Journal of Environmental Management 153 (2015) 40–47

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Combination of surfactant enhanced soil washing and electro-Fenton process for the treatment of soils contaminated by petroleum hydrocarbons

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ARTICLE INFO

Article history:
Received 1 July 2014
Received in revised form
21 January 2015
Accepted 23 January 2015
Available online 31 January 2015

Keywords:
Soil pollution
Soil washing
Column experiment
Tween® 80
Electro-Fenton

ABSTRACT

In order to improve the efficiency of soil washing treatment of hydrocarbon contaminated soils, an innovative combination of this soil treatment technique with an electrochemical advanced oxidation process (i.e. electro-Fenton (EF)) has been proposed. An *ex situ* soil column washing experiment was performed on a genuinely diesel-contaminated soil. The washing solution was enriched with surfactant Tween® 80 at different concentrations, higher than the critical micellar concentration (CMC). The impact of soil washing was evaluated on the hydrocarbons concentration in the leachates collected at the bottom of the soil columns. These eluates were then studied for their degradation potential by EF treatment. Results showed that a concentration of 5% of Tween® 80 was required to enhance hydrocarbons extraction from the soil. Even with this Tween® 80 concentration, the efficiency of the treatment remained very low (only 1% after 24 h of washing). Electrochemical treatments performed thereafter with EF on the collected eluates revealed that the quasi-complete mineralization (>99.5%) of the hydrocarbons was achieved within 32 h according to a linear kinetic trend. Toxicity was higher than in the initial solution and reached 95% of inhibition of *Vibrio fischeri* bacteria measured by Microtox® method, demonstrating the presence of remaining toxic compounds even after the complete degradation. Finally, the biodegradability (BOD_5/COD ratio) reached a maximum of 20% after 20 h of EF treatment, which is not enough to implement a combined treatment with a biological treatment process.

1. Introduction

Soil pollution by hydrocarbons is a worldwide environmental concern. For instance, in France, these pollutants are present in about 32% of the polluted sites referenced in the BASOL database (BASOL, 2015). Among this class of pollutants, 23% of the sites are contaminated by total petroleum hydrocarbons (TPH). These compounds are often associated with fuel, oils, jet fuel, etc. Their impact on human health and environment is well known because of their hydrophobic characteristics (Lapinskiene et al., 2006) permitting them to reach and accumulate in the food chain. They are indeed likely to cause toxic effects to human and environmental receptors (Rowland et al., 2001). Furthermore this toxicity is closely related to their structures; the light fractions being less toxic than heavier ones (van Gestel et al., 2001). Their physical and chemical properties such as solubility and K_{ow} favour their accumulation in organic matter and human bodies via food chain. The fate of these molecules in the environment is often leaching in soils to groundwater, dispersion, and mostly sorption and biodegradation (Cozzarelli et al., 2014). Due to their harmful effects, TPH have been regulated in France where a concentration of 500 mg kg^{-1} of dry matter is the legal threshold, above which soil is considered as a waste and has to be treated (JORF, 2010).

Biological, physical and chemical *in situ* treatment methods are often used but these techniques are very often time-consuming (Tang, 2005) and require high engineering costs (Majone et al., 2015). Besides, before implementing an *in situ* soil treatment technique at full-scale, laboratory tests should be performed in order to adapt the technique to the field conditions (Gomes et al., 2013). As a consequence, *ex situ* techniques such as soil washing are getting more and more interest despite that soil excavation is necessary (Lee et al., 2005; Khalladi et al., 2009). Since 2007, French policy on polluted sites is strongly oriented towards the use and operation of *in situ* treatment methods. *In situ* treatment of TPH

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http://dx.doi.org/10.1016/j.jenvman.2015.01.037

contaminated soils could be achieved by soil flushing (Lee et al., 2005). However, this remediation approach is still being developed by companies as it does not require soils excavation, allowing this technique still to be more cost-effective than *ex situ* processes. Surfactants are chemical compounds frequently used for the extraction of hydrocarbons from soil. Their amphiphilic properties are useful to promote the mobilization of hydrophobic compounds sorbed onto soil particles. Non-ionic surfactants like Tween® 80 are particularly of interest when dealing with hydrocarbons. Since its first use more than 20 years ago (Laha and Luthy, 1992), Tween® 80 has been widely used in soil remediation to mainly clean up hydrocarbons (Wong et al., 2004; Mousset et al., 2013a). Compared to other surfactants, its chemical characteristics together with its low cost, and low toxicity (Varma et al., 1985) on soil microorganisms (Bautista et al., 2009) compared to other surfactants, are of great interest for soil remediation companies.

Although this washing technique is generally efficient to clean soil, the major concern remains in the treatment of the leachates containing both TPH and surfactants. Such solutions contain a significant amount of high COD (Chemical Oxygen Demand), which require an advanced oxidation treatment to be degraded. Electrochemical Advanced Oxidation Processes (EAOPs) have shown promising results to treat many poorly biodegradable organic compounds in solutions (Brillas et al., 2009; Panizza and Cerisola, 2009) even for highly loaded solutions like reverse osmosis concentrates and landfill leachates (Zhou et al., 2012). These techniques, considered as environmental friendly, promote the *in situ* electro-generation of hydroxyl radical ($^{\bullet}OH$) that is a very powerful oxidizing agent (E° ($^{\bullet}OH/H_2O$) = 2.80 V/SHE (Standard Hydrogen Electrode). Among these EAOPs, electro-Fenton (EF) technique has shown good performances towards various organic pollutants (Dirany et al., 2012; El-Ghenymy et al., 2013; Loaiza-Ambuludi et al., 2013; Oturan et al., 2012) and more especially with synthetic soil washing solutions (Mousset et al., 2014a). EF allows the production of $^{\bullet}OH$ through the Fenton reaction (Eq. (1)):

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + {}^{\bullet}OH \quad (1)$$

Compared to chemical Fenton process, the EF process allows minimizing the use of reagent since H_2O_2 is *insitu* produced and a catalytic amount of soluble iron is enough because it is continuously electro-regenerated at the cathode via the reactions 2 and 3 (Sires et al., 2007):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

Thanks to these enhancements, higher degradation rate, high mineralization degree of organic pollutants and no sludge production are observed (Rodrigo et al., 2014).

This study aims at implementing an innovative combination of soil column washing with Tween® 80 and EF treatment of the collected leachates. To the best of our knowledge, this is the first time that such a combination is applied on a diesel-contaminated soil. Some studies dealing with electrocoagulation (López-Vizcaíno et al., 2012) and Fenton oxidation (Rosas et al., 2013) have been performed but never used soil column washing together with EF. Iglesias et al. (2014) performed an EF treatment on marine sediment contaminated with phenanthrene considering the solution and the slurry after the sediment washing. Another study performed column soil washing in the presence of Tween® 80 and phenanthrene combined with an electrochemical treatment (Gómez et al., 2010). However, this electrochemical treatment is not considered as an EAOP, since it is not based on the oxidation with $^{\bullet}OH$. In this paper, the washing of TPH-contaminated soil with Tween® 80 has been studied using a soil column experimental set up. The experimental configuration is close to what could be used on the site where the contaminated soil was sampled. The collected leachates containing TPH were then studied for their degradation features with EF as an advanced electrochemical technique. Finally, the biodegradability of the treated leachates was also monitored.

2. Materials and methods

2.1. Surfactant

Polyoxyethylene (20) sorbitan monooleate, also known as Tween® 80, was purchased from Sigma–Aldrich (France) and was used for the soil washing experiments. This non-ionic surfactant has a molecular mass of 1310 g mol^{-1} and a critical micellar concentration (CMC) of 0.012 mM (0.0016% w/v) at 25 °C. Distilled water was used to prepare solutions containing different concentrations of Tween® 80.

2.2. Soil

Soil samples were collected at the depth of 100 cm in an urban site where a genuine contamination by TPH was discovered. The samples were collected on July 12, 2012 and were stored in sealed buckets protected from sunlight until the column experiments. The soil collected on that site was characterized as a sandy loam soil with more than 60% sand, 25% loam and 15% clay. The main soil characteristics are as follows: $pH_{(H2O)}$ 8.4; organic matter content, 44.6 g kg^{-1} DW; cationic exchange capacity, 15.7 cmol kg^{-1} DW. Three different samples were used for the experiments and were named soil S1, soil S2 and soil S3. TPH concentrations are shown in Table 1.

2.3. Materials

Polyvinyl chloride (PVC) columns of 30 cm height and 20 cm diameter were used. These PVC columns were put on a polymethyl methacrylate (PMMA) (Plexiglas®) slab of 0.8 cm width. This slab was pierced by 2 mm diameter holes in order to evacuate the leachates. Eluates were then collected in a high-density polyethylene (HDPE) funnel.

2.4. Washing experiment

Columns were filled with 15 kg of contaminated soil (S1, S2 and S3) without any preparation. Experiments were performed at room temperature (approx. 20 °C). Washing solutions were stored in a plastic tank during the experiment. The required volumes were injected by a 4-channels peristaltic pump IPC-N (Ismatec, Switzerland). Tygon® tubes with an internal diameter of 0.76 mm were used.

Washing solution was prepared with Tween® 80 dissolved in tap water. Tween® 80 solution was prepared at different concentrations

Table 1
Hydrocarbons concentrations in mg kg^{-1} DW (dry weight). S1, S2 and S3 stand for the three different soils. Fractions C10 to C40 stand for the number of carbon atoms in the molecule. Total means the sum of the 4 different fractions.

	Hydrocarbons concentrations (mg kg^{-1} DW)				
	C10–C12	C12–C16	C16–C21	C21–C40	Total
S1	700	2400	2300	660	6100
S2	320	1600	1600	480	3900
S3	650	2300	2500	1000	6100