Chemical Engineering Journal 318 (2017) 2–9

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

UV assisted electrochemical technologies for the removal of oxyfluorfen from soil washing wastes

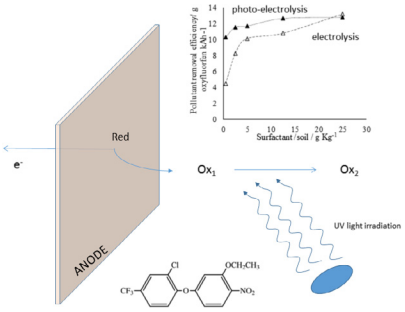
E.V. dos Santos [a], C. Sáez [b], P. Cañizares [b], C.A. Martínez-Huitle [c], M.A. Rodrigo [b,*]

[a] School of Science and Technology, Federal University of Rio Grande do Norte, Campus Universitario, 59078-970 Natal, Brazil
[b] Department of Chemical Engineering, Enrique Costa Building, Campus Universitario s/n, 13071 Ciudad Real, Spain
[c] Institute of Chemistry, Federal University of Rio Grande do Norte, Campus Universitario, 59078-970 Natal, Brazil

HIGHLIGHTS

- Photo-electrolysis can mineralize completely soil washing fluids.
- Photolysis only produces a very soft oxidation of soil washing fluids.
- Mineralization of oxyfluorfen by electrolysis is improved with UV irradiation.
- Mineralization of SDS by electrolysis is almost not affected by the UV irradiation.
- Sulfate released by the oxidation of SDS catalyzes photo-electrolysis.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Available online 8 March 2016

Keywords:
Oxyfluorfen
Photolysis
Photo-electrolysis
Soil washing
Boron doped diamond
Electrolysis

ABSTRACT

In this work, it is studied the treatment of soil polluted with oxyfluorfen by Surfactant-Aided Soil-Washing (SASW) and after that, photo-electrolysis was used for the treatment of the soil-washing fluid produced. This liquid waste is characterized by the high concentration of micelles of pesticide and surfactant (sodium dodecyl sulfate, SDS), whose initial size depends on the ratio soil-surfactant used in the soil washing treatment. The waste treatment is studied in terms of the decrease in size of the particles and the depletion of the pollutants. Results clearly demonstrate that photo-electrolysis with diamond electrodes is a very effective treatment technology with results that overcome those obtained by single photolysis and/or single electrolysis with diamond electrodes. The greater improvements attained by combining UV irradiation to the electrolysis were observed in the removal of the pesticide while the removal of the surfactant was little affected. Electrolysis does not only deplete the complete concentration of pesticide but it also shows to be very efficient in the depletion of the surfactant, preventing its potential recycle. The significant concentration of sulfate released during the attack to the surfactant and the effect of the peroxosulfate anions that are formed from the anodic oxidation of that anion, explain the improved performance of the technology in the treatment of washing fluids with higher concentrations of SDS.

1. Introduction

Over the last years, the search for novel sources of water has become a topic of the major interest, in particular in countries with serious problems of permanent or stationary lack of water. Global warming is definitively contributing to make the problem even greater and hence, to increase the necessity of developing solutions to this serious problem. Consequently, the development of novel and efficient technologies capable to remove complex pollutants and provide water of high quality, from wastewater, is not only a topic of the major interest nowadays; but for sure it will be the

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

http://dx.doi.org/10.1016/j.cej.2016.03.015
1385-8947/

target of significant research in the next years. Unfortunately, we are far away from the development of an efficient treatment technology, robust enough to transform wastewater into high quality water and this fact explains the huge interest paid by the scientific community to advanced oxidation processes in the recent years [1–3]. Among those technologies, electrolysis with diamond anodes has received considerable interest for the removal of very different types of pollutants in the recent years [4–9] because of its outstanding efficiency, explained in terms of the combination of direct (by electron transfer) and mediated (through the formation of oxidizing/reducing agents at the electrode) oxidation approaches [8,10]. In particular, the formation of highly powerful oxidants from the salts contained in wastewater seems to be one to the clear advantages of the diamond electrolytic technologies [11] and, hence, the role of not only hypochlorite but also that of peroxocarbonates, peroxophosphates, peroxosulfates, hydrogen peroxide and ozone is important in order to explain the high efficiency of these technologies. To improve the performance of the processes, the activation of these reagents is a process of the major importance. The final aim is to produce species that can enable the rapid degradation of the pollutant species. Three important aspects should be taken into account: (i) the dosage of the precursor for the production of oxidants (i.e., Cl^-, SO_4^{2-}, CO_3^{2-} etc), but preferentially it should be contained in wastewater to avoid the undesired salinization of the waste, (ii) the oxidant produced on the electrodes should be efficient for the oxidation of pollutant contained in wastewater, (iii) sometimes, the oxidant produced is not active for the oxidation of the pollutant but it could be activated.

Activation of oxidants, that is, the formation of highly reactive species from poorly reactive oxidants [12], can be attained by combination of oxidants or by UV light or ultrasounds irradiation [13–15]. Among them, the irradiation of UV light seems to be particularly promising [16–18] and photolytic treatments may be used for generation of oxidant species and also for the direct dissociation of organic pollutants through a radiation source. The irradiation of UV light is attained with lamps and among the different sources of radiation, mercury vapor lamps are widely used, because of their low cost, ease of operation, good energy efficiency (proportion of electrical power converted into radiation) and good spectral efficiency (proportion of radiation emitted as UV) [19].

Recent research has pointed to the use of combined processes because it takes advantage not only of the good features of the single technologies but also that of their potential synergistic effects. This fact has been confirmed during the treatment of many types of pollutants, such as dyes [20,21], pharmaceuticals [16,22], pesticides [14,23,24], plasticizers [25], carboxylic acids [26], phenol [27] and surfactants [19]. In those works, it was found that in addition to the well-known UV light based processes; combination with electrochemical technology allows the formation of powerful radicals during the treatment [28–30] as indicated in Eqs. (1)–(4).

$$H_2O_2 + h\nu \rightarrow 2{\cdot}OH \quad (1)$$

$$H_2O + O_3 + h\nu \rightarrow 2{\cdot}OH + O_2 \quad (2)$$

$$S_2O_8^{2-} + h\nu \rightarrow 2\left(SO_4^-\right)^{\cdot} \quad (3)$$

$$ClO^- + h\nu \rightarrow O^{-\cdot} + Cl^{\cdot} \quad (4)$$

A clear example of this synergistic combination was described in the literature [27], by studying the well-known mineralization of phenol in the presence of chloride. After 6 h of treatment, photolysis resulted in 29% phenol mineralization and electrochemical treatment resulted in 35% and 52% mineralization using BDD and ruthenium oxide on titanium (DSA-Cl_2) anodes, respectively. After the same treatment period, the photo-assisted electrochemical process removed 88% and 96% of total organic carbon (TOC) by using BDD and DSA-Cl_2 anodes, showing clearly a synergistic combination.

Taking into account this background, the objective of this study is to investigate the remediation of soils polluted with oxyfluorfen (Fig. 1) by a combined treatment consisting of the Surfactant-Aided Soil Washing (SASW) with a sodium dodecyl sulfate (SDS) solution followed by the photolysis and/or photo-electrolysis with conductive-diamond anodes of the soil-washing fluid.

The resulting soil-washing fluid is a complex wastewater characterized by the presence of soluble pollutants, 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. Hence, this work not only focus on the interest of the removal of this pollutant (development of the environmental remediation technology) but also (and very important) in the treatment of colloids-containing wastewater, trying to give significant insights about the treatment of this type of complex wastes.

2. Materials and methods

2.1. Chemicals

Oxyfluorfen (2-chloro-1-(3-ethoxy-4-nitrophenony)-4-(trifluor omethyl), 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 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 extraction process. 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). 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 °C. 20 μL aliquots were injected, using as mobile phase, a mixture of acetonitrile/water (70:30 (v/v)) at 0.3 $cm^3\ min^{-1}$. TOC concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. The oxyfluorfen and surfactant removals 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). The colorimetric method used to determine the concentration of the SDS surfactant has been reported elsewhere [31]. The anions present in the target wastewater were characterized using ion chromatography by means of a Shimadzu LC-20A system.

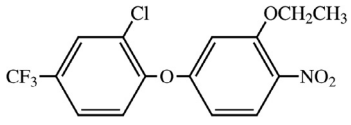


Fig. 1. Chemical formula of oxyfluorfen.