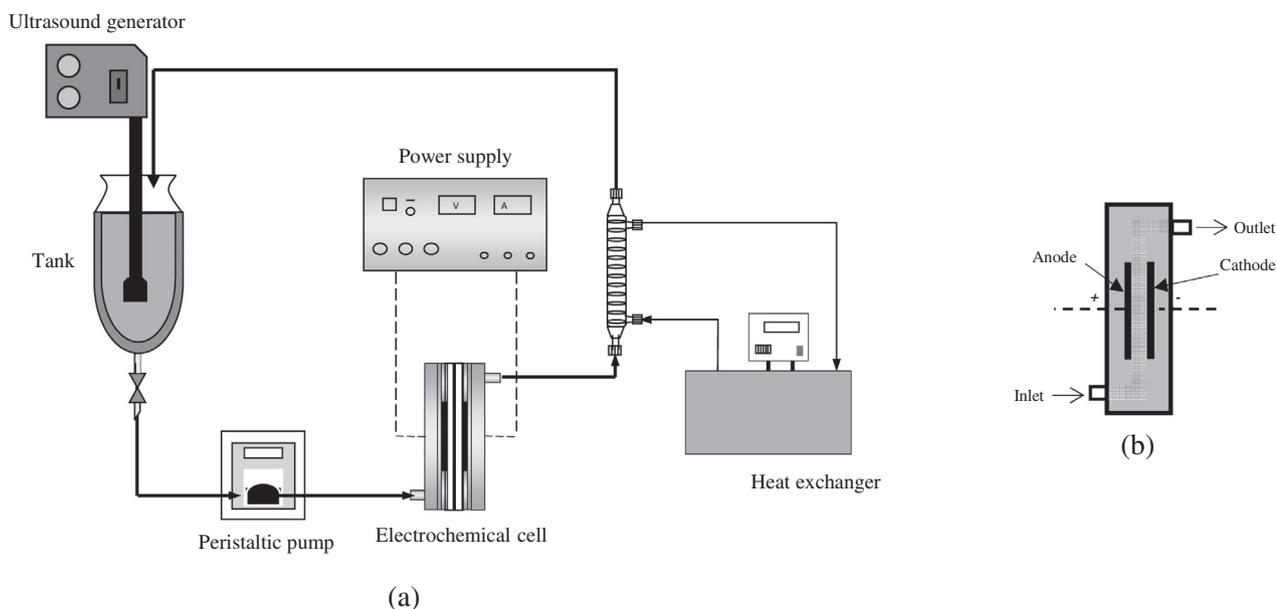


Fig. 1. (a) Bench-scale plant of sonoelectrolysis. (b) Detail of the electrochemical reactor.

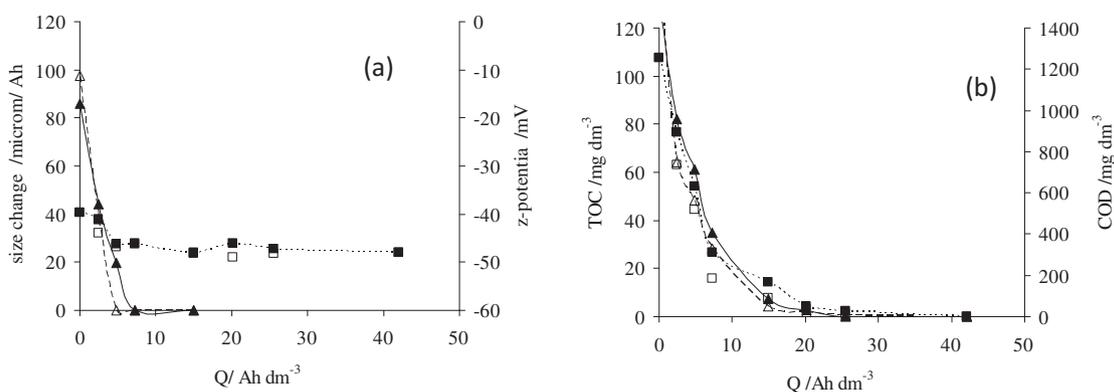


Fig. 2. Changes during the electrolysis and sono-electrolysis of soil-washing fluid obtained after the treatment of soil spiked with 100 mg kg^{-1} of oxyfluorfen with a solution containing 500 mg dm^{-3} of SDS. (a): (\blacktriangle) particle mean size and (\blacksquare) z-potential during electrolysis; (\triangle) particle mean size and (\square) z-potential during sono-electrolysis; (b): (\blacktriangle) TOC and (\blacksquare) COD decays during electrolysis; (\triangle) TOC and (\square) COD during sono-electrolysis. Current density: 30 mA cm^{-2} ; US power rate: 250 w dm^{-3} .

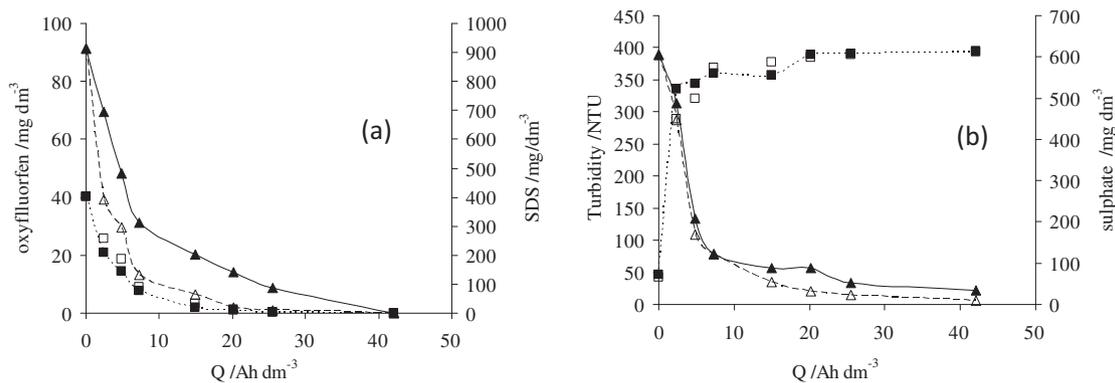


Fig. 3. Changes during the electrolysis and sono-electrolysis of soil-washing fluid obtained after the treatment of soil spiked with 100 mg kg^{-1} of oxyfluorfen with a solution containing 500 mg dm^{-3} of SDS. (a): (\blacktriangle) oxyfluorfen and (\blacksquare) SDS concentration abatements during electrolysis; (\triangle) oxyfluorfen and (\square) SDS concentration decays during sono-electrolysis. (b): (\blacktriangle) turbidity and (\blacksquare) sulfate behavior during electrolysis treatment; (\triangle) turbidity and (\square) sulfate concentration changes during sono-electrolysis. Current density: 30 mA cm^{-2} ; US power rate: 250 w dm^{-3} .

are drastically attacked during the first stages to form smaller particles with more negative surface charge. In this point, it is impor-

tant to take in mind that it is used an anionic surfactant and thus, the expected superficial charge of micelles is negative. After this

initial rapid reduction in size of the micro-drops, size continues decreasing till the end of the test although at a lower rate, while the z-potential value kept almost constant (in fact a small trend towards more negative values is observed). In observing the figures, another important point to remark is that size decreasing (Fig. 2a) and mineralization (Fig. 2b) occur at the same time for the single electrolysis and for the sono-electrolysis and that changes in the TOC and COD are almost overlapped (Fig. 2b), in both cases. This fact suggests that few intermediates are being formed during the treatments and that the mechanisms followed are the same. This behavior can only be attributed to the attack of oxidants electrochemically formed to the micelles with simultaneous mineralization of the organics and inorganic species release (sulfate in the case of the SDS).

Nevertheless, a competitive oxidation between SDS and oxyfluorfen is attained, but the surfactant is more efficiently removed in both US irradiated and silent electrolysis. It can be easily understood taking into account that surface of pesticide micelles is covered by the SDS and hence its oxidation becomes most effective because SDS is first attacked during the destruction of the micelles. In addition, free SDS is also contained in the solution because the pesticide is the limiting reagent in the SASW process. In any case, oxidation of pesticide is simultaneously achieved from the very first moment, pointing out the harsh oxidation conditions attained during the electrochemical processes with diamond anodes.

Another important observation is that US irradiation seems to influence more on the pesticide degradation than on the SDS degradation and a very outstanding difference is observed in this parameter (Fig. 3a). The important concentration of SDS when compared to that of pesticide makes that changes observed in TOC and COD are closer to those observed for SDS and hence the effect of UV irradiation on these parameters is not as large as that observed for the pesticide. On the other hand, similar changes in the size changes and turbidity are observed during the treatment at both approaches. However, the decreasing rate in both parameters is also slightly improved when US irradiation is applied. This fact indicates that oxidation proceeds through the continuous attack to micelles, which results in their disappearance from waste. One important point in this discussion is an estimation of the energy consumption of both technologies, silent electrolysis and sono-electrolysis. Value of the energy consumption for electrolytic processes can be estimated by multiplying the cell voltage by the specific current charge required to attain a given removal. As an example, according to the experimental results shown in Fig. 2b, for a removal of 97% of the TOC, it is required almost 90 kW h m^{-3} for the sono-electrolysis and 108 kW h m^{-3} for the silent electrolysis (assuming a typical cell voltage of 6.0 V). Energy applied by the horn is significantly higher and can be estimated in almost 1460 kW h m^{-3} (taking into account the duration of the test). Unfortunately, this value is very high in comparison with the value provided by the electrolysis, but it should be taken into account that according to the calorimetric measurements carried out at least 25% of the power supplied in our experimental device produces heat and hence optimization may be carried out in full scale processes.

Hence, from the results discussed up to now, it seems that combination of US irradiation with electrolysis seems to be a very effective technology, with an improved affinity for the aromatic oxyfluorfen than for the aliphatic chain of SDS when compared to the single electrolysis. However, an important point to be considered is that the effluents of the soil washing process differs significantly from each other when different SDS concentrations are used in the soil washing. In particular, the size of micelles is completely different as it was pointed out in a previous work of our group [29], and this is a very interesting point, scarcely studied in the literature. Because of that, this paper does not only focus

on the oxidation of a single washing fluid but it takes into account the very different colloids dispersions which can be obtained when pesticide and SDS are combined in different ratios. According to these assumptions, in comparing the effect of irradiating US for different types of soil washing wastes (Fig. 4), it can be observed that the irradiation of US during electrolysis results in a much more effective process, because it leads to a slightly higher size-reduction rate and hence for the same charge passed, lower resulting mean-size is obtained when US are irradiated. As can be observed from secondary axis of this Fig. 4, it is also shown that the mean size of the micelles obtained in the SASW process decreases with the surfactant/soil ratio. Hence, it can be stated that size reduction rate is related to the characteristic of the colloids dispersion and particularly to the initial size of the particles contained in the washing fluid: the higher the initial size, the faster is the size reduction attained. Likewise, it can also be observed that single sonolysis (carried out for two effluents) is not very effective in the reduction in size of the colloids, although it cannot be considered a reluctant treatment, because a noticeable decrease in size is clearly observed during the treatment.

Size reduction of micelles leads to changes in the surface charge of micelles, because structure of the micelles is modified. This change is not always in the same way because it leads to more negative values for the washing fluid containing the larger micelles and to less negative values for the other washing fluids. However, the final z-potential measured after the electrolytic process tends to the same value (Fig. 5), regardless the initial value of the z-potential of the micelles contained in the washing fluid. This suggests that when the size of the micelles decreases during the electrochemical oxidation process, the same structure of micelles is obtained regardless of the initial point. No influence of the US-irradiation is observed at this point suggesting that chemical mechanisms during the oxidation should be, at least, comparable.

Once clarified how the electrolytic and sono-electrolytic processes behaves with respect to the micelles contained in these wastes, it is important to focus on the changes in the two main organic species contained in the raw washing fluids treated (Fig. 6). Fig. 6a focuses on the removal of the surfactant. SDS removal efficiency (and rate because all the experiments are carried out in galvanostatic conditions at the same current and hence, the rate can be obtained by dividing the efficiency by the current intensity) depends on the amount of SDS contained in the waste as it could be expected for most electrochemical wastewater treatment processes in which mass transport and/or first order mediated oxidation reactions can control the overall rate of the process [34,35]. Oxidation of SDS means that this surfactant cannot

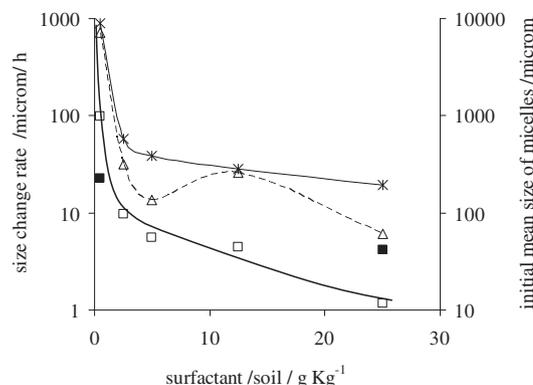


Fig. 4. Influence of the initial characteristics of soil washing fluid in the micelles size reduction rate: (Δ) electrolysis; (*) sono-electrolysis; (■) sonolysis and (□) initial mean size of micelles obtained in the SASW process. Current density: 30 mA cm^{-2} ; US power rate: 250 w dm^{-3} .

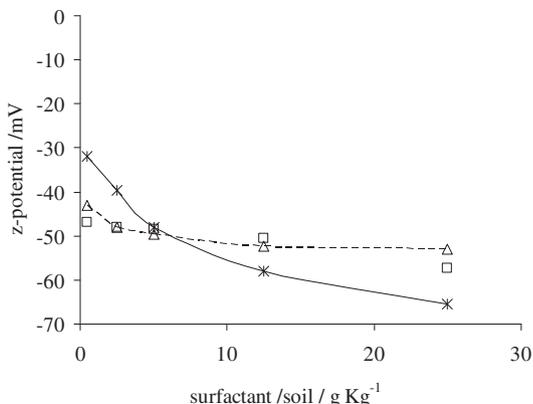


Fig. 5. Changes in the z-potential during the treatment (after the application of 2.4 Ah dm^{-3}) compared to the initial z-potential of the raw soil-washing waste. * initial; □ electrolysis; △ Sono-electrolysis.

be recovered and recycled for the SASW process when electrolysis or sono-electrolysis are applied. Regarding the comparison of silent electrolysis and sono-electrolysis, results obtained for the removal of the micelles are very different from those obtained for the surfactant. As can be observed from Fig. 6b, only a very small influence of the irradiation of ultrasound is observed in the rate of removal of SDS. A last point to be discussed is the performance of single electrolysis, which is shown for two soil-washing wastes in the Figure, indicating its low relevance as compared to the electrolysis. A last point to be discussed regarding SDS is the amount of sulfate release during the oxidation of SDS, which clearly increases with the surfactant soil /ratio, as expected due to the higher concentration of the precursor SDS. It is important to point out that sulfate released during the sonolysis is not negligible, confirming the occurrence of oxidation processes during single sonolysis, although at lowest rate.

Fig. 7 focuses on the influence of soil-washing characteristics on the removal rate of oxyfluorfen. As can be observed, it compares the oxyfluorfen removal rates attained with the different effluents of the SASW processes, indicating that there is a very important increase, which clearly depends on the initial size of the particles and on the irradiation of ultrasound. In comparing the results obtained for the different washing fluids, the smaller the micelles and the greater the SDS/pesticide ratio, the faster is the removal obtained. To explain this observation, an important condition must be taken into consideration, high SDS/pesticide ratios lead to the formation of higher concentration of sulfates, which afterwards

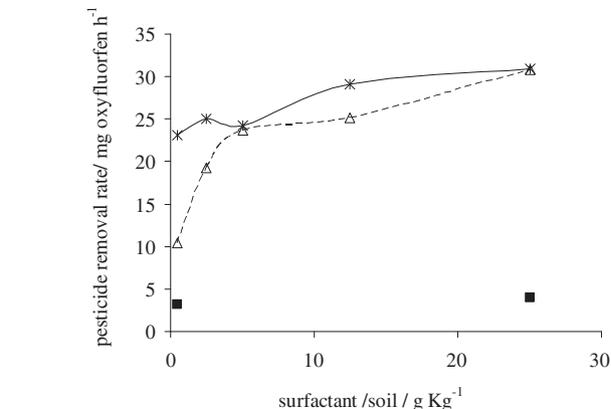


Fig. 7. Influence of the initial characteristics of soil washing fluid on the oxyfluorfen removal rate. Conditions: (△) electrolysis; (*) sono-electrolysis; (■) sonolysis. Current density: 30 mA cm^{-2} ; US power rate: 250 w dm^{-3} .

may be oxidized to peroxosulfates [36], increasing the amount of oxidants contained in the bulk and hence the rate of the oxidation processes. It is very important to point out that pesticide is removed from the very first moment, simultaneously with the micelles size reduction.

Regarding the irradiation of US, the improvement is more clearly observed for larger micelles; suggesting that, in addition to the higher production of sulfates at high surfactant/soil washing ratios, the enhanced mixing conditions caused by the US irradiation and also the promotion in the formation of sulfate radicals from the decomposition of persulfate is playing a more important role with this type of washing-fluid wastes. Again, a very low rate of the single sonolysis process is observed. This fact points out that process is clearly synergistic because the combined process is faster than the addition of the two single processes. This observation is very clear for the effluents obtained at low surfactant/soil ratios. The activation of persulfates with ultrasound is a very interesting observation because in these experiments low frequency US were used and results obtained demonstrate that despite this irradiation is not enough to produce hydroxyl radicals it is suitable to produce sulfate radicals and hence to produce the synergisms observed.

Fig. 8 shows the TOC and COD removal rate for the five washing fluids studied. As expected, taking into account the low concentrations of pollutants, the higher the organic load, the higher is the TOC and COD removal. This explains that efficiencies obtained for washing wastes with higher ratio of SDS are higher. As it can be observed, no great differences between the sono and the silent

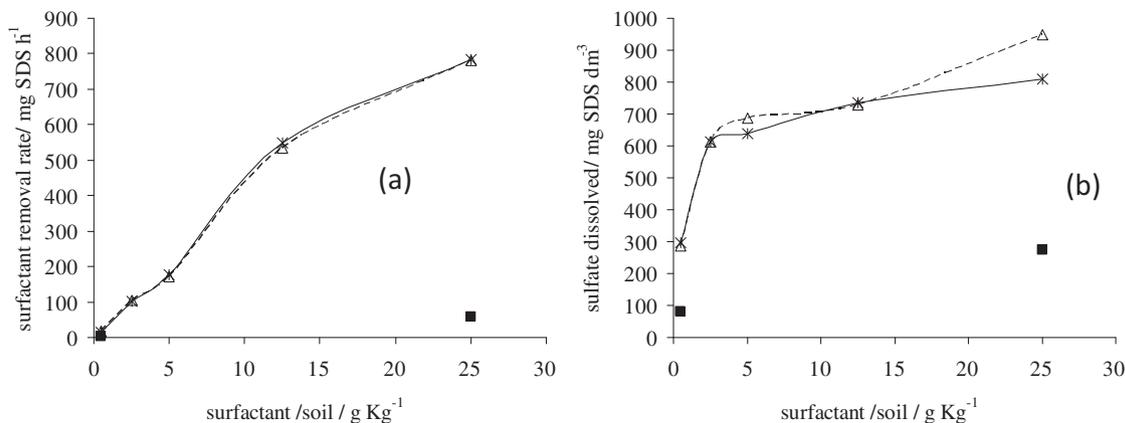


Fig. 6. Influence of the initial characteristics of soil washing fluid in the SDS removal rate and sulfate released at the end of the oxidation tests. (a): SDS removal rate; and (b): Sulfate released. Conditions: (△) after electrolysis; (*) after sono-electrolysis; (■) after sonolysis. Current density: 30 mA cm^{-2} ; US power rate: 250 w dm^{-3} .

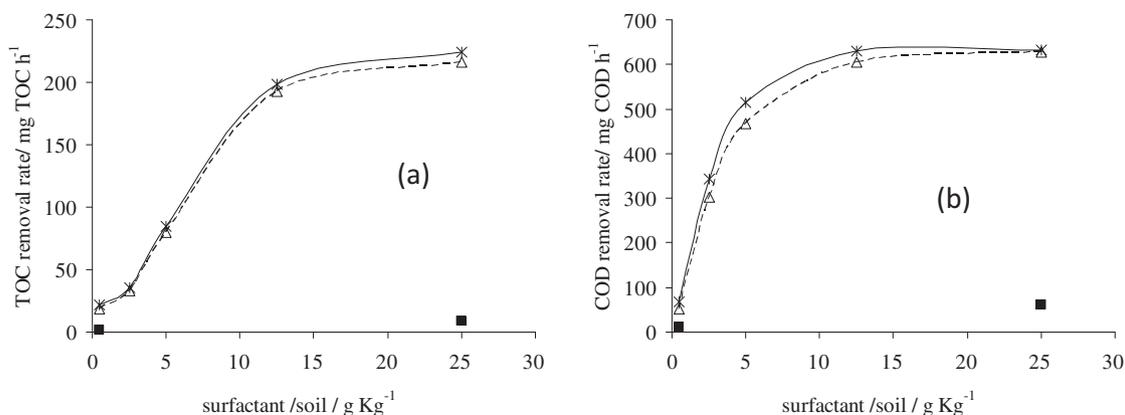


Fig. 8. Influence of the initial characteristics of soil washing fluid on the TOC and COD removal rate. Conditions: (Δ) electrolysis; (*) sono-electrolysis; (\blacksquare) sonolysis. Current density: 30 mA cm^{-2} ; US power rate: 250 w dm^{-3} .

experiments are obtained in comparing mineralization. This behavior is explained because the main contribution to TOC and COD is that of SDS. However there is a slightly more efficient COD removal when applying US which can be explained in terms of the higher contribution of oxyfluorfen.

Regarding intermediates, it is important to point out that decay curves of TOC and COD are almost overlapped (data not shown) suggesting that compounds are rapidly mineralized once the oxidation of the micelles started. This is verified with the HPLC analysis that only shows two very small peaks related to intermediates. Table 1 compares the maximum concentration of intermediates in these experiments. As it can be observed, in addition to the low values detected, there is not a clear correlation with the maximum value and the characteristic of the raw soil-washing effluent. This observation points out the scarce relevance of the intermediates formed and confirm that electrolysis and sono-electrolysis of pesticide-polluted soil-washing fluids is a very efficient technology.

Opposite to other advanced oxidation processes, production of intermediates is almost negligible in this process. Only 4-(trifluoromethyl)-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 concentration of SDS in several of the effluents. This indicates that intermediates formed during the process are very rapidly oxidized and that most important processes occur on the micelles surfaces.

4. Conclusions

From this work, the following conclusions can be drawn:

- Characteristic of effluents obtained by applying Surfactant-Aided Soil-Washing to soil spiked with oxyfluorfen depends strongly on the dose of surfactant used. The higher the surfactant concentration used, the smaller are the micelles formed

Table 1

Maximum concentration of intermediates during the sono-electrolysis of the five soil-washing fluids.

SDS/g kg ⁻¹	Intermediate 1 3.7 (min)	Intermediate 2 9.0(min)
0.5	1064	1462
2.5	1403	781
5	739	829
12.5	927	510
25	537	839

and the more negative is the z-potential of their surfaces. These characteristics of the soil-washing waste have strong influence on results of the sono-electrolysis treatment.

- Sono-electrolysis with diamond electrodes is a very efficient technology for the removal of oxyfluorfen and SDS from soil washing fluid. In comparing the US irradiated technology with the single electrolysis, it was observed a clear improvement in the removal of pesticide and almost nil effect on the removal of the SDS. This opposite behavior reflects on the evolution of TOC and COD during the treatment. Sulfate plays a very important role in the sono-electrolysis of soil-washing waste polluted with oxyfluorfen. During the oxidation of SDS significant amounts of sulfate are released. The catalytic effect of the peroxosulfate produced anodically helps to understand better the process and explain the higher depletion rate observed in the experiments in which the SDS concentration of the washing fluid was higher. This means that US irradiation can produce sulfate radicals from persulfates. Only two intermediates (and in very low concentrations) were obtained during the treatment. This observation means that once the micelles are attacked, the surfactant and pesticide release are rapidly mineralized.
- Sonolysis of soil-washing waste containing oxyfluorfen results in a very soft oxidation of the micelles. The addition of the effects of sonolysis and electrolysis is below the observed for the combination of the technologies in a single stage. This means that sono-electrolysis is a synergistic technology.

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