



# Removal of pendimethalin from soil washing effluents using electrolytic and electro-irradiated technologies based on diamond anodes



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## ABSTRACT

This work describes the treatment of soil polluted with the herbicide pendimethalin by the combination of surfactant-aided soil-washing (SASW) and electrochemical advanced oxidation processes. Results show that it is possible to completely extract the herbicide from soil using SDS (sodium dodecyl sulfate) solutions as soil washing fluid (SWF) and ratios SWF/soil higher than  $10 \text{ dm}^3 \text{ kg}^{-1}$ . Soil washing effluents obtained after the application of the SASW consisted of a mixture of surfactant (high concentration) and pesticide (low concentration) and their degradation by electrolysis, photo-assisted electrolysis (photoelectrolysis) and sonoelectrolysis with diamond anodes has been compared with that obtained by the application of single photolysis and sonolysis. Opposite to photolysis and sonolysis, the different electrolytic techniques allow decreasing the concentration of herbicide and surfactant in the effluents. Competition between the surfactant and the herbicide oxidation is important and irradiation of high-frequency ultrasound or UV light do not seem to outperform very importantly the results obtained by single electrolysis in the effluents of the SASW obtained with low SDS/soil ratios. Opposite, photoelectrolysis becomes the most efficient technology for the treatment of SWF obtained at high SDS/soil ratios (those required for an efficient SASW). Catalytic effect of the sulfate released during the degradation of SDS (in particular the formation of sulfate radicals) can help to explain the differences observed. The removal efficiency is higher during sonoelectrolysis, reaching a final removal of the pesticide after 8 h of treatment of 86.22%. Photoelectrolysis (57.59%) shows higher efficiencies for the removal of SDS followed by sonoelectrolysis (52.64%) and, finally, electrolysis (48.29%), after 8 h of treatment.

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## 1. Introduction

Over the last seventy years, the increasing use and the hazardousness of organic pesticides has alarmed to environmental authorities which, in turn, have favor the application of a stricter regulation about the manufacturing and application of these agro-

chemicals. Nowadays, many products, which have been widely applied for decades, are banned in many countries and there is an important search of technologies capable to minimize the impact of the pesticides which are still in use, in order to control their diffusion and to minimize their negative impacts on human health and environment.

Among pesticides, herbicides are able to rapidly remove the weed of crops. They have to be applied in large concentrations and the interaction with the soil matrix may be important. For this reason, their presence is not only limited to soils but they can also be present in groundwater in significant concentrations. Further-

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more, these compounds can be found in soils because of accidental discharges and, in this case, the concentration of herbicides can be much higher than that found from agricultural activities. Hence, it is necessary to develop clean and efficient technologies that allow an efficient removal of these compounds from both, soil and water.

One of the most applied technologies for the treatment of different pollutants from soils is soil washing, which is considered as an excellent technique due to its simplicity and high efficiencies reached in the removal of various types of pollutants [1–3]. This process consists of a physical treatment, where the pollutant is transported from soil to a liquid stream, commonly called Soil Washing Fluid (SWF). To obtain high efficiencies with this technology, it is essential to attain an efficient mass transfer of the pesticide from soil to the liquid stream and, in the case of pollutants with low solubility in water, it can be needed the use of surfactants during the treatment and this process is known as SASW, Surfactant-Aided Soil-Washing [4,5]. Anyhow, the outcome of soil washing technology is a treated soil and a highly-polluted soil washing fluid, which needs for additional treatment.

Electrochemical processes are among the most promising technologies for the treatment of soil washing effluents polluted with organics [6–10]. Specifically, electrolyses with diamond electrodes have been proven efficient in the removal of different types of pollutants from wastewater, reaching a total mineralization of the organic matter [11–16]. This technology is based on the generation of powerful oxidants from the oxidation of the ions naturally contained in wastewater [17]. Likewise, diamond anodes favor the generation of large amounts of hydroxyl radicals during wastewater treatment which, in turn contribute to the mineralization of the organic matter [18]. Nonetheless, the main drawback of the electrolytic technology is the mass transfer limitations associated to the transport of the pollutant to the anode surface. For this reason, to overcome this limitation, the electrochemical oxidation can be coupled with other processes such as US (sonoelectrolysis) and UV light irradiation (photoelectrolysis) [19,20]. In this context, the use of ultrasound waves or UV light may promote the activation of the oxidants electrogenerated, favoring the formation of free radicals. These species significantly contribute to the mineralization of the organic matter [21–23].

One of the most commonly-used herbicides is pendimethalin ( $C_{13}H_{19}N_3O_4$ ). This is a nitro-organic compound that allows preventing the growth of weeds in different crops such as garlic, artichoke, cotton, barley and onion. However, this compound can promote different types of cancer in humans and, therefore, should be removed from water [24]. Despite its extended application, there are few works in literature related to its degradation. Thus, Pinto et al. [25] studied the removal of pendimethalin by fungi cultures. They described the application of different fungi for the biodegradation of pendimethalin showing that *Lecanicillium sak-senae* (*L. saksenae*) could remove 99.5% of the chemical in batch liquid cultures. Another study was carried out by Fenoll et al. [26], who described the photodegradation of pendimethalin in drinking water at pilot plant scale. They proposed the use of the ZnO catalyst for the removal of the pesticide, reaching a final concentration lower than  $0.8 \mu\text{g dm}^{-3}$ . More recently, Ahammed Shabeer et al. [27] carried out the removal of pendimethalin by a combined adsorption-coagulation-flocculation using aluminum and polyaluminum chloride as coagulants and modified montmorillonites and bentonite as adsorbents. They demonstrated that the combined treatment was much more efficient than single processes. Thus, this combined technology allowed removing higher than 90% of the herbicide.

Nevertheless, its treatment by electrochemical technology has not been reported and, in addition, the literature only includes the degradation of the herbicide in water but not in soils, where the impact can even be higher. Taking into account this background,

the main aim of the present work is to evaluate the application of a combined soil washing–electrolysis treatment for the removal of pendimethalin from spiked soil. The influence of the ratio surfactant/soil has been studied during soil washing and electrolysis because it seems to have a clear influence in the kinetics and the removal efficiency. Furthermore, in order to try to improve the process performance, the coupling of US and UV light irradiation to the electrochemical process (sonoelectrolysis and photoelectrolysis, respectively) was evaluated during the electrochemical treatment.

## 2. Material and methods

### 2.1. Chemicals

Pendimethalin (3,4-dimethyl-2,6-dinitro-N-pentan-3-ylaniline) and sodium dodecyl sulfate (SDS) (Sigma-Aldrich, Spain) were analytical grade and used as received. Acetonitrile HPLC grade (Sigma-Aldrich, Spain) was used for the mobile phase. Sodium tetraborate decahydrate, sodium hydroxide, phenolphthalein, methylene blue and chloroform (Sigma-Aldrich, Spain) were used for the determination of surfactant. Sodium carbonate and acetone (Sigma-Aldrich, Spain) were used as mobile phase for the determination of sulfate. Double deionized water (Millipore Milli-Q system, resistivity:  $18.2 \text{ M}\Omega \text{ cm}$  at  $25^\circ\text{C}$ ) was used to prepare all solutions.

### 2.2. Analytical techniques

Samples were filtered with  $0.22 \mu\text{m}$  nylon filters Scharlau provided by Scharlab. The concentration of pendimethalin was followed by reversed-phase chromatography. A L-L extraction was carried out before analytical analysis. The herbicide was extracted from water using ethyl acetate (1:1 v/v) in Eppendorf tubes ( $15 \text{ cm}^3$ ) at 4000 rpm. The chromatography system was an Agilent 1200 series coupled a DAD detector. A ZORBAX Eclipse Plus C18 analytical column was used. The mobile phase consisted of 85:15 acetonitrile/water (flow rate:  $0.8 \text{ cm}^3 \text{ min}^{-1}$ ). The DAD detection wavelength was 240 nm, the temperature was maintained  $25^\circ\text{C}$  and the injection volume was  $20 \mu\text{L}$ . The TOC concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. Particle size was measured using a Mastersizerhydro 2000SM (Malvern) and SDS concentration was monitored with the colorimetric method reported by Jurado et al. [28]. Sulfate concentration was measured by ion chromatography using a Metrohm 930 Compact IC Flex coupled to a conductivity detector. A Metrosep A Supp 7 column was used for the determination. The mobile phase consisted of 85:15 v/v  $3.6 \text{ mM Na}_2\text{CO}_3$ /acetone with a flow rate of  $0.8 \text{ mL min}^{-1}$ . The temperature of the oven was  $45^\circ\text{C}$  and the volume injection was  $20 \mu\text{L}$ . The concentration of persulfate was determined iodometrically according to Kolthoff & Carr [29] and Standard methods [30].

### 2.3. Preparation of spiked soil

To pollute soil, pendimethalin was solubilized in hexane (solubility in water:  $0.3 \text{ mg dm}^{-3}$ ) and the solution was sprayed to clay soil. The main characteristics of the soil have been reported elsewhere [31]. Then, soil was aerated for 1 day to evaporate the solvent used (hexane). Thus, the pesticide was homogeneously distributed in soil with an average concentration of  $100 \text{ mg kg}^{-1}$ .

### 2.4. Preparation of soil washing effluents

Soil washing was carried out in a stirred tank and discontinuous mode, by mixing different ratios between volumes of SWF

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