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Oxidation by Fenton's reagent combined with biological treatment applied to a creosote-comtaminated soil

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ABSTRACT

In this study, we investigated the feasibility of using Fenton oxidation to remove sorbed polycyclic aromatic hydrocarbons (PAHs) in aged soil samples with creosote oil from a wood preserving site. The optimal dosage of reagents was determined by a statistical method, the central composite rotatable experimental design. The maximum PAH removal was 80% with a molar ratio of oxidant/catalyst equal to 90:1. In general low molecular weight PAHs (3 rings) were degraded more efficiently than higher molecular weight PAHs (4 and 5 rings). The hydrogen peroxide decomposition kinetic was studied in the presence of KH_2PO_4 as stabilizer. The kinetic data were fitted to a simple model, the pseudo-first-order which describes the hydrogen peroxide decomposition. The PAH kinetic degradation was also studied, and demonstrated that non-stabilized hydrogen peroxide was consumed in less than 30 min, whilst PAH removal continued for up to 24 h. In a second part of the work, a combined chemical and biological treatment of the soil was carried out and shown to be dependent on the pre-oxidation step. Different reagent doses (H_2O_2:Fe) were used (10, 20, 40, 60:1) in the pre-treatment step. An excess of hydrogen peroxide resulted in a poor biological removal, thus the optimal molar ratio of H_2O_2:Fe for the combined process was 20:1. The combined treatment resulted in a maximum total PAH removal of 75% with a 30% increase in removal due to the biodegradation step. The sample with highest PAH removal in the pre-oxidation step led to no further increase in removal by biological treatment. This suggests that the more aggressive chemical pre-oxidation does not favour biological treatment. The physico-chemical properties of the pollutants were an important factor in the PAH removal as they influenced chemical, biological and combined treatments.

1. Introduction

Abandoned gasworks, asphalt factories and wood impregnation facilities contribute to coal tar and creosote oil contamination in industrialized countries. Creosote oil is manufactured by distilling coal tar and may consist of up to 200 compounds [1]. Contaminated soils typically consist of 85% polycyclic aromatic hydrocarbons (PAH), 1–10% phenols, 5–13% heterocyclic aromatics containing nitrogen, sulphur or oxygen, and 1–3% monoaromatic compounds. PAHs are a group of compounds that consist of two or more benzene rings and are classified as hydrophobic organic compounds. PAHs tend to persist in the environment and to occur in natural media such as soil, sediments, water and air. They are widely distributed due to their hydrophobic nature and low water solubility [2,3]. In fact, PAHs are considered the most widely distributed class of potent human carcinogens. In aquatic systems, the toxicity of PAHs increases as molecular weight increases. Therefore, they have been listed by the United States Environmental Protection Agency (USEPA) and by the Environmental European Agency (EGA) as priority environmental pollutants [2–5].

Thermal desorption after excavation is the most widely used treatment technology for highly contaminated soils. For lower contamination levels, biological treatment has proved feasible, but its applicability may be limited because of low PAH bioavailability due to the sequestration [6,7]. Chemical techniques are promising alternatives that may be highly efficient in a relatively short time. They can also be combined with bioremediation to design complete soil treatment processes [8–11].

In situ chemical oxidation (ISCO) is an emerging technology and a relatively simple process. It involves the use of a strong oxidant, with or without a catalyst, to oxidize organic contaminants. Exam-

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ples of potential contaminants that are amenable to treatment by ISCO include BTEX, PCE, TCE, MTBE and PAHs [12]. Chemical oxidation technologies are predominantly used to address contaminants in a source area's saturated zone and capillary fringe. Cost concerns may preclude the use of chemical oxidation technologies to treat large and dilute petroleum contaminant plumes [13].

Like most remediation technologies, in situ chemical oxidation has its limitations, which generally fall into two categories: (i) reactivity with contaminants of concern and (ii) the mass transfer of contaminants from the sorbed phase and dense non-aqueous phase liquids (DNAPLs) to the medium in which the reactive species exists, which is usually water. These contaminants are problematic as almost all reactants used in soil and groundwater remediation (e.g. bacteria, hydroxyl radicals and reductants) exist in the aqueous phase. Therefore, sorbed contaminants must desorb or dissolve into the aqueous phase before transformation can occur [14]. As the contaminants are degraded in the aqueous phase, the concentration gradient between the sorbed phase and the aqueous phase increases, which drives the subsequent desorption or dissolution. This treatment process, which is referred to as desorption or dissolution-limit requires a long time for site cleanup. However, the Fenton reaction can potentially treat sorbed contaminants and DNAPLs at a faster rate than the desorption and dissolution processes [15].

The Fenton reaction is often used to treat wastewater from different types of industries [16,17]. It can also be applied to the remediation of contaminated sediments, sludges and soils [8,14,18,19]. Furthermore, Fenton oxidation is a process that can be used in combination with bioremediation techniques, either as a pre-treatment for the oxidation of contaminants to more degradable compounds or as a post-treatment for residual contaminants. [8,20].

The Fenton reaction is based on hydrogen peroxide decomposition in the presence of ferrous iron to produce hydroxyl radicals, which are the main oxidizing species:

$$\mathrm{Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + {}^{\bullet}OH} \quad k_1 = 53\text{–}76\,\mathrm{M^{-1}\,s^{-1}} \tag{1}$$

Hydroxyl radicals are strong, relatively unspecific oxidants that react with most organic contaminants, including PAHs, at rates close to their theoretical limit, which is controlled by the diffusion rate in water [21,22]. Treatment with the Fenton reaction is conducted in an acid medium (pH 2–3) to prevent iron salt precipitation [8]. The Fenton reaction process has some limitations such as excessive H_2O_2 decomposition via non-productive reactions; pH change (e.g. acidification), which is problematic in well-buffered aquifers; radical scavenging; problematic delivery of H_2O_2, Fe(II), acid, and stabilizers due to reactive transport; and health and safety issues regarding the release of volatiles and strong oxidant solutions [3,12,13].

Biodegradation studies suggest that PAHs sorbed onto or partitioned into a solid phase are not readily degraded by microorganisms, so hydrocarbons must be released from the solid phase to the aqueous phase in which they are available [23,24]. As a result of low mass-transfer rates in the soil matrix, this release often limits the effectiveness of bioremediation.

The combination of chemical oxidation and biodegradation has a great advantage over either of the two treatments alone in the remediation of organic contaminants [1,2,25]. It was established that pre-oxidation of PAH and by Fenton/Fenton like reactions leads to oxidation products that are more soluble in water and also with better availability to microorganism [1,8,9].

Previous studies have shown that the efficiency of the chemical treatment was dependent on the soil characteristics and on the PAH physico-chemical properties of PAHs [25,26]. In addition several specific conditions are required to efficiently apply each method. The extent of PAH removal by the Fenton-like-treatment depended on the applied H_2O_2/soil weight ratio and the addition of a catalyst to a creosote spiked soil [1]. Partial removal of PAHs from iron-rich creosote oil-contaminated soil was achieved by a modified Fenton reaction without iron addition or pH adjustment, and subsequent incubation [27].

Use of chemical treatment in conjunction with biodegradation to remove organic pollutants in creosote contaminated soil has not been widely studied, especially for aged soils with a history of contamination, laboratory experiments have shown that spiked PAHs can be more easily oxidized than native pollutants, which are usually sorbed onto solid matrices over years or decades and make their desorption and subsequent chemical or biological treatment difficult.

The present study was thus conducted to evaluate the efficiency of the chemical oxidation treatment and the combination of chemical oxidation and biodegradation in the remediation of sandy aged soil contaminated with creosote oil. The optimal reagent doses were determined in the chemical process and a kinetic study was performed in order to evaluate the impact of chemical pre-treatment on PAH biodegradation.

2. Materials and methods

2.1. *Contaminated soil*

Sandy creosote oil contaminated soil samples from a wood preserving site were used. The contamination origin is 30–40 years ago. The polluted soil contained high amounts of PAH compounds. Creosote oil was also found as a free phase on top of the bedrock and as a dense non-aqueous phase in liquid blobs in the overlying soil. At the sampling site, the bedrock is at a depth of 5 m. Soil core samples were taken from a depth of 3–5 m. The soil was sieved to a particle size of <2 mm before the experiments were performed. The total PAH concentration in the soil was 1203 mg kg^{-1}. Eleven different PAH compounds were detected. The total iron concentration in the soil was 4 g kg^{-1}. The percentage of organic matter was 1.5 wt%. The humidity of the soil was 7.7%.

The concentrations of the 11 PAHs detected in the untreated soil are shown in Table 1. The concentrations of the PAHs in the soil exceed the screening threshold values established in Spain to regulate the potentially unacceptable risk of contamination,

Table 1
The concentrations and standard deviations of PAHs in the contaminated soil (mg PAH kg^{-1} dry soil) and general levels of reference for PAHs (mg kg^{-1} dry weight) based on the soil use, defined in the Spanish Royal Decree 9/2005 [28].

PAHs concentration in the soil sample and generic levels of reference defined by the Spanish Royal Decree 9/2005				
PAH	mg kg^{-1} ± S.D. dry soil	Industrial use	Urbane use	Others
Naphthalene	nd	10	8	1
Acenapthtylene	nd			
Acenaphthene	165 ± 12	100	60	6
Fluorene	124 ± 4	100	50	5
Phenanthrene	258 ± 16			
Anthracene	68 ± 4	100	100	45
Fluoranthene	228 ± 18	100	80	8
Pyrene	153 ± 10	100	60	6
Benzo(a)Anthracene	41 ± 4	20	2	0.2
Chrysene	58 ± 4	100	100	20
Benzo(b)Fluoranthene	44 ± 5	20	2	0.2
Benzo(k)Fluoranthene	25 ± 3	100	20	2
Benzo(a)Pyrene	40 ± 5	2	0.2	0.02
Dibenzo(a,h)Anthracene	nd	3	0.3	0.03
Benzo(g,h,i)Perylene	nd			
Indeno(1,2,3-cd)Pyrene	nd	30	3	0.3
Total	1203 ± 70			

nd = not detected.