Journal of Electroanalytical Chemistry 799 (2017) 1–8

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Electrokinetic oxidant soil flushing: A solution for *in situ* remediation of hydrocarbons polluted soils

Ciprian Sandu[a,b], Marius Popescu[a,b], Emilio Rosales[a], Marta Pazos[a], Gabriel Lazar[b],
M. Ángeles Sanromán[a,*]

[a] *Department of Chemical Engineering. University of Vigo, Campus As Lagoas-Marcosende, 36310 Vigo, Spain*
[b] *Faculty of Engineering, "Vasile Alecsandri" University of Bacau, Calea Marasesti 157, 600115 Bacau, Romania*

ARTICLE INFO

Keywords:
Electrokinetic
Real polluted soil
TPH removal
Sodium persulfate
Potassium permanganate
Sodium hypochlorite

ABSTRACT

Nowadays, the majority of the remediation studies have been carried out using artificially spiked soils with individual target pollutants. One of the bottlenecks is the application of developed technologies to the removal of pollutants in real aged contaminated soils, which is much more difficult than in spiked ones. Thus, in this study, the performance of a combined technology as flushing using different oxidants coupled with the electrokinetic technique was performed and its feasibility was evaluated to remediate a real industrial polluted soil with low permeability in which is not possible the conventional flushing system. Initially, the characterization of this soil showed a wide distribution of hydrocarbons with a total petroleum hydrocarbons content of 29,666 $mg \cdot kg^{-1}$. Based on the hydrocarbons distribution, the source of the pollutants was identified as a spillage of motor oil and diesel. Moreover, the aging of the pollution was evaluated (around 16 years) resulting in a historically polluted soil. Initially, an *ex-situ* oxidative treatment was considered. This treatment demonstrated the feasibility of the different oxidants on the removal of the hydrocarbons, achieving removal values higher than 65% in all the experiments. Furthermore, a critical parameter in the treatment, as pH, was also evaluated resulting in an acidic environment for $KMnO_4$ and $Na_2S_2O_8$ and basic environment for NaOCl. Later, the simulated bench scale *in situ* removal of the contaminants was considered, but the delivery of the oxidants into the polluted soil is hard, and for this reason, the coupling of flushing and electrokinetics was carried out. Working at the optimal conditions determined before, the treatment with the selected oxidants was performed. The total petroleum hydrocarbons (TPH) removal (40–60%), the profile of hydrocarbons and metals in the different sections of the soil after the treatments proved the efficiency of the system. The viability of the selected hybrid technique in the removal of TPH from historically polluted soils was demonstrated.

1. Introduction

The persistence of pollutants, which are strongly sorbed into the soils, is causing important environmental problems. Nowadays, the variety of complex mixtures of hydrocarbons depends upon manufacturer, geographic location, and seasonal use. For this reason, it is known that the compositions of these products are made up of hundred hydrocarbon compounds, which are accumulated in environmental media, mainly in soil [1,2]. Thus, total petroleum hydrocarbon (TPH) also known as mineral oil or hydrocarbon oil, has been used as measurable amount of the mixture of hydrocarbons, which are found in the environmental matrix [3].

Soil pollution caused by hydrocarbons represents a serious threat to the environment; as for example, Romania has three major "hot spots" (Prahova, Dolj, and Bacau) that correspond to areas within which oil extraction and Romanian petrochemical industry operates. Almost half of the accidental contaminant releases in Romania are caused by oil extraction or transportation. These accidental releases have multiple causes, but most of them are related to the obsolete equipment, improper conditions for pipes used for crude oil transportation and in the petrochemical industry [4]. This is an important concern since the agriculture contributes 20% to the national income and the agricultural lands productivity is diminished by 20–30% due to certain limiting factors as chemical pollution due to the unreasonable utilization of fertilizers and pesticides, emissions of metals, and hydrocarbons [5].

Nowadays, the management of these polluted soils is a common problem among industrialized countries, requiring the development of innovative, cost-effective, and eco-friendly technologies [6,7]. Although a variety of biological, chemical, or physical techniques for environmental remediation of hazardous waste sites have been devel-

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[*] Corresponding author.
E-mail addresses: emiliorv@uvigo.es (E. Rosales), mcurras@uvigo.es (M. Pazos), glazar@ub.ro (G. Lazar), sanroman@uvigo.es (M.Á. Sanromán).

http://dx.doi.org/10.1016/j.jelechem.2017.05.036
Received 18 February 2017; Received in revised form 14 May 2017; Accepted 18 May 2017

oped, it has been detected that by a combination of these technologies a better approach is possible. In these cases, the major challenge is to know when to switch from one technology to the next in a treatment train [8,9].

Chemical oxidation is considered as one of the treatment alternatives able to reduce or eliminate the volume and toxicity of pollutants. In recent years, the coupling of this technology with others, such as *in-situ* flushing, has attracted much attention for its potential to treat and degrade various soil contaminants, *e.g.* chlorinated compounds and pesticides [7,10,11]. The application of this technology permits to include in the flushing solution oxidant agents able to transform chemically hazardous contaminants into non-hazardous or less toxic, mobile or inert compounds [12]. Among the most common oxidants used in soil remediation are ozone, hydrogen peroxide, hypochlorite, chlorine, permanganate, and persulfate [13–15].

In-situ flushing technology can be applied to soils with high permeability; however, it is not able to be effective for a soil of low hydraulic permeability like clays. One possible solution is to generate the *in-situ* flushing of oxidants by electrokinetic technology (EK). The principle of EK relies upon the application of a low-intensity direct current that generates several transport phenomena causing the movement of the species present in the soil towards the electrodes [16]. Thus, for the treatment of this kind of polluted soil, the use of electrokinetic oxidant soil flushing (EKOSF) is proposed as an alternative technology. In EKOSF, the oxidants are mobilized along the soil by electroosmotic flow, and they can oxidize the organic pollutants during their migration [17,18].

In this context, for the treatment of soil with low permeability is necessary to develop a combined technology, as EKOSF, in order to transport the oxidants and chemically transform the hazardous pollutants into non-hazardous or less toxic, mobile or inert compounds in the soil. In addition, in the literature, the majority of the reported studies are focused on the evaluation of artificially spiked soils with individual target pollutants. In order to assess the system in a near real environment, the present study was performed with an aged contaminated soil of an industrial area of elevated activity in the nearby of Bacau (Romania). The EKSOF was performed using different oxidants such as sodium hypochlorite (NaOCl), permanganate ($KMnO_4$), and sodium persulfate ($Na_2S_2O_8$) that were flushing into the soil by electric field action from the electrolyte chambers. Previously, the soil was characterized and several *ex-situ* experiments were carried out in order to determine the efficiency of each oxidant to degrade the TPH present into the soil.

2. Material and methods

2.1. Reagents

Sodium hypochlorite (NaOCl), potassium permanganate ($KMnO_4$), sodium persulfate ($Na_2S_2O_8$), and sodium sulfate (Na_2SO_4) were obtained from Sigma-Aldrich.

2.2. Industrial polluted soil

A hydrocarbon contaminated soil sample was collected from an area of elevated industrial activity in the nearby of Bacau (Romania). The sample was collected from the topsoil by using an Eijkelkamp sampler. It was kept in polyethylene bags, carried to the laboratory, passed through a sieve (2 mm) and homogenized. Then, the sample was stored at room temperature until its use.

2.3. Ex-situ and simulated bench scale in-situ treatments

2.3.1. Ex-situ experiments

Preliminary *ex-situ* experiments were carried out in order to determine the feasibility of this process with the proposed strategies. Experiments were performed in Erlenmeyer flasks with a working volume of 0.15 L where 7.5 g of the soil were mixed with 0.15 L of the selected oxidant (Table 1). The concentration and pH range used in each oxidant were selected based on the optimized conditions described in previous studies reported in the literature [14,15]. In the case of experiments with persulfate, citric acid (0.1 M) was added to favor the solubilization of the iron present in the soil. The soil sample was maintained in suspension by shaking in an orbital shaker avoiding concentration gradients in the cell. All reaction samples were prepared in triplicate.

Table 1
Oxidant concentrations and pH for the different *ex-situ* experiments developed.

Oxidant	Concentration	pH
NaOCl	1 g/L	8, 9.5, 12
$KMnO_4$	9 g/L	3.5, 5.5, 7.5
$Na_2S_2O_8$	20%	5, 7, 9

2.3.2. In-situ experiments: EKOSF

Simulated bench scale *in-situ* experiments were performed to evaluate the efficiency of this technology applied to historically hydrocarbon polluted soil. EKOSF was studied using an EK cell developed by our research group (Fig. 1) [19]. This set-up consisted of two electrode chambers (working volume 0.3 L) and a central tube (length 100 mm x diameter 32 mm). The soil samples with initial moisture around 40% were compacted manually in the central tube, favoring their homogeneous distribution to avoid preferential paths for the fluid transport. In order to separate the soil samples from the electrode chambers, porous stones and filter papers were used. Graphite bar electrodes were used as anode and cathode, and a constant voltage drop ($3\ V\cdot cm^{-1}$) was applied with a power supply HP model 3662 [19].

In all experiments, the electrode flushing solution was Na_2SO_4 (0.1 M) as electrolyte at the pH determined as optimal in the *ex-situ* experiments. Furthermore, in the electrolytic chambers, the oxidants were added. For the acquisition of electrical parameters over time, an automatic data acquisition software it has been developed, called EK-Data. The purpose of this software is the automatization of the data recording and storing tasks needed for the control of the experiments. Thus, there is a continuous flow of information about the evolution of electrical parameters in the systems.

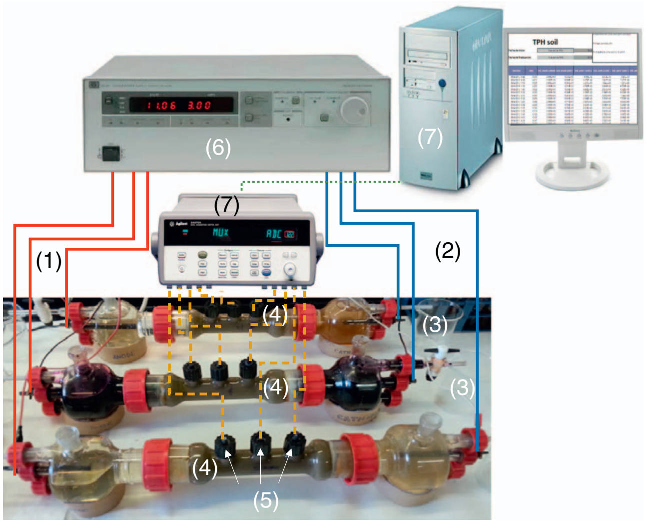

Fig. 1. Experimental set-up for the simulated bench scale *in-situ* experiments: (1) anode, (2) cathode, (3) electro-osmotic flow reservoir, (4) soil sample, (5) auxiliary electrodes, (6) power supply, (7) data acquisition system.