

## Strategies for oxidation of PAHs in aged contaminated soil by batch reactors

Marina Peluffo<sup>a</sup>, Janina A. Rosso<sup>a</sup>, Irma S. Morelli<sup>b,c</sup>, Verónica C. Mora<sup>b,\*</sup>

<sup>a</sup> Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas, INIFTA (UNLP; CCT-La Plata, CONICET), La Plata, Argentina

<sup>b</sup> Centro de Investigación y Desarrollo en Fermentaciones Industriales, CINDEFI (UNLP; CCT-La Plata, CONICET), La Plata, Argentina

<sup>c</sup> Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC-PBA), Argentina

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### ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) are neutral, nonpolar and hydrophobic molecules that tend to sorb onto soil organic matter. Chemical oxidation is a good choice to avoid the limitations of bioremediation.

To evaluate the efficiency of different types of oxidation (permanganate, hydrogen peroxide, and persulfate) and activation (heat, alkaline, and iron), batch reactors were prepared. The soil was contaminated with phenanthrene and pyrene ( $1200 \pm 200$  and  $2800 \pm 100$  mg per kg of dry soil, respectively) and aged for fifteen months. Treatments were prepared with 10 g of contaminated dry soil and 20 ml of water and incubated at room temperature for 7 days. Analyses of phenanthrene and pyrene concentrations, soil pH and electric conductivity were performed. Counts of heterotrophic cultivable bacteria on R2A medium and PAH-degraders were carried out after 7 days of treatment. The persulfate treatment at room temperature, without the addition of activators, achieved better results than treatments with the same doses of permanganate or hydrogen peroxide. All the strategies to improve persulfate treatments yielded higher degradation of pyrene than the biological control, as expected from the structural description of this compound by Clar's model. The thermal activation of persulfate ( $65^\circ\text{C}$  for 6 h) led to the degradation of more than 90% of both PAHs after 7 days of treatment.

### 1. Introduction

Industrial activities have left behind large areas contaminated with persistent organic pollutants, especially polycyclic aromatic hydrocarbons (PAHs) (Barnier et al., 2014). These pollutants represent a threat to human health because of their recognized carcinogenic and mutagenic effects. Up to now, approximately 130 PAHs have been identified, but only 16 PAHs have been listed by the US Environmental Protection Agency (US EPA) as priority contaminants due to their prevalence (Lemaire et al., 2013a). These neutral, nonpolar and hydrophobic molecules are slightly volatile, slightly soluble in water, and tend to sorb onto soil organic matter (SOM). In the case of high contamination levels, thermal desorption is commonly used to treat soil after excavation (Ranc et al., 2016), while less contaminated soils are generally left to naturally attenuate or are treated by monitored biological treatments (Lu et al., 2011). PAH bioremediation usually needs more time than other technologies (Singh et al., 2009) and can be incomplete because of the low availability and recalcitrance of PAHs (Posada-Baquero and Ortega-Calvo, 2011). Chemical oxidation can be used to degrade PAHs and not merely transfer them to another compartment. However, the remediation of PAH-contaminated soil using chemical oxidation technology remains a big challenge (Lemaire et al.,

2013a) because the efficiency of the chemical oxidation of PAHs in soils depends on the soil characteristics (such as organic matter and oxide contents, specific surface area, etc.) and PAH properties (such as molecular weight, water solubility, amount of aromatic rings, etc.) (Gan et al., 2009).

Permanganate has been widely used to break down organic and inorganic compounds. The main advantage of this oxidant is that it persists in soils and groundwater. It is also relatively cheap and easy and safe to use compared to hydrogen peroxide. However, its natural oxidant demand is generally high, leading to high permanganate consumption, which is a drawback. The oxidation of organic compounds by permanganate ions produces manganese dioxide ( $\text{MnO}_2$ ) as well as  $\text{CO}_2$  or organic intermediates. The excess of  $\text{MnO}_2$  could reduce soil permeability, an obviously undesirable side effect that may affect soil quality (Siegrist et al., 2002; Sirguey et al., 2008).

Chemical oxidation by Fenton reagents is a well-developed technology for the remediation of soils and water contaminated with organic compounds. In particular, they were applied to remediate soils contaminated with pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and total petroleum hydrocarbons (TPHs) (Cheng et al., 2016a). A Fenton reaction is based on the generation of reactive hydroxyl radicals ( $\text{HO}\cdot$ ) (Usman et al., 2016).

\* Correspondence to: calle 50 y 115 (CINDEFI), La Plata, Buenos Aires, Argentina.  
E-mail address: [vcmorad@quimica.unlp.edu.ar](mailto:vcmorad@quimica.unlp.edu.ar) (V.C. Mora).

The strong standard oxidation potential [ $E^\circ(\text{HO}\cdot/\text{H}_2\text{O}) = +2.8 \text{ V}$ ] and nonselective reactivity of  $\text{HO}\cdot$  are primarily responsible for the high efficiency in removing recalcitrant organic compounds (Bokare and Choi, 2014). The production of  $\text{HO}\cdot$  by Fenton reagents occurs with the addition of  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{2+}$  salts. Studies have demonstrated that Fenton/Fenton-like reactions cannot only be catalysed by free iron ions ( $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ ) but also by endogenous (Lemaire et al., 2013a) or synthesized iron oxides ( $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ) (Cheng et al., 2016b). Therefore, it is not always necessary to add external iron to produce  $\text{HO}\cdot$ .

Persulfate (PS) has been investigated because it can be activated by heat (Mora et al., 2009), transition metals (Anipsitakis and Dionysiou, 2004), bases (Furman et al., 2010), and ultraviolet light (Lin and Lee, 2015) to form the highly reactive sulfate radicals. These radicals are an alternative method for the degradation of organic contaminants due to the high removal efficiency of pollutants that cannot be eliminated by traditional treatments (Ranc et al., 2016). They have a high oxidation potential ( $E^\circ(\text{SO}_4^{\cdot-}/\text{SO}_4^{2-}) = +2.60 \text{ V}$ ) and are nonselective (Matzek and Carter, 2016). Activated persulfate has widespread applications for remediation because formed radicals react with organic chemicals to cause either partial or complete mineralization. In situ remediation with activated persulfate oxidation may be preferred over hydrogen peroxide-based processes because the persulfate anion is more stable and may be transported further into the subsurface before being activated for contaminant degradation (Waldemer et al., 2007; Yan et al., 2013). For in situ applications,  $\text{Fe(II)}$  and  $\text{Fe(III)}$  are the most commonly used activators due to their natural abundance in porous media and benign nature (Tsitonaki et al., 2010). In a previous work, we found that soil natural conditions were sufficient to decompose PS without the addition of activators and that the persistence of PS was approximately 7 days (Mora et al., 2014).

The choice of an oxidant for a given remediation situation is governed by several factors, as reported by some authors (Anipsitakis and Dionysiou, 2004; Lemaire et al., 2013a; Pardo et al., 2015). The soil composition (SOM nature and content), texture and porosity strongly affect PAH availability (Lemaire et al., 2013a). Another important factor is pH, since a low pH is preferred for Fenton reactions (Pardo et al., 2015) and the metal activation of persulfate (Anipsitakis and Dionysiou, 2004) because of the behaviour of soluble iron species.

Remediation of some recalcitrant xenobiotic chemicals may require a combination of chemical, physical and biological steps to increase the efficacy of contaminant destruction (Singh et al., 2009). Frequently in aged contaminated soil remediation, a low PAH removal rate is attained with chemical oxidation. Then, in order to efficiently combine chemical oxidation with bioremediation posttreatment, it is necessary to control the impact of the oxidation on the soil properties such as pH and salinity (Haapea and Tuhkanen, 2006; Sutton et al., 2011; Valderrama et al., 2009). Moreover, the addition of high doses of the oxidant affects the viability of later biodegradation.

In some cases, treatment effectiveness increases with the oxidant dosage (Ferrarese et al., 2008; Huang et al., 2005; Ravikumar and Gurol, 1994). However, when the mechanism of the chemical reaction involves radicals, the reaction may be stopped by radical scavenging, and so a high oxidant dose can cause negative effects (Lemaire et al., 2013a). For these reasons, a bench scale study is required for each remediation situation in order to choose the best operational conditions and predict the expected PAH degradation rate.

The aim of this contribution is to investigate the efficiency of low doses of potassium permanganate, hydrogen peroxide, Fenton reactions, persulfate and activated persulfate to degrade phenanthrene and pyrene (as model PAHs) in batch systems with artificially spiked and aged soil.

## 2. Materials and methods

### 2.1. Chemicals

Sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ,  $\geq 99.0\%$ , Merck), sodium hydroxide ( $\text{NaOH}$ ,  $\geq 97.0\%$ , Cicarelli), ethyl acetate ( $\text{C}_4\text{H}_8\text{O}_2$ ,  $\geq 99.5\%$ , Cicarelli), anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ,  $\geq 97.0\%$ , Carlo Erba), iron sulfate heptahydrate ( $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ ,  $\geq 97.0\%$ , Mallinckrodt), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30% w/v (100 vol.), Biopack), phenanthrene ( $\text{C}_{14}\text{H}_{10}$ ,  $\geq 99.5\%$ , Carlo Erba) and pyrene ( $\text{C}_{16}\text{H}_{10}$ ,  $\geq 98.0\%$ , Sigma) were used. Potassium permanganate ( $\text{KMnO}_4$ ,  $\geq 99.0\%$ ), monobasic potassium phosphate ( $\text{KH}_2\text{PO}_4$ ,  $\geq 99.4\%$ ) potassium phosphate ( $\text{K}_2\text{HPO}_4$ ,  $\geq 98.0\%$ ), disodium ethylenediaminetetraacetic acid ( $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8\cdot 2\text{H}_2\text{O}$ ,  $\geq 99.0\%$ ) were provided by Anedra.

### 2.2. Soil

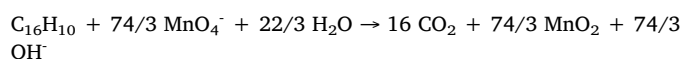
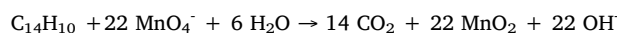
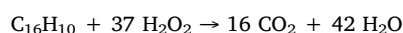
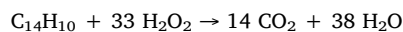
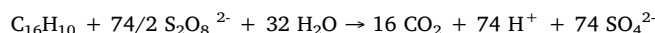
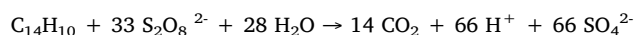
The soil selected for the study was an uncontaminated soil from an area near La Plata City, Argentina ( $34^\circ 50' \text{ S}$ ,  $58^\circ 10' \text{ W}$ ). It was analysed in the Laboratory of Soil Science at the University of La Plata and showed the following physicochemical properties: a pH of 6.6, 4.67% organic carbon (Walkley-Black method), 8.05% SOM, 3.89 mg/kg total nitrogen (wet digestion, and evaluation by Micro-Kjeldahl method), 4.0 mg/kg available phosphorus (Bray Kurtz No. 1 method), electrical conductivity of  $3.3 \pm 0.3 \text{ dS m}^{-1}$  (on the saturated paste extract) and  $109.9 \pm 0.9 \text{ mg}$  of Fe per kg of dry soil (extracted with EDTA and determined according to EPA method 7950).

The soil was contaminated with 2000 mg of phenanthrene and 3000 mg of pyrene per kg of dry soil ( $\text{kg}_{\text{DS}}$ ) and aged at  $4^\circ \text{C}$  for 15 months. The concentrations of both PAHs were determined before each set of experiments. The PAHs were delivered in an acetone solution and mixed manually into the soil with a spatula, as reported (Mora et al., 2014).

### 2.3. Oxidant doses

For the field application of ISCO (in situ chemical oxidation), one major issue is the determination of the optimal doses of the reagents in the oxidizing solution. The oxidant/pollutant dose is the molar or mass amount of oxidant needed to degrade a known amount of pollutants (Ranc et al., 2016).

The calculation of the oxidant doses was based on the stoichiometric balances for each PAH/oxidant couple, and we considered the reaction leading to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Lemaire et al., 2013b).



### 2.4. Treatments

Batch reactors consisting of 10 g dry soil ( $\text{g}_{\text{DS}}$ ) and 20 ml of aqueous phase (which contains the oxidant, the activator or distilled water) were placed in a glass container with continuous stirring. All the treatments were carried out in triplicate trays and incubated at  $24 \pm 2^\circ \text{C}$  (regional climate conditions) for 7 days. For the experiments of thermal activation of PS, the reactors were held at  $65 \pm 2^\circ \text{C}$  for the first 6 h and then were incubated at  $24 \pm 2^\circ \text{C}$  for 7 days.

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