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Soil flushing and simultaneous degradation of organic pollutants in soils by electrokinetic-Fenton treatment

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ABSTRACT

This study focuses on the evaluation of a combination of electrokinetic technology and Fenton's process to remediate a soil polluted with organic compounds. To determine the influence of the several variables such as hydrogen peroxide dosage, iron soil concentration and porosity, different experiments using kaolinite spiked by Rhodamine B were performed. The use of this coloured sample permitted an easy monitoring of the oxidation reactions across the soil bed. From the obtained results, it is concluded that the highest colour removal rate was reached when a solution of hydrogen peroxide around 10% was used, and slight influence of iron soil concentration was detected at the range of concentrations used in these experiments. In all cases, citric acid was added in the anolyte and catholyte solutions in order to solubilize the iron as Fe-citrate complex and to keep the pH in acid environment favouring that the Fenton's reactions take place into the soil. Based on these preliminary experiments, the electrokinetic-Fenton process was applied to total petroleum hydrocarbons (TPH) polluted soil. After 15 and 27 days of treatment, a homogeneous removal of pollutants, around 54.4% and 58.2% of TPH removal efficiency, was reached, respectively. In addition, the Microtox bioassays confirmed the reduction of the *Vibrio fischeri* inhibition after the soil treatment. Summing up, *in situ* electrokinetic-Fenton treatment seems to be a suitable technique for the remediation of organics such as hydrocarbons present in polluted soils.

1. Introduction

Soil contamination by organic compounds has significantly increased due to several activities and factors such as farming, accidental emissions of harmful pollutants, industrial wastewater and the landfill leachate (Cheng et al., 2016). The presence of these compounds in soil has been causing serious incidents of soil pollution. This fact has led to a grave decline in the quality of agricultural products and is evolving in a growing interest among those involved in environmental remediation (Manz et al., 2001).

Nowadays, extensive studies have been carried out for the development of soil remediation techniques such as thermal desorption, excavation or dredging, pumping and treating, surfactant enhanced aquifer remediation, solidification and stabilization, soil vapour extraction, bioremediation, nanoremediation or *in situ* oxidation (Ramírez et al., 2015a, 2015b; Cobas et al., 2013; Gómez et al., 2010; Pazos et al., 2010, 2011,

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2013; He et al., 2014; Huguenot et al., 2015; Mousset et al., 2016). Among these treatment techniques, advanced oxidation processes (AOPs) have the potential for rapidly treating or pretreating soils contaminated with toxic and biorefractory organic compounds (Cheng et al., 2016; Pazos et al., 2013; Watts et al., 2002).

AOPs are chemical oxidation processes based on the *in situ* generation of hydroxyl radicals, which are very reactive and short-lived oxidants able to destroy target pollutants up to their mineralization or, at least, transform them into harmless or biodegradable products in short treatment times (Rosas et al., 2013). The main limitation in the AOP is the necessity of homogeneous distribution of the reactants into the soil to ensure the contact between the pollutants and reactive species, in order to reduction/oxidation reactions take place. The inclusion of the reactive agents into the soil must be carried out by soil flushing. However, it is impossible the application of this technique to fine and low-permeability soils. To overcome this problem, electrokinetic-Fenton treatment has been proposed as a solution (Oonnittan et al., 2013; Kang et al., 2014; Kim et al., 2005, 2009). There are several papers available in the literature in which the electrokinetic process with Fenton oxidation have been demonstrated as a useful method to remediate soils co-contaminated with organic pollutants and heavy metals (Bocos et al., 2015; Seo et al., 2015; Ng et al., 2014).

In the electrokinetic treatment, a low-density direct current is applied by two electrodes inserted into wet-polluted soil. This current promotes the movement of the pollutants in the pore fluid towards the electrode chambers where they are finally collected and treated. Therefore, this technique is recommended for application into fine and low-permeability soils (Pazos et al., 2010; Lopez-Vizcaino et al., 2016) and it has been mainly applied to treatment of soils polluted by metals, due to the facility to move the ionic species (Robles et al., 2015; Acar, 1993).

Regarding Fenton's process, this technique has been evaluated to destroy different organic pollutants present in soil and wastewater over the last decades. The Fenton's reaction is based on the generation of hydroxyl radicals by the combination of hydrogen peroxide and ferrous ions. Hydroxyl radicals can react even with most of the organics persistent pollutants until their complete mineralization (Mousset et al., 2016; Pardo et al., 2015; Sirés et al., 2014; Thiam et al., 2016; Oturan and Aaron, 2014). The main advantages of the process are: (i) pollutants can be destroyed operating in different modes (*in situ*, on-site or off-site); (ii) Fenton's reagents are abundant, non-toxic, easy to handle and environmentally benign; and (iii) the process requires short treatment time in comparison to other technique such as bioremediation.

In the Fenton's treatment, iron is one of the most important variables and it can be present and available in soil. However, it is necessary to transport the hydrogen peroxide across the soil in order to promote the Fenton's reactions. The hydrogen peroxide, transported in the soil through the electrokinetic phenomena and electro-osmotic flow, is decomposed by iron or other transition minerals into the active oxygen species which are capable of oxidizing pollutants (Watts and Stanton, 1999). The transport through the application of electric field enables a uniform and rapid transport of hydrogen peroxide into a soil with low permeability. The electro-osmotic flow could be enhanced by the presence of enhancing agents such as electrolytes, surfactants and chelating agents (citric acid, ethylenediaminetetraacetic acid, Na_2SO_4, $NaNO_3$, etc.) in the processing fluid and also applying pH control at the electrode chambers (Rozas and Castellote, 2015; Masi et al., 2015). In addition, to improve the electrokinetic process, it is necessary to enhance pollutants desorption from soil and to create a favourable environment to their transport towards the electrode chambers. In the electrokinetic-Fenton treatment, the addition of complexing agents facilitates the desorption of the entrapped pollutants and the solubilization of the iron from soil (Reddy and Chandhuri, 2009). Recently, Bocos et al. (2015) reported that citric acid is the most suitable complexing agent, increasing iron solubilization as soluble Fe-citrate that remains available for the Fenton's oxidation and enhancing the electro-osmotic flow (around 18.7%) with respect to the conventional electrokinetic remediation. In addition, the generation of hydroxyl radicals is only effective under low pH (Valentine and Ann Wang, 1998) and the buffer capacity of the citric acid will allow remaining in an appropriated pH value along the soil in the electrokinetic cell (Bocos et al., 2015).

In terms of free radicals formation and consumption, there are three mechanisms whereby hydrogen peroxide is consumed: (i) namely reaction with Fe^{2+}; (ii) reaction with Fe^{3+} and (iii) reactions with organic pollutants and/or free radicals. The efficacy of Fenton's oxidation is therefore dependent on the hydrogen peroxide oxidant to iron catalyst ratio. Considering that scavenging effect exist within soil systems and the fact that the major cost of applying Fenton's oxidation comes from the quantity of the main oxidant used, it is recommended that the reactant dosage and other operating parameters have to be carefully optimized before field applications (Venny et al., 2012). Therefore, in this study, the effect of different factors such as iron content, hydrogen peroxide dosage and soil porosity has been evaluated in order to reach a clear understanding of the complex interactions between all processes implicated in the soil electrokinetic-Fenton treatment.

2. Materials and methods

2.1. *Spiked Rhodamine B kaolinite samples*

Rhodamine B and kaolinite were purchased from Sigma–Aldrich. The kaolinite has a particle size average of 3 μm and a specific surface of 13.5 m^2/g. The mineralogy analysis by X-Ray Diffraction indicated the presence of kaolinite clay 85%, mica 14% and quartz 1%. Polluted kaolinite was prepared mixing thoroughly 150 g of kaolinite clay spiked at different iron concentrations with a solution of Rhodamine B. This mixture was stood for more than 24 h to allow the sorption of the dye on the surface of kaolinite particles until a final concentration of 0.16 g dye/kg dry kaolinite. The initial pH of the mixture was around 4. In this sample, Rhodamine B was effectively adsorbed on the kaolinite particles since no dye was released in extraction tests with deionised water.

2.2. *Soil*

TPH polluted soil samples were collected in the northwest of Spain from an area of high industrial activity. Samples were taken from 0 to 30 cm depth by using an Eijkelkamp sampler, transported to the laboratory in polyethylene bags and then sieved and homogenized. Only the fraction containing particles smaller than 2 mm was selected. Some of the most typical characterization data of used soil sample such as pH, conductivity, total organic carbon, total inorganic carbon, total carbon, organic matter and the presence of some metals are depicted in Table 1. In terms of the overall concentration of

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