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Reversible electrokinetic adsorption barriers for the removal of atrazine and oxyfluorfen from spiked soils

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HIGHLIGHTS

- REKAB technology efficiently removes atrazine and oxyfluorfen from soil.
- Synergistic interaction between electrokinetics and GAC permeable reactive barrier.
- Significant carbon bed-adsorption mechanism for atrazine and oxyfluorfen.
- Volatilization of herbicides is prevented in the REKAB technology.
- Reversible changes in the polarity control avoid extreme pH values.

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ABSTRACT

This study demonstrates the application of reversible electrokinetic adsorption barrier (REKAB) technology to soils spiked with low-solubility pollutants. A permeable reactive barrier (PRB) of granular activated carbon (GAC) was placed between the anode and cathode of an electrokinetic (EK) soil remediation bench-scale setup with the aim of enhancing the removal of two low-solubility herbicides (atrazine and oxyfluorfen) using a surfactant solution (sodium dodecyl sulfate) as the flushing fluid. This innovative study focused on evaluating the interaction between the EK system and the GAC-PRB, attempting to obtain insights into the primary mechanisms involved. The obtained results highlighted the successful treatment of atrazine and oxyfluorfen in contaminated soils. The results obtained from the tests after 15 days of treatment were compared with those obtained using the more conventional electrokinetic soil flushing (EKSF) technology, and very important differences were observed. Although both technologies are efficient for removing the herbicides from soils, REKAB outperforms EKSF. After the 15-day treatment tests, only approximately 10% of atrazine and oxyfluorfen remained in the soil, and adsorption onto the GAC bed was an important removal mechanism (15–17% of herbicide retained). The evaporation loses in REKAB were lower than those obtained in EKSF (45–50% compared to 60–65%).

1. Introduction

Over the past decades, concerns about the application of herbicides have been increasing, particularly about their effects on the environment [24]. Currently, the use of herbicides is very common in most agricultural regions of the world, providing great advantages related to improved crop production. Consequently, since the mid-1940s, the industrial production of organic herbicides has continuously increased, and even now it continues to progressively increase. The negative environmental impact of herbicides is related to water and soil contamination, which has received a considerable amount of attention from the scientific community [23,10,9,5,7,26]. From an environmental perspective, a very interesting classification of herbicides is related to their solubility. Low-solubility herbicides are typically formulated as emulsions to favour their application. The transport properties of such herbicides when they become pollutants strongly depend on the matrices used in the commercial formulation. Among the low-solubility herbicides, there are two that are of particular interest and are the focus of this manuscript: oxyfluorfen and atrazine. Oxyfluorfen (2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene) is a diphenyl-ether herbicide that is used for broad spec-

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trum pre- and post-emergent control of various annual broadleaf and grassy weeds [15]. This herbicide has low water solubility (0.1 mg/dm^{-3} at 22 °C), low vapour pressure (0.026 mPa at 25 °C), high Koc (log Koc = 3.46–4.13) and high Kow (log Kow = 4.86). Atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) is characterized by a low biodegradability, long half-life, low vapour pressure (0.0385 mPa at 25 °C) and low solubility in water (33 mg dm^{-3} at 22 °C) [14,20], and because of its hazardousness, it was banned in the European Union, although it remains in use in many other countries around the world.

One of the worst types of events related to the pollution caused by these herbicides is associated with accidental leakage, which may become a major source of diffuse pollution. To prevent serious environmental problems under accidental discharges of these species, it is very important to take rapid actions against accidental discharges of hazardous species using efficient technologies that help to rapidly remediate the soil [22]. Electrokinetic (EK) remediation integrated with permeable reactive barriers (PRBs) has been investigated by several authors in recent years [21,2,3,31,16], and this technology appears to be a very promising alternative. This technological approach was implemented primarily because EK also enables the use of PRB in low-permeability soils [11]. Thus, when a PRB is coupled with EK remediation, the flow of pollutants through the PRB is not provided by the transport driven by the hydraulic gradient of groundwater; rather, it is driven by the electro-osmotic flow of soil pore fluid, electromigration or electrophoresis (particularly in low-permeability soils) [6,30,13]. As the contaminated groundwater passes through the PRB, contaminants may be degraded or sequestered and clean groundwater exits the PRB. The reactive materials commonly considered include reductions using elemental metals, adsorption with porous high-surface-area materials, ion exchange with resin-based materials, biological degradation, limestone, çhydroxyapatite, active carbon and zeolites [11]. The use of inexpensive reactive materials as permeable barriers, such as granular activated carbon (GAC), should contribute towards improving the cost effectiveness of the combined treatment and increasing environmental sustainability [12]. Consequently, PRBs have been extensively proposed for the remediation of inorganic and organic pollutants in groundwater [28,30,13,8].

Regarding the use of EK-PRB with herbicides, a first experience in the application of the combination of EKSF with adsorption barriers was reported for the removal of trichlorophenol (not exactly a herbicide but highly related to these toxic pollutants from a chemical perspective) from spiked soils [25], where its high efficiency and easy performance were demonstrated. Another interesting experience came from the use of biobarriers in the removal of diesel, where it was concluded that the application of polarity reversal allows for considerably better performance [16,18,19]. The advantages of reversible changes in polarity were also noted by many other authors [1]. The reversible changes in polarity help to suppress acidification and basification of the contaminated soil in the close vicinity of the electrodes' surfaces and prevents the depletion of ionic species. This fact is of special relevance in combinations of EKSF with biological barriers because non-reversible processes lead to the exhaustion of nutrients in soil.

To date, no studies on the removal of atrazine and oxyfluorfen from soil by EK-PRB coupling have been reported. Consequently, the authors of the present work considered that it would be interesting to investigate the feasibility of coupling EKSF and GAC-PRB to remove atrazine and oxyfluorfen from low-permeability soil using an innovative process called reversible electrokinetic adsorption barrier (REKAB) technology. For the setting of this process, the previous experience of our group, gained in the development of easier technologies such as EK combined with non reversible adsorption permeable barriers and biobarriers has been used. In this context, this work aims to describe the removal of atrazine and oxyfluorfen from clay soils using electrokinetically assisted soil flushing (with sodium dodecyl sulfate (SDS) as the flushing solution) coupled with a PRB consisting of beds of GAC and to assess the influence of the electric field on the efficiency of this technology.

2. Materials and methods

2.1. Chemicals

Kaolinite, provided by Manuel Riesgo Chemical Products (Madrid, Spain), was used as a model of clay soil [17]. Atrazine and oxyfluorfen (Sigma-Aldrich), were of analytical grade and used as received. HPLC-grade acetonitrile (Sigma-Aldrich, Spain) was used as the mobile phase in high-performance liquid chromatography (HPLC) analyses. Hexane and ethyl acetate (Sigma-Aldrich, Spain) were used as solvents for the extraction of liquid and solid samples. Granular activated carbon (granule size of 1.25–3.15 nm) was purchased from Panreac (Spain). Graphite electrodes (100.0 cm^2) provided by Carbosystem (Madrid, Spain) were used as the electrode material.

2.2. Experimental procedure

The bench setup used in this work was constructed from transparent methacrylate and divided into seven compartments (Fig. 1) [29].

The central compartment with a length of 20 cm was loaded with herbicide-polluted soil and an active carbon PRB, which was manually compacted and separated from the electrode compartments by a 0.5 mm nylon mesh. One of these compartments contained the anode, and the other contained the cathode. Each electrode compartment was connected to additional compartments to collect the liquid overflowing from the wells that is transported due to the EK processes. The experiments were performed in potentiostatic mode, i.e., setting a voltage of 1.0 V cm^{-1}. The duration of the experiments was 15 days, which is long enough to provide a clear overview of the main process occurring in the soil and short enough to avoid the depletion of herbicides (this was intentionally sought to evaluate the removal mechanisms).

Because the carbon PRB areas were placed in an intermediate section of the installation, far away from the electrodes, it was necessary to use a surfactant to promote the transport of the atrazine and oxyfluorfen. A flushing fluid that consisted of a SDS surfactant solution (1000 mg dm^{-3}) was used as the solubilizing agent. Because SDS is an anionic surfactant, the superficial charge of the atrazine-SDS or oxyfluorfen-SDS micelles is expected to be negative [27,4], and consequently, they are expected to be transported from the cathodic zone towards the anodic compartment, with the atrazine and oxyfluorfen being adsorbed when passing through the carbon PRB. The polarity of the electric field applied between the electrodes was reversed once a day (value selected arbitrarily), and this periodic change will help to explain the zig-zag changes observed in the pH values of the electrolytes contained in the wells throughout the experiment.

The model soil was spiked with 960 mL of herbicide aqueous solutions (100 mg dm^{-3}) until an initial pollutant concentration of 30 mg per kg of soil was obtained. In the case of atrazine and oxyfluorfen solutions, SDS was used as the solubilizing agent (1000 mg dm^{-3}). The initial target moisture level of the soil was 30%. The polluted soil was manually compacted in an attempt to avoid the formation of heterogeneities in the soil, which may result in preferential paths for fluid transport. The levels of the anode wells were maintained using a level regulation loop. Water was pumped daily from the cathode well and electroosmotic flux (Jeo)

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