Science of the Total Environment 640–641 (2018) 629–636

Contents lists available at ScienceDirect

Science of the Total Environment

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

Reversible electrokinetic adsorption barriers for the removal of organochlorine herbicide from spiked soils

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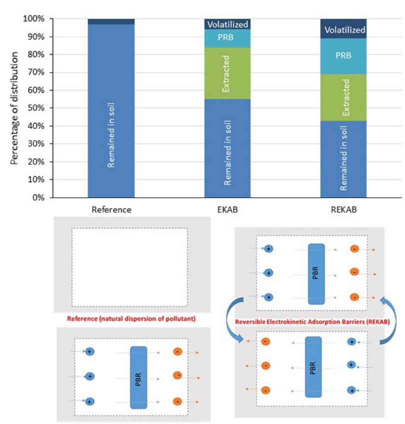
HIGHLIGHTS

- EKAB and REKAB technology allows removing 45 and 57% of clopyralid in 30 days.
- Reverse polarity increases the retention of clopyralid in GAC PRBs.
- Reverse polarity allows a better regulation of pH and higher water content of soil.
- Volatilization of clopyralid is partially prevented with the insertion of PRBs.
- Mobilization of clopyralid to electrolyte wells is lower with GAC PRBs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 February 2018
Received in revised form 10 May 2018
Accepted 28 May 2018
Available online xxxx

Editor: Yolanda Picó

Keywords:
Electroremediation
Soil remediation
Clopyralid
Granular activated carbon
Permeable reactive barrier
Reversible electrokinetic adsorption barriers

ABSTRACT

This work aims to describe the removal of clopyralid from clay soils using electrokinetically assisted soil flushing (EKSF) coupled with a permeable reactive barrier (PRB), consisting of beds of Granulated Activated Carbon (GAC). To do this, two strategies have been evaluated on bench-scale electroremediation facilities (175 dm^3): electrokinetic adsorption barrier (EKAB) and reversible electrokinetic adsorption barrier (REKAB). Likewise, to clarify the contribution of the different mechanisms to remediation process results are compared to those obtained in a reference test (without applying an electric field) and to results obtained in the EKSF of soils polluted with compounds with different polarity and vapour pressure. Results show that during EKAB and REKAB tests, clopyralid is removed from the soil by adsorption in PRB, electrokinetic transport and, very less decisively, by evaporation. The application of polarity reversion attains a higher retention of clopyralid in the activated carbon-PRB and a better regulation of pH because of the neutralization of H^+ and OH^- generated in the electrolyte wells. After 30 days of operation, the removal of clopyralid by EKAB is 45% while it reaches 57% in the case of REKAB.

1. Introduction

In recent years, the increase of the agricultural activity has enlarged the occurrence of pesticides in soils and groundwater. These products are extremely hazardous to human health and, thus, their diffusion in

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https://doi.org/10.1016/j.scitotenv.2018.05.364
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the environment should be controlled (Gavrilescu, 2005; Eason et al., 2013). Therefore, the search of treatments for the efficient degradation of this type of compounds has become a worthy topic of study. One of the most important families of pollutants gathers the chlorinated hydrocarbon pesticides. Nowadays, scientific community has focused their interest on it, mainly because they may become an important source for diffuse pollution (Lu and Yuang, 2009; Lei et al., 2018). Among them, clopyralid (3,6-dichloro-2-pyridinecarboxylic acid, $C_6H_3Cl_2NO_2$) is one of the most commonly used pesticides and it is considered as model pollutant (Ozcan et al., 2010). It is an organochlorinated compound with a very high solubility in water. Because of this, it can be rapidly transported, promoting the problem of diffuse pollution.

Conventional technologies for the treatment of contaminated groundwater, such as the well-known *pump & treat*, have shown important drawbacks due to their high cost, long treatment periods and/or difficulties to reduce the concentration of pollutants down to permitted levels (Ribeiro et al., 2005; Pazos et al., 2010; Ribeiro et al., 2011; Yeung and Gu, 2011; Alcantara et al., 2012). Thus, new in-situ technologies such as electrokinetic flushing (EKSF) or permeable reactive barriers (PRB) and even the combination of EKSF with PRB are being developed (Rodrigo et al., 2014) (Bebelis et al., 2013). PRB is a type of semi-passive in-situ treatment that uses a medium that promotes chemical, biochemical reactions or sorption processes to transform or immobilize contaminants (Hayes and Marcus, 1997; Scherer et al., 2000; Palmer, 2001; Choi et al., 2007; Chung and Lee, 2007; Henderson and Demond, 2007; Weng, 2009). Hence, PRB can consist, among others, of biological barriers (Mena et al., 2015; Mena et al., 2016b), ion exchange resins (Garcia et al., 2015), ZVI (Choi et al., 2008; Suzuki et al., 2012) or activated carbon (Saeedi et al., 2009; Yang et al., 2010; Ruiz et al., 2014; Huang et al., 2015) barriers. On the other hand, EKSF is based on the application of an electric field between the electrodes immersed in the soil capable to transport the pollutants contained in the soil by electromigration (ionic pollutants), electrophoresis (colloids and micro-drops of emulsified pollutants) or by dragging with the electro-osmotic flux (Alshawabkeh et al., 1999; Virkutyte et al., 2002; Trellu et al., 2016) (Kolosov et al., 2001; Hamdan et al., 2014). In a combined process, this mobilization could be used to transport the pollutants through the PRB and, thus, it may favor their retention and immobilization.

In previous works of our group, the use of electrokinetic adsorption barriers was proposed for the removal of many types of chlorinated hydrocarbons (Ruiz et al., 2014; Vieira dos Santos et al., 2016; Souza et al., 2017; Sun et al., 2017). Ruiz et al., evaluated the combination of EKSF with adsorption barriers for the removal of trichlorophenol from spiked soils, where its high efficiency and easy performance were demonstrated. Vieira dos Santos et al. and Souza et al. demonstrated the application of reversible electrokinetic adsorption barrier (REKAB) technology to soils spiked with low-solubility pollutants (oxyfluorfen and atrazine) and with soluble pollutants (2,4-D and clorsulfuron), respectively. These studies focused on evaluating the interaction between the EK system and the GAC-PRB, attempting to obtain insights into the primary mechanisms involved in each case (which include electrokinetic transport, adsorption and evaporation). Sun et al., evaluated the combination of EKSF with zero valent iron/activated carbon permeable barriers for the remediation of soil polluted with phenantrene and trichlorophenol, concluding that Fe/C-PRB exhibited a good and relatively stable performance by removing approximately 80% of PHE and 90% of TCP from the contaminant flux passing the PRB. This is one of the first works in which a combined Fe/carbon permeable barrier was evaluated. In general, results obtained showed that this combined technology was efficient but it depended on the contact of the pollutant with the adsorption beds. Thus, the periodic reversion in the polarity seemed to be a good way to improve the efficiency and to prevent extreme pH and the depletion of ionic species in the soil. It is important to highlight that all these studies were carried out in small lab-scale plants containing <5 kg of polluted soil. In this context, scale up of soil remediation processes has been found to be very important in order to understand the fundamentals of the electrochemically assisted technologies and their influence on the performance of the treatment. In previous works (Lopez-Vizcaino et al., 2017a, 2017b), we shed light on how size affects the results of soil remediation. We demonstrated that the removal of herbicides from soil were affected by the size of the plant used and that conclusions from small scale tests should not be extrapolated for full-scale applications. In fact, we confirmed that the controlling mechanisms in the small scale tests were the electrokinetic transport processes (electroosmosis or electromigration). However, the relevance of these processes in the prototype scale test was very low and, conversely, volatilization of organics was very important. For this reason,

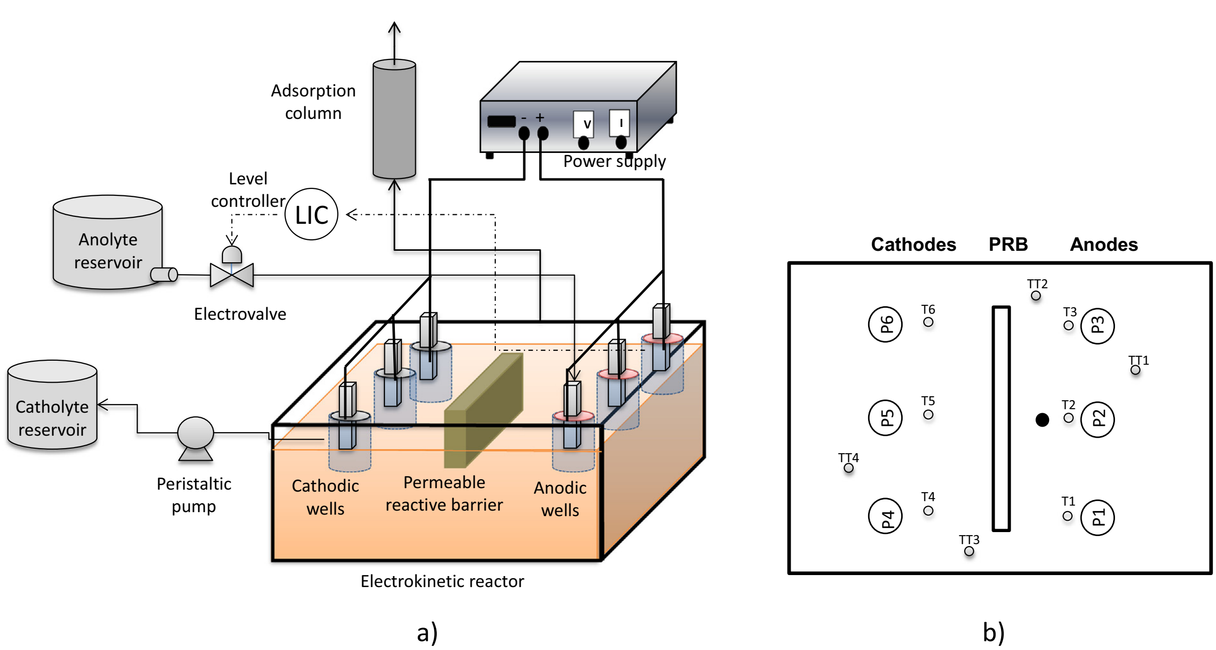

Fig. 1. a) Diagram of the electrokinetic remediation plant; b) configuration of the instrumentation. PRB: permeable reactive barrier; PP: pollution point; TT_i: thermocouple no. i; T_i: tensiometer no. i; P_i: well no. i. ● Spill point.