Electrocoagulation as the key for an efficient concentration and removal of oxyfluorfen from liquid wastes

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Abstract

Electrocoagulation is usually applied to remove pollutants from the liquid phase, but in this work it is investigated to concentrate pollutants, with the final aim to get a later much more efficient treatment by electrolysis. Results obtained during the treatment of wastes polluted with commercial oxyfluorfen (Fluoxil®) show that electrocoagulation exhibits a good efficiency in removing this model non-ionic halogenated pesticide. It was observed that the chemicals contained in Fluoxil® with higher solubility than oxyfluorfen are less efficiently removed, explaining the lower removal of TOC as compared to that of oxyfluorfen. An improvement in the design of the electrocoagulation was faced by increasing the amount of particles in the reactor, allowing to deplete the pesticide concentration down to levels 2-log below the inlet concentration. The herbicide is concentrated in a solid phase, from where it can be released to a concentrated waste just by changing the pH.

Keywords: Oxyfluorfen; non-ionic pesticide; electrocoagulation; concentration

1. INTRODUCTION

Nowadays, the continued use of pesticides and the development of new agricultural technologies to transform upland into irrigation crops has dramatically improved the agricultural production [1, 2]. One of the herbicides most commonly used for different crops is oxyfluorfen, a non-ionic halogenated organic herbicide, used to control annual broadleaf and grassy weeds in a variety of tree fruit, blackberries, sunflowers and field crops. Oxyfluorfen presents low water solubility (0.116 mg dm^{-3} at 20ºC), low vapor pressure (0.026 mPa at 25 ºC), high K_{oc} (log $K_{oc} = 3.46 – 4.13$) and high K_{ow} (log $K_{ow} = 4.86$) [3]. Oxyfluorfen contaminates surface water through spray drift and runoff, although it is unlikely to contaminate ground water [4]. It is classified as slightly mobile to immobile in soil, and it is nearly insoluble in water with a tendency to adsorb in soils [5]. Oxyfluorfen was also classified as low acute toxicity compound by the World Health Organization (WHO) [6] and by the Environmental Protection Agency (EPA) [4]. It is assessed as very toxic to aquatic organisms and affect terrestrial plants and aquatic ecological systems at all levels [7-9]. In addition, it is stable to hydrolysis at pH 4 to 9 but degraded rapidly by the sunlight in aqueous solution and it is dangerous [3, 10]. The commercial brands that contains Oxyfluorfen commonly include other chemicals with higher water solubility (surfactant, cyclohexanone, etc.) in order to enhance its dosage to the crops.

The previous studies of oxyfluorfen removal found in the literature dealt about its soil dissipation and persistence in crops. Ying and Williams (1999) studied the photoproducts of oxyfluorfen and found that the half-life of the herbicide was significantly shorter in water than in soils [11]. Our group recently studied the oxyfluorfen removal in soils using a surfactant-aided soil-washing (SASW) process [12] or electrokinetic soil flushing (EKSF) processes [13-15]. Tejada et al also studied the bioremediation effects of a soil polluted with an oxyfluorfen herbicide with and without three earthworms [16]. Evaporation is also commonly used in contaminated soils with higher moisture [17]. It is worth noting that the conventional treatment in Wastewater Treatment Plant (WWTP) does not always achieve efficient depletion of the pesticide and it is necessary to develop novel and clean technologies capable to attain efficient removals. Traditional physical–chemical processes are comparatively expensive, and may lead to secondary pollution [18]. Biological treatment does not always get an efficient removal of the pollutants due to the inability of bacteria to degrade this pesticide.

The drawbacks mentioned above has promoted the search for alternative treatment technologies for pollutants removal. Among them, electrochemical technologies are gaining more and more attention in the last two decades[19]. Electrolysis is a robust technology, which shows impressive results in terms of mineralization. Recent studies using diamond coatings as anodes demonstrates that it is efficient in the removal of pesticides from liquid wastes[20-23]. These studies also point out that this technology can be easily combined with soil treatment processes, assisting efficiently in their remediation[24]. One of the main drawbacks in the application of electrolysis is the decrease in the process efficiency observed for low concentrations of pollutant, where the process becomes diffusion controlled [25, 26] and a first order kinetic fits well to the decay of pollutants. These problem is very clear in the treatment of pesticides and a promising way to overcome it is by concentrating the pollutant in the waste either by membrane technology [27] or by any other concentration technology. To the knowledge of authors, this challenge has not been faced for oxyfluorfen removal from soils and water.

One of the technologies that can be used to concentrate oxyfluorfen from liquid wastes is electrocoagulation (EC). This electrochemical technique consists in the dissolution of aluminium or iron anodes, thus generating active coagulant species and hydroxides that can destabilize and aggregate pollutants, facilitating their further removal by conventional separation processes [28]. At this point, it is worth noting that electrocoagulation (EC) can be applied not only to remove the pollutant from the liquid phase but also to concentrate it by dissolving the solid in a small volume (as compared to the initial volume of wastewater), enhancing the efficiency of further degradation technologies. Electrocoagulation is a simple, reliable and cost-effective operation for the treatment of wastewater [29, 30] that has been efficiently applied, among others, to the removal of pollutants from industrial wastewater [31-34], to the production of drinking water [35-38] and to the reclaiming of wastewater [39, 40].

With this background, the main goal of the present work is to evaluate the treatment of water polluted with Fluoxil®, a commercial brand that contains oxyfluorfen, using electrocoagulation with iron anodes. This treatment would allow its removal from the liquid phase and its further concentration by dissolving the solid produced in the electrocoagulation stage. The main removal mechanisms involved in the removal of oxyfluorfen were investigated in order to develop an electrocoagulation device that allows the efficient removal and concentration of oxyfluorfen.

2. MATERIALS AND METHODS

2.1. Chemicals

Fluoxil ® 24 EC (provided by CHEMINOVA AGRO S.A., Spain) was used as the commercial source of oxifluorfen (24% wt.). Apart from the pesticide, the formulation of Fluoxil® includes cyclohexanone, calcium dodecylbenzene sulphonate (surfactant) and xylene. Sodium sulfate anhydrous (> 99 %), Phosphoric acid (> 85%, solvent with TOC-grade), Hydrochloric acid (>37%) was obtained from Panreac. Deionized water (Millipore Mili-Q system) was used to prepare all solutions.

2.2. Analytical techniques

To determine the efficiency of EC device, both total organic carbon (TOC) and oxyfluorfen concentration were monitorized. TOC was measured with a Multi N/C 3100 Analytik Jena analyzer, meanwhile the evolution of oxyfluorfen concentration in EC device was measured by High Permeation Liquid Chromatography (HPLC). It uses analytical column Phenomenex Gemini 5 µm C18 with as mobile phase a mixture of acetonitrile/water (70:30 (v/v)) at 0.3 $cm^3 min^{-1}$. The detection wavelength of 220 nm was selected and the temperature of the oven was maintained at 25ºC. Aliquots of 20 µL were injected and oxyfluorfen detection limit was 0.2 mg dm^{-3}. Prior to each analysis, all samples were filtered with 0.22 µm nylon filters Scharlau provided by Scharlab.

The total iron concentration was measured off-line using an inductively coupled plasma spectrometer (Liberty Sequential, Varian) (detection limit < 1.5 ppb) according to a previously published standard method [41]. To determine the total metal concentration, samples were diluted to 50:50 (v/v) using 4 N HNO_3 to make sure total solubility of the metal.

The particle size was monitored off-line using a Mastersizer hydro 2000SM (Malvern) without using any filters just allowing the sedimentation of bigger and heavier flocs. In this way, two phases are formed in the sample and only colloidal particles from upper phase are measured. It was used a volume of particle size distribution because the number of particle size distribution does not show significant results due to the lower particles of oxyfluorfen in the total volume of dissolution.

pH and conductivity were measured using a CRISON pH25+ and CRISON CM35+, respectively and zeta potential was determined using a Zetasizer Nano ZS (Malvern, UK).

2.3. Experimental device

Electrocoagulation experiments were carried out in a bench-scale plant with a single-compartment electrochemical flow cell described elsewhere [42]. Iron and stainless steel electrodes were used as anode and cathode, respectively. Both electrodes were square in shape (100 mm side), each with a geometric area of 100 cm^2 and with an inter-electrode gap of 12 mm. The electrical current was provided by a Delta Electronika ES030-10 power supply (0-30 V, 0-10 A). The wastewater was stored in a 5000 cm^3 glass tank stirred by an overhead stainless steel rod stirrer Heidolph RZR 2041. The synthetic water was flowed through the electrolytic cell by means of a peristaltic pump.

2.4. Experimental procedure

All experiments were carried out under galvanostatic conditions. The electrocoagulation device was operated in discontinuous mode to perform the tests that allow the characterization of the coagulation mechanisms involved in the removal of oxyfluorfen. Current density applied in experiments ranged from 20 to 200 mA cm^{-2}. Prior to use in galvanostatic assays, the electrodes were treated by rinsing with a solution of 1.30 M HCl in order to remove any kind of impurity from its surface. Moreover, an additional final test was performed working with two different stages: 1) discontinuous mode at 200 mA cm^{-2} during 2 hours to increase the concentration of iron hydroxide in the reactor: 2) continuous mode at 50 mA cm^{-2} by feeding a constant volumetric rate to the system and extracting the same volume of treated water and solids.

3. RESULTS AND DISCUSSION

3.1. General behavior of the process

Figure 1 compares the time-course of TOC and oxyfluorfen concentrations during the electrocoagulation (EC) of synthetic wastewater polluted with 100 mg dm^{-3} of the pesticide oxyfluorfen (Fluoxil®) and 3,000 mg dm^{-3} of Na_2SO_4 as supporting electrolyte.

As it can be observed, a different behavior is observed in the removal of TOC and oxyfluorfen. In both cases, the concentration of pollutant (either TOC or oxyfluorfen) decreases until a constant value, from which it seems not possible to remove more pollutant from the liquid phase by electrocoagulation. The main difference between the removal of TOC and oxyfluorfen is the efficiency of the treatment: it is possible to reduce around 35 % of initial TOC meanwhile the removal of oxyfluorfen is higher than 90 %.

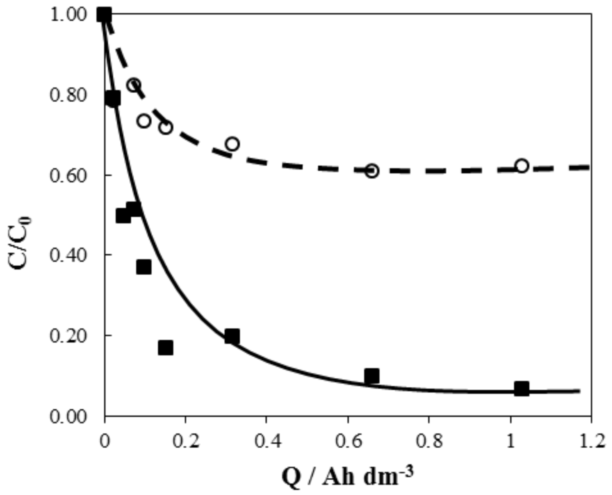

Fig.1. TOC (○) and oxyfluorfen (■) removal as a function of the applied electric charge in the eletrocoagulation of synthetic wastewater containing 100 mg dm^{-3} of pesticide and 3000 mg dm^{-3} of Na_2SO_4. j=50 A m^{-2}.

There are two possible explanations for this discrepancy: reactivity or presence of species that cannot coagulate. Regarding the first (formation of reaction intermediates due to anodic oxidation during the electrocoagulation tests), although various works have reported a partial oxidation of organic molecules on iron anodes during electrocoagulation [43, 44], it is well-known that other reactions such as the water oxidation or the dissolution of the anode are favored in electrocoagulation processes [45]. In fact, the oxidation rates of organics described in those works are not high enough to explain the huge differences observed between the removal of TOC and oxyfluorfen in the present work. Regarding the second, in order to completely discard the contribution of anodic oxidation, the results of EC were compared to that of chemical coagulation, where the removal of organic compounds is produced only by physicochemical processes and not by oxidation. In this case, a further adjustment of pH is necessary to assure similar conditions in both chemical coagulation and EC, because the key difference between the coagulation and the electrocoagulation is in the pH changes and how they affect to the removal of pollutants [46]. Thus, the TOC and oxyfluorfen concentration remaining in the waste after the coagulation as a function of iron dosed are shown in Figure 2.

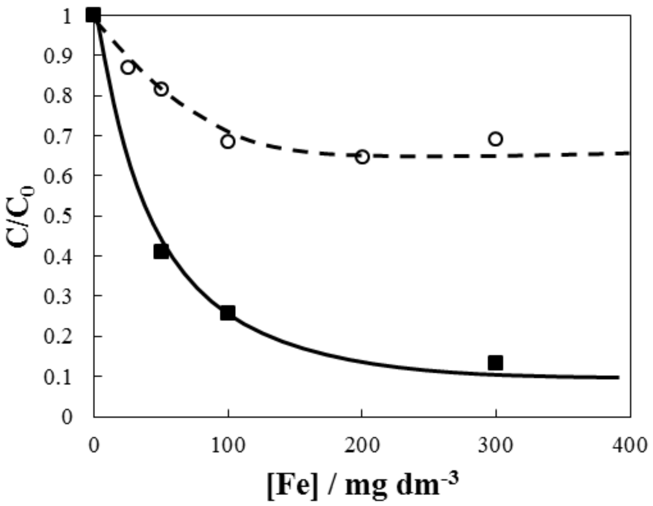

Fig. 2. TOC (○) and oxyfluorfen (■) removal as function of the iron concentration in chemical coagulation of synthetic wastewater containing 100 mg dm^{-3} of oxyfluorfen and 3000 mg dm^{-3} of Na_2SO_4.

As it can be observed, the removal of oxyfluorfen is higher than the removal of TOC in coagulation trials, as it was the case previously described in EC tests. Thus, the great differences in the removal of TOC and oxyfluorfen in EC are not explained by the formation of reaction intermediates caused by the anodic oxidation of the pesticide as they are not possible in the chemical coagulation. At this point, it is important to bear in mind that a commercial source of oxyfluorfen (Fluoxil®) is being used in the present work and this is a realistic situation in the treatment of oxyfluorfen polluted wastes, in which the pure compound is not used. As commented in the experimental section, Fluoxil® formulation includes not only oxyfluorfen but also other chemicals as surfactant (calcium dodecylbenzene sulphonate) and cyclohexanone. Thus, the different removal of TOC and pesticide can only be due to a different separation efficiency of the different components of Fluoxil® by the coagulants dosed to the solution, either chemically or electrochemically. To understand the removal mechanisms that explain this dissimilar separation efficiency, key variables such as pH, conductivity, iron dosed, conductivity and Z potential were monitored throughout the electrocoagulation test, and they are presented in Figure 3.

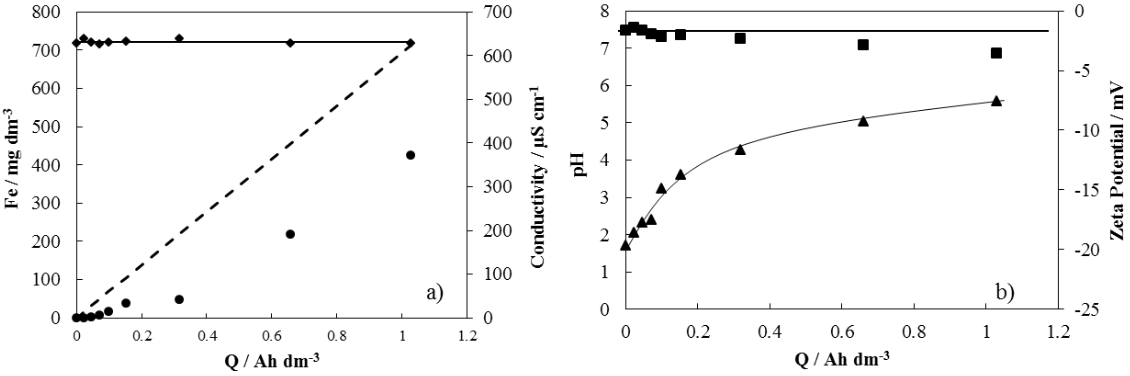

Fig. 3. Electrocoagulation of synthetic waste containing 100 mg dm^{-3} of herbicide and Na_2SO_4 as supporting electrolyte. a) iron dissolved (●); conductivity (♦); theoretical iron

concentration predicted by Faraday's law (dashed line) b) pH (■); zeta potential (▲). j=50 A m^{-2}

Both pH and conductivity did not vary appreciably during the experiments (average pH between 7 to 8, average conductivity from 600 to 650 μS cm^{-1}), which is an expected result in electrocoagulation treatment and a key advantage of the technology over the chemical coagulation in which the addition of salts and the neutralization of pH produce an effluent with a higher salinity. Regarding iron dosed, iron predicted by Faraday's law is higher than the experimental measured, what means an under-Faradaic dosing of iron. This result has been previously reported at slightly basic pH and with the presence of organics and can be attributed to the significant contributions of side reactions, in particular water oxidation [45, 47]. Under these operating conditions and according to the literature, the dominant coagulant species are iron hydroxide ($Fe(OH)_3$) precipitates [46, 48]. With respect to Z potential (represented in Fig. 3.b), it was observed a partial neutralization of charge throughout the test (from a very negative initial potential), although the charge was not fully neutralized and z-potential tends to stabilize in values below -5 mV. It is important to remind that zeta potential is a measurement of the magnitude of the surface charge of particles, being one of the fundamental parameters that affect the removal mechanisms in coagulation processes. The initial value is negative (nearly to -20 mV) due to the sulfonic groups of the surfactant used (calcium dodecylbenzene sulphonate) in commercial Fluoxil®. As it has previously mentioned, pH is nearly constant around 7-8, value at which iron precipitates have slightly positive charge [46], thus explaining the partial neutralization of zeta potential observed.

According to these results, namely the presence of iron hydroxide and not fully charge neutralization, it can be concluded that the main coagulation mechanism is sweep flocculation, which occurs when the metal coagulant precipitates are formed and sweep the colloidal contaminants as they settle or move in the suspension. The dissimilar efficiency in TOC and oxyfluorfen removal can be attributed to the different water solubility of the components of Fluoxil®. Oxyfluorfen, with a very limited solubility in water, and present as micelles, is easily trapped into the growing flocs meanwhile other components as cyclohexanone and surfactant, with a higher water solubility, are not efficiently trapped, causing the limited removal of TOC from the target effluent.

The removal of oxyfluorfen by growing flocs can be monitored by measuring particle size distribution. Thus, Figure 4.a shows the evolution of particle size, where the average size of the particles is represented by dots and the dispersion of this particle size is included as error bars. Moreover, Figure 4.b represents the specific surface area (SSA) and the concentration of particles measured by light scattering.

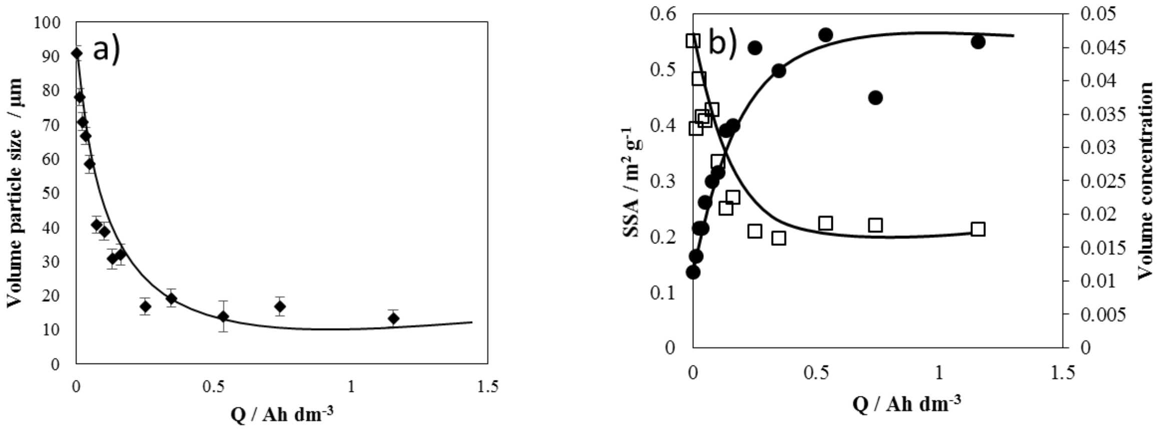

Figure 4. a) Evolution in the volume particle mean size as function of applied electric charge. 4b) Evolution in the Specific surface area (SSA, ●) and volume concentration (□) as function of applied electric charge. Initial oxyfluorfen concentration: 100 mg dm^{-3}; j=50 A m^{-2}.

Results indicate a reduction in the particle size together with a decrease in the concentration and an increase in the SSA of particles. As described in analytical techniques section, the samples were previously allowed to sediment because the growing flocs present a size much higher than the upper detection limit of the measurement device (1 mm). Thus, it must be mentioned that the particle size does not correspond to the size of the precipitated flocs but to the size of the aggregates of pesticide that kept suspended in the samples. Moreover, as previously commented, the solubility of oxyfluorfen in water is very limited (0.116 mg dm^{-3}) so the pesticide forms a dispersion of oxyfluorfen molecules stabilized by the formation of micelles and by the presence of cyclohexanone. The removal of oxyfluorfen aggregates in this dispersion corresponds to the decrease in the particle size and the subsequent increase in the SSA due to the smaller size of the particles. Moreover, the removal of the aggregates of pesticide is also confirmed by the decrease in the concentration of particles.

The sludge produced during the electrocoagulation was further processed. It was concentrated by sedimentation up to a final volume of 65 mL and then acidified up to pH 2.0 (three drops of concentrated acid). Under those conditions the flocs were dissolved and hence the oxyfluorfen was released to solution reaching concentrations as high as 1400 mg dm^{-3}, 14 times higher than the initial concentration contained in the raw waste. Figure 5 shows the oxyfluorfen mass balances including the distribution before and after the coagulation step between the liquid and the solid phase (which was solved in a much lower volume).

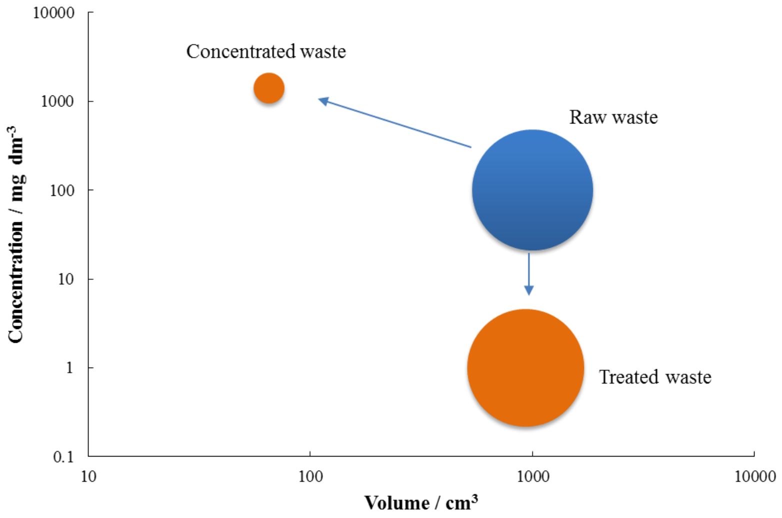

Fig. 5. Evolution of concentration and volume of the target effluent, the treated waste and the concentrated solid before (blue circle) and after (orange circles) the EC process.

As it can be observed, electrocoagulation allows to concentrate into the solids most of the oxyfluorfen, changing between one and two log-units above the initial concentration in the raw waste studied with a volume which decreases in the same ratio. It is well assumed that the efficiency of an electrochemical degradation process is greater for higher concentration of the target pollutant [49]. Thus, if EC were place before an electrochemical degradation process, this pre-concentration step would dramatically increase the efficiency of the degradation stage.

To complete the characterization of the process, the influence of the current density (one of the key variables of the process) on the performance of the process was evaluated. Results are presented in Figure 6, where the TOC and oxyfluorfen concentration are represented with respect to the amount charge applied to the solution at two different current densities.

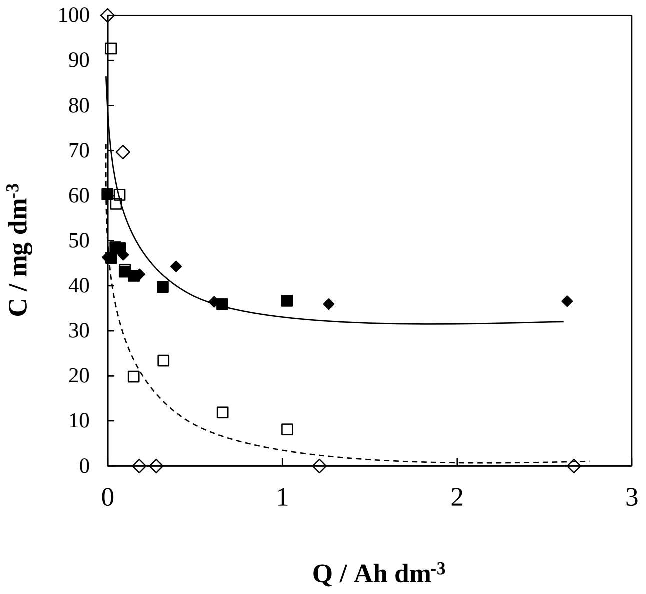

Fig.6. Influence of the current density on the TOC and oxyfluorfen removal as function of the applied electric charge during electrocoagulation process of synthetic wastewater polluted with 100 mg dm^{-3} of oxyfluorfen. Supporting electrolyte: 3,000 mg dm^{-3} Na_2SO_4. TOC: full symbols; Oxyfluorfen: empty symbols. ■ 50 A m^{-2} ; ◆ 200 A m^{-2}.

As it can be observed, the concentration of TOC decreases for higher charge applied, although there exists a plateau at around 35 mg L^{-1} regardless the value of the working current density. Thus, it can be stated that the removal of TOC depends on the amount of iron dosed and not on the current density applied to the system. The removal of oxyfluorfen is more efficient than the removal of TOC regardless the value of the working current density. In the case of the higher current density (200 A m^{-2}), the concentration of oxyfluorfen remaining in the liquid phase was close to zero from a charge applied of 0.18 A h dm^{-3}. The evolution of pH and other parameters was similar to that described in previous figures. These points out that current density does not limit the applicability of this technology for the concentration of herbicides applied as colloids dispersions.

3.2. Optimization of TOC and oxyfluorfen removal.

From the results presented in the previous section, it is confirmed that the main removal mechanism is the trapping of oxyfluorfen aggregates into the growing flocs, which preferentially trap the insoluble components of the solution (pesticide). For this reason, an optimization of the process must consist in an optimization of the flocculation in the system. A feasible way to enhance the flocculation is to increase the concentration of solids, in order to rise the number of collisions between particles and thus the trapping of pollutants in the growing flocs.

Based on this idea, a final test was performed. Throughout an initial stage, the system worked in discontinuous mode with the aim of increasing the concentration of iron hydroxide. Afterwards, the system was operated in continuous mode, feeding a given volume of solution (polluted with 100 mg L^{-1} of oxyfluorfen) and extracting from the reactor the same volume of treated solution and purged solids. In this case, the current density was 50 A m^{-2} and the feeding rate (0.6 dm^3 h^{-1}) was selected in order to work with a specific charge of 0.836 A h dm^{-3}, a value high enough to obtain the maximum removal of TOC and oxyfluorfen according to the results in discontinuous mode. Results of TOC and oxyfluorfen concentration in the feed and in the treated solution are shown in Figure 7.

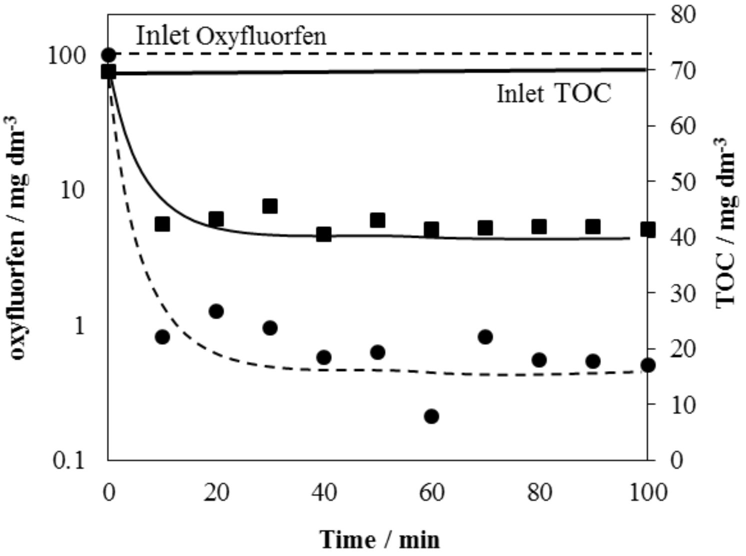

Figure 7. Evolution of oxyfluorfen (●) and TOC (■) concentration with time in the continuous experiment with. Supporting electrolyte: 3,000 mg dm^{-3} Na_2SO_4. j= 50 A m^{-2} ; q = 0.6 dm^3 h^{-1} ; Q = 0.836 A h dm^{-3}.

As it can be observed, results were as expected according to previous tests and demonstrates that coagulation can be used to concentrate this herbicide and that with an enhance flocculation the efficiency of the system can be greatly increased. Thus, TOC removal is slightly increased with respect to the removal obtained at discontinuous tests (45% vs. 35 %), which can be explained by the higher amount of solids and hence the enhanced adsorption capabilities of the flocs produced. Regarding the removal of the pollutant from the liquid, a 2-log removal in the concentration of oxyfluorfen in the treated solution was obtained from the first sample, confirming the more efficient removal of the pesticide and the expected positive effect of enhancing the flocculation by increasing the number of particles in the system. Finally, a specific energy consumption as low as 4.01 Wh dm^{-3} was achieved, outstanding the promising performance of the proposed technology.

4. CONCLUSIONS

Electrocoagulation exhibits a promising behavior in removing non-ionic pesticides from polluted wastewater, allowing its concentration in the solid phase, which in turn, can be used to produce a much more concentrated waste. This waste can be treated more efficiently by electrolysis. The main coagulation mechanism is sweep flocculation, being the compounds with lower solubility, namely the pesticide, more efficiently trapped in to the flocs than the chemicals with higher solubility in water (cyclohexanone or surfactant). This dissimilar removal of the different chemicals explain the lower removal of TOC compared to that of oxyfluorfen. The improvement in the flocculation of the system by increasing the amount of particles of iron hydroxide in the reactor allows to deplete the pesticide concentration down to 2-log its concentration in the inlet stream.

Notes

The authors declare no competing financial interest.

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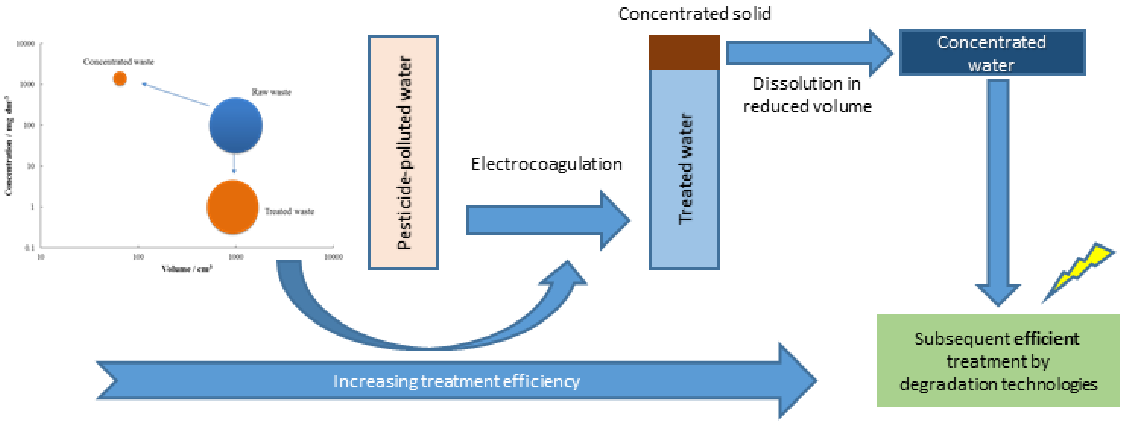
Concentrated waste
Raw waste
Treated waste
Concentration / mg dm^{-3}
10000
1000
100
10
1
0.1
10
100
1000
10000
Volume / cm^{3}
Pesticide-polluted water
Electrocoagulation
Concentrated solid
Treated water
Dissolution in reduced volume
Concentrated water
Subsequent **efficient** treatment by degradation technologies
Increasing treatment efficiency