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Oxidant selection to treat an aged PAH contaminated soil by in situ chemical oxidation

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ABSTRACT

This work is a part of the OXYSOL project aiming at the conception of a global treatment pathway including In Situ Chemical Oxidation to clean up soils of former metallurgical sites. It deals with the selection of the most adapted oxidants. Batch experiments were performed with aged contaminated soil samples of a former steel-making plant to degrade the 16 US EPA PAHs. In this research, hydrogen peroxide, modified Fenton's reaction, potassium permanganate, sodium percarbonate and sodium persulfate were compared at high and moderate doses. Hydrogen peroxide, modified Fenton's reagent, percarbonate and activated persulfate led to a maximum degradation ratio of 45%. A higher ratio (70%) was obtained with a high dose of permanganate. Except for permanganate, increasing oxidant dose did not improve degradation rates, especially with radical-based oxidative systems probably due to radical scavenging. Oxidant doses had an effect on pH that drastically increased or dropped in some cases, which was a drawback. Permanganate efficacy was mainly assigned to its persistence. In all cases, the low availability of PAHs, partly sequestrated in the aged soil, was identified as the most limiting factor for degradation performance. Oxidants were ranked according to their efficiency for PAH oxidation in soils. Efficiency was not correlated to the doses.

Introduction

Former steel-making factories, manufactured gas plants and wood treatment facilities has given birth to huge brownfields contaminated by polycyclic aromatic hydrocarbons (PAHs) [1,2]. PAH content may range from a few thousands to a few tens of thousands ppm. Around 130 PAHs have been identified but the most studied are the 16 PAHs listed by the US Environmental Protection Agency (US EPA) as priority contaminants. Some of them are known to be toxic, carcinogenic and mutagenic [3]. PAHs are neutral and hydrophobic molecules, rather thermally stable, and slowly degraded by microorganisms; they are low volatile, low soluble in water and strongly sorbed onto soil organic matter (SOM) [2]. The initial reversible sorption is followed by a slow diffusion into the matrix, known as aging process. PAHs that have been present for years in a soil matrix are very little extractable and bioavailable [4–6].

For these reasons, PAH remediation is a complex task [3]. Generally, the most contaminated soil fractions are treated by thermal desorption after excavation while for lower contamination levels, biological treatments are more appropriate and cheaper [7]. Biological treatments are effective for low-molecular weight PAHs but degradation is limited by PAH low availability [5,6,8]. In this context, *in situ* chemical oxidation (ISCO) is a promising alternative, which can be very efficient in a relatively short time period. ISCO aims at the degradation of the target contaminants after their reaction with an oxidant injected into the groundwater or soil [9–12].

The conventional oxidants are ozone, permanganate, Fenton's reagent, percarbonate and activated persulfate. Permanganate, used as sodium or potassium permanganate has been extensively investigated and applied [9,10,13]. With a standard oxidation potential of 1.7 V, it is considered as a strong oxidant able to break carbon–carbon double bonds, aldehyde and hydroxyl groups, but not benzene rings. Then it was believed that permanganate was not suitable for PAH oxidation, but many contributions have shown its effectiveness for these pollutants

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[14–18]. Permanganate has the advantage to be very persistent in soils, but it can be consumed by many side reactions (e.g. SOM oxidation) leading to a high natural soil demand. Recently, it has become available in the form of slow-release paraffin-$KMnO_4$ candles allowing a progressive distribution and able to degrade PAHs in groundwater [19]. Another oxidant that has been widely studied is hydroxyl radical, which is a very strong oxidant (standard oxidation potential 2.8 V) [9–12,20–23]. It is generated by the decomposition of hydrogen peroxide in the presence of ferrous ions. This reaction is known as ''Fenton reaction'' when run at acidic pH (*ca* 3) and ''Modified Fenton Reaction'' (MFR) when run at near neutral or natural soil pH. Chelating agents are often used to maintain iron in solution, preventing iron precipitation (citric acid, EDTA, sodium pyrophosphate) [24]; sodium pyrophosphate was found the most effective for PAH treatment. Instead of using iron solutions, some authors have shown the effectiveness of iron oxides for heterogeneous catalysis: goethite, hematite, ferrihydrite or magnetite [25,26]. In some cases, no iron is added and activation is done by endogenous iron [12], the reaction is called ''Fenton-like reaction''. Hydrogen peroxide is hazardous since its decomposition is highly exothermic, then slow-release compounds have been developed, namely sodium percarbonate [27,28]. It has seldom been used for PAH remediation and was less effective than catalyzed hydrogen peroxide [29]. More recently, sulfate radical, a strong oxidant (standard oxidation potential 2.6 V) obtained by activation of sodium persulfate has been tested for pollutant removal [9–11,15,30–32]. Activation can be performed by several methods: thermal photochemical or chemical using dissolved iron or solid iron (e.g. magnetite), in alkaline conditions or with hydrogen peroxide [15,30,33–35].

The choice of an oxidant for a given remediation situation is governed by several factors. The soil composition (SOM nature and content), the texture and porosity strongly affect PAH availability. pH is also of importance since a low pH is preferred for Fenton's reaction while persulfate treatment is favored at a high pH. Operational conditions (temperature, injection procedure, reaction time) also have a significant influence. In some cases, treatment effectiveness increases with oxidant dosage but when radicals are involved, reaction may be stopped by radical scavenging and so a high oxidant dose can cause negative effects. For these reasons, a bench scale study is required for each remediation situation with the aim to choose the best operational conditions and predict the expected PAH degradation rate. However, in many situations of aged soil remediation, a very high PAH removal rate is not directly attained with oxidation and a post-treatment by bioremediation is performed to achieve clean-up objectives [8,36–38].

The present work was the first step of the OXYSOL project (http://www.oxysol-anr.org). OXYSOL aimed at combining ISCO, bioremediation and soil restoration [39] for the remediation of contaminated topsoil of a former steel-making factory contaminated by PAHs and metals. The objective of the present contribution was to compare the effects of oxidants at the bench scale to select the best candidates to degrade the 16 US EPA PAHs with doses of oxidants as low as possible, in order to minimize treatment cost and environmental impacts. Were used (i) persistent oxidants obeying redox reactions: potassium permanganate and sodium persulfate and (ii) radical-based oxidant systems: hydrogen peroxide, Fenton's reagents with different additives, sodium percarbonate and activated persulfate. For Fenton's system, we tested citric acid to avoid iron hydroxide precipitation and a cyclodextrin to enhance PAH desorption/availability. The experiments were started with relatively high amounts of oxidants to test the limits of the reactions and then the doses were lowered.

Materials and methods

Chemicals

A standard solution of the 16 USA EPA PAHs standard (1 mg L^{-1} each) and sulfuric acid (96%) were supplied by Sigma–Aldrich, sodium percarbonate by Solvay Chemicals, sodium persulfate (>99%) by Acros Organics, ortho-phosphoric acid (85%) by Merck, potassium permanganate (>99%) by Fluka Chemika, citric acid (>99%) by Prolabo, hydroxypropyl-beta-cyclodextrin by Molekula, hydrogen peroxide (50%), ferrous sulfate heptahydrate Rectapur and sodium carbonate Normapur by VWR.

Soil sample

The sample was a sandy loam soil collected at a former steel-manufacturing site (Neuves-Maisons, Northeastern France) [33,40–44]. This soil was previously thoroughly characterized: the composition of all the size fractions and the distribution of PAHs and metals among these fractions had been determined; morphologies had been observed by SEM [41,44]. It had been shown that 69 wt% of the material was formed of particles larger than 2 mm, composed of various materials formed in blast-furnace. In the present study, a 20 kg sample was air-dried, and sieved to 2 mm. Soil analyses were performed by the Laboratory of Soil Analyses (Arras, France): particle size distribution, pH, total carbonate, total organic carbon. Soil pH was measured in water suspension at the ratio 1/5 (v/v) (NF ISO 10390). Total carbonate (NF ISO 10693) was determined by measurement of the emitted volume of CO_2 during sample acidification with HCl. Total C (NF ISO 10694) was determined by dry combustion and quantification of the emitted volume of CO_2. Organic carbon was calculated from the difference between total carbon and total carbonate. Trace elements were measured by ICP-OES (Cr, Cu, Ni and Zn) and by ICP-MS (Pb) after lithium metaborate attack and acid digestion. PAHs were analyzed as described in *Analytical methods* section.

The sieved sample was composed of 62.9 wt% sand, 24.1 wt% silt and 13.0 wt% clay. It contained 71.5 g kg^{-1} organic carbon, 1.55 g kg^{-1} of the 16 US EPA PAHs and heavy metals: Zn (2.6 g kg^{-1}), 1), Pb (684 mg kg^{-1}), Cr (325 mg kg^{-1}), Ni (260 mg kg^{-1}), and Cu (110 mg kg^{-1}). The distribution of the 16 PAHs was (in mg kg^{-1}): naphthalene 30.0, acenaphtylene 1.7, acenaphtene 62.0, fluorene 57.0, phenanthrene 170.0, anthracene 63.0, fluoranthene 250.0, pyrene 200.0, chrysene 110.0, benzo(a)anthracene 130.0, benzo(b)-fluoranthene 120.0, benzo(k)fluoranthene 68.0, benzo(a)pyrene 120.0, dibenzo(a,h)anthracene 13.0, benzo(g,h,i)perylene 71.0, indeno(1,2,3-cd)pyrene 85.0. The calcium carbonate content was 35 g kg^{-1} and pH in water 7.4.

Batch experiment design

Stoichiometric molar ratio

To compare the results, oxidant doses were expressed in terms of stoichiometric molar demand (SOD) calculated from the stoichiometric molar ratio (SMR) previously defined [16,20,28,43]. SMR is the number of moles of an oxidant required to degrade one mole of a target component into CO_2 and H_2O. Stoichiometric coefficients were obtained by listing the reactions between each oxidant and each PAH and SMR was calculated as the weighted average of these coefficients for the soil sample.

Then the stoichiometric oxidant demand yields:

$$\mathrm{SOD} = M_{\mathrm{ox}}\mathrm{SMR}[\mathrm{PAH}] \tag{1}$$

where SOD is expressed in g $kg_{\text{dry soil}}^{-1}$, M_{ox} is the molar mass of the oxidant (g mol^{-1}), SMR the stoichiometric molar ratio (–) and