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Effect of the polarity reversal frequency in the electrokinetic-biological remediation of oxyfluorfen polluted soil

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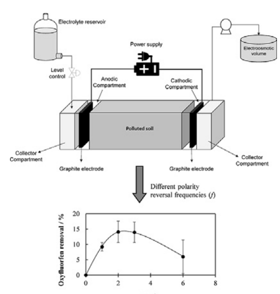
HIGHLIGHTS

- Electrobioremediation of oxyfluorfen polluted soil was studied in laboratory tests.
- Polarity reversal strategy improved the electrobioremediation performance.
- Different reversal frequencies affected electro-osmosis and remediation efficiency.
- Optimum frequency values around 2–3 d^{-1} obtained 15% removal efficiency in 14 days.

GRAPHICAL ABSTRACT



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ABSTRACT

This work studies the feasibility of the periodic polarity reversal strategy (PRS) in a combined electrokinetic-biological process for the remediation of clayey soil polluted with a herbicide. Five two-weeks duration electrobioremediation batch experiments were performed in a bench scale set-up using spiked clay soil polluted with oxyfluorfen (20 mg kg^{-1}) under potentiostatic conditions applying an electric field between the electrodes of 1.0 V cm^{-1} (20.0 V) and using PRS with five frequencies (f) ranging from 0 to 6 d^{-1}. Additionally, two complementary reference tests were done: single bioremediation and single electrokinetic. The microbial consortium used was obtained from an oil refinery wastewater treatment plant and acclimated to oxyfluorfen degradation. Main soil conditions (temperature, pH, moisture and conductivity) were correctly controlled using PRS. On the contrary, the electroosmotic flow clearly decreased as f increased. The uniform soil microbial distribution at the end of the experiments indicated that the microbial activity remained in every parts of the soil after two weeks when applying PRS. Despite the adapted microbial culture was capable of degrade 100% of oxyfluorfen in water, the remediation efficiency in soil in a reference test, without the application of electric current, was negligible. However, under the low voltage gradients and polarity reversal, removal efficiencies between 5% and 15% were obtained, and it suggested that oxyfluorfen had difficulties to interact with the microbial culture or nutrients and that PRS promoted transport of species, which caused a positive influence on remediation. An optimal f value was observed between 2 and 3 d^{-1}.

1. Introduction

Pesticide pollution is becoming a very serious environmental problem with a highly negative impact on the quality of water

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reservoirs and the surrounding ecosystems (Chowdhury et al., 2008). Persistent pesticides remain in the environment for very long periods and they can produce different harmful effects on humans. Oxyfluorfen is framed within this category. This herbicide has low solubility in water (0.116 mg L^{-1}) and low vapour pressure (0.026 mPa at 25 °C) and its biodegradation is known to be very poor: plants cannot metabolize this compound and it is only slowly assimilated by microorganisms (Sondhia, 2010; Calderón et al., 2015).

Because of the soil is a non-renewable natural resource, its remediation should be mandatory. Nowadays, there are different technologies available for the remediation of polluted soils, based on very different biological, chemical, electrochemical, physical or thermal processes. Among them, the electrochemically assisted technologies are becoming more and more studied, because they allow to remediate efficiently soils *in situ*, and they can be easily combined with other technologies, even as different as the bioremediation, sometimes showing important synergisms.

Thus, the electrokinetic (EK) treatments consist of applying an electric field among electrodes placed the soil. This field mobilizes molecular and ionic species through the soil, including pollutants, nutrients or microorganisms in the case of combination of EK with bioprocesses (Reddy and Cameselle, 2009). Different EK phenomena such as electromigration, electrophoresis and electroosmosis are known to be responsible of this transport of species (Rodrigo et al., 2014).

Currently, EK treatment is started to be marketed as a cost-effective in-situ technique for removing pesticides from soils with low permeability (Reddy and Cameselle, 2009). However, EK remediation is known to have various important limitations, such as the low mobilization of non-polar pollutants, the important raise in soil temperature or the formation of pH gradients in the treated soil. In addition, EK is a non-destructive technology. It means that the contaminant is not degraded, but it is transported to wells where is accumulated. Then, the pollutant has to be removed and treated off-site (Risco et al., 2016). Because of it, as a way to improve the outcomes of this technology, it was recently proposed the combination of EK technology with other conventional technologies (Yeung and Gu, 2011). In the recent years, interest has increase in coupling EK treatment to bioremediation, and this combination is known as electro-bioremediation (EBR). The aim of EBR is combining the EK movement with microbiological degradation, which may be an advantage for enabling the *in situ* pollutant elimination (Wick et al., 2007) because EK can be efficient in the transport of microorganisms, nutrients or pollutants.

EBR can be achieved by different biological strategies such as biostimulation, bioaugmentation or biological permeable barriers (Mena et al., 2016c). In all these alternatives, EBR processes have to face several drawbacks being the most important the pH control, which is the most critical parameter in order to keep the microorganisms alive (Yeung and Gu, 2011; Gill et al., 2014). As it is well-known, large pH gradients are caused by the transport of protons and hydroxyl ions generated by water electrolysis on the electrodes surfaces.

Different strategies have been proposed to maintain a suitable pH in the soil during EBR processes (Pazos et al., 2010; Yeung and Gu, 2011; Gomes et al., 2012; Gill et al., 2014). One of the most interesting is the periodic change of the polarity of the electric field (so-called as periodic polarity reversal) (Mena et al., 2016b). Periodic polarity reversal has been used in some different treatments such as electroremediation of soils with emerging contaminants (Yang et al., 2016) and electrobioremediation of diesel polluted soils (Mena et al., 2016a, 2016b). In both cases, successful results were obtained, and pH was properly controlled, while the process has obtained a good treatment efficiency. Based on the experience gained by this research group, it may be guessed that one of the critical factors that can influence this technology is the frequency in the polarity changes, and to the best of our knowledge this factor has not been deeply studied yet. In this context, the aim of this work is to know how the reversal frequency influences on the performance of the periodic polarity reversal strategy in an EK-biological process for the remediation of oxyfluorfen polluted clayey soil. This evaluation of the influence of the frequency represents the main novelty of this work as compared to the previous existing literature.

2. Materials and methods

The experimental devices, and the experimental, sampling and analytical methods have been described elsewhere in previous research performed by the same authors (Ramírez et al., 2015; Mena et al., 2016c) and related to the same research programme. The following subsections only describe the important details required for a good understanding of this work, and additional details have been included as Supplementary Material.

2.1. Electrokinetic installation

The experiments were carried out in a bench scale set-up (Fig. SM-1, Supplementary material). The cell was made is transparent methacrylate and it was divided into five compartments. Pesticide polluted soil was located in central compartment. The anodic and cathodic compartments were placed at both sides of the soil compartment, separated by nylon mesh (0.5 mm mesh size). They behaved as electrode wells, containing the electrolyte which is transported through the soil. In turn, each electrode compartment was connected to a collection compartment, which the liquid transported by electro-osmosis accumulates. Graphite plates (10.0 cm × 10.0 cm × 1.0 cm) are used as anodes and cathodes. They are connected to the power supply.

2.2. Materials

Clayey soil characteristics are shown in Table SM-1 (supplementary material). Fluoxil 24 EC (Cheminova Agro, Madrid), a commercial herbicide whose composition contains oxyfluorfen, was used to pollute the soil. This product contains 24% oxyfluorfen, solvents such as xylene (<60%) and cyclohexanone (<13%) and a surfactant, the calcium dodecylbencene sulfonate (<4%), which is added to the formulation to promote the correct spreading of oxyfluorfen in soils.

The oxyfluorfen-degrading microbial consortium was obtained by a standard acclimation procedure described elsewhere (Moliterni et al., 2012). Activated sludge obtained from the biological reactor of an oil-refinery wastewater treatment plant (Puertollano, Spain) was used to seed the bioreactor. The feeding solution consists of Bushnell-Hass Broth (BHB) culture media (0.20 g Mg SO_4 L^{-1}, 0.02 g $CaCl_2$ L^{-1}, 1.00 g KH_2PO_4 L^{-1}, 1.00 g $(NH_4)_2HPO_4$ L^{-1}, 0.05 g $FeCl_3$ L^{-1} and 1.00 g KNO_3 L^{-1}) and Fluoxil 24 (with a concentration of oxyfluorfen of 200 mg L^{-1}) as organic substrate (sole carbon source). Once the acclimation period was expected to be completed, the microbial culture performance was checked by several batch biodegradation tests (Moliterni et al., 2012). Both the acclimation procedure and the batch oxyfluorfen biodegradation tests were conducted under no aerated conditions and using enough amounts of nitrates which acted as electron acceptor. The authors considered that the main biodegradation mechanism is anoxic, that is, heterotrophic denitrification, as also occurred in previous similar research (Ramírez et al., 2015).