Journal of Environmental Management 171 (2016) 260–266

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Short communication

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

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ARTICLE INFO

Article history:
Received 23 August 2015
Received in revised form
29 December 2015
Accepted 21 January 2016
Available online 1 February 2016

Keywords:
Oxyfluorfen
Electrolysis
Soil remediation
Soil washing
Boron doped diamond

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 (oxyflourfen, 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-electrolyzes. 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.

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 $_{Koc}$ = 3.46–4.13) and high K_{ow} (log $_{Kow}$ = 4.86) (Mantzos 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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http://dx.doi.org/10.1016/j.jenvman.2016.01.027
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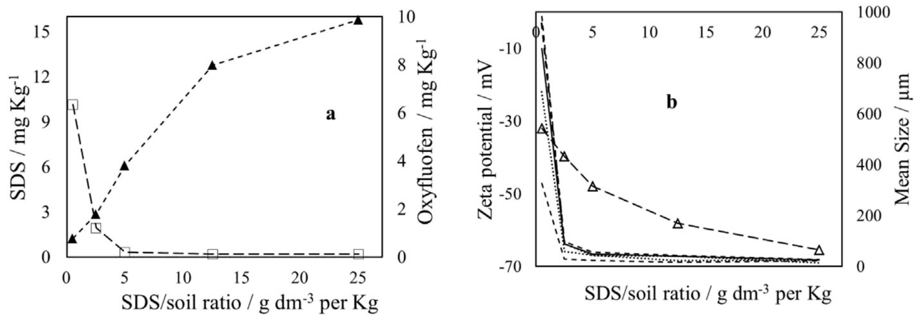

Fig. 1. Evaluation of soil polluted with oxyfluorfen after washing process with different SDS concentrations, as a function of SDS/soil ratio: (a) (▲) remaining SDS and (□) oxyfluorfen concentrations in the soil; (b) (Δ) Zeta potential and size limits including (- - - -) 50% of the particles; size limits 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; Martinez-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; Martinez-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 (●OH) formed by water electrolysis (Marselli et al., 2003) to $S_2O_8^{2-}$, Cl_2, ClO_2^- or $C_2O_6^{2-}$ 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 oxyflourfen 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 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 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 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 oxyflourfen. 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 cm^3. Low-permeability soil (1000 g) polluted with oxyfluorfen and 800 cm^3 of solubilizing agent (containing deionized water, 500 mg dm^{-3} of $NaHCO_3$, and different