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Persulfate treatments of phenanthrene-contaminated soil: Effect of the application parameters

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ABSTRACT

The aim of this work was to study the effects of the parameters involved in persulfate (PS) application, namely, the cation counterion, mode of persulfate addition and soil-moisture content, to optimize the use of low doses of PS coupled with bioremediation technologies. Soil microcosms were contaminated with 110 ± 20 mg of phenanthrene per kilogram of dry soil. The efficiency of each treatment in phenanthrene elimination was evaluated. Additionally, the impact on cultivable autochthonous heterotrophic bacteria populations was examined.

The addition of sodium persulfate in successive doses (14.9 g/kg_{DS}) showed the greatest efficiency in phenanthrene elimination (36%) after 7 days of treatment, but inhibited further bioremediation. Sodium persulfate was more efficient than ammonium. Increased moisture enhanced the bioremediation but inhibited the oxidative treatment. The persulfate-ion decomposition rate decreased at high moisture levels, possibly through diluting activators within the soil.

The results suggest that, for oxidative treatments of contaminated soil, the application of low doses of sodium PS at low soil-moisture levels is the most effective option for an elimination of phenanthrene that is compatible with bioremediation.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are composed of two or more aromatic rings that are fused together in a linear, angular or cluster arrangement when a pair of carbon atoms is shared between them (Dhote et al., 2010). PAHs are mainly formed during natural and anthropogenic combustion processes of fuels (Samburova et al., 2016). There are sixteen PAHs that are considered as priority pollutants by the United States Environmental Protection Agency (US EPA) and the European Community, due to their toxic, mutagenic, and carcinogenic properties(Schneider et al., 2002; Tobiszewski and Namieśnik, 2012; Usman et al., 2016) and their recalcitrant nature.

A strategy frequently used for the treatment of soils polluted with PAHs is bioremediation through the degradative action of microorganisms because of the low cost and the low impact on the site to be treated. Although accelerated bioremediation processes have been applied (Ward et al., 2003), most of the soil bioremediation processes are relatively slow processes, and frequently it either takes a long time or desired end points may not be achieved due to the lack of suboptimal environmental conditions for selection and growth promotion of the biological system employed (Singh et al., 2009).

Chemical-oxidation technology is a potent option for soil restoration that can effectively eliminate an extensive range of contaminants, including PAHs. In addition, chemical oxidation offers the potential of a complementary remediation strategy that could deliver effective and efficient results while avoiding the principal drawbacks associated with bioremediation alone (Sutton et al., 2011).

In ISCO, inorganic oxidants are injected into the subsurface to degrade organic contaminants into carbon dioxide or other less toxic products (Siegrist et al., 2011). Two common oxidants applied in ISCO are hydrogen peroxide and persulfate, both of which oxidize organic contaminants by generating highly reactive radical species, such as hydroxyl and sulfate radicals (Deng et al., 2014). Hydrogen peroxide decomposes very quickly and can produce substantial heat, which not only induces potential safety problems but also causes the escape of volatile organic compounds. As a result, persulfate has been increasingly used in recent years for the remediation of organic contaminated sites, because persulfate tends to have much longer lifetime in the subsurface and it is safer to handle and more applicable to subsurface than hydrogen peroxide (Tsitonaki et al., 2010).

Persulfate (PS) has several advantages such as high aqueous solubility, high stability at room temperature and relatively low cost

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(Peluffo et al., 2016). It reacts slowly with many organic compounds (Furman et al., 2010), but can be chemically (Tsitonaki et al., 2010), photochemically (Lin and Lee, 2015; Rosso et al., 1999) or thermally (Mora et al., 2009) activated to generate the more strongly oxidizing sulfate radicals, $SO_4^{\cdot -}$ with a redox potential E° ($SO_4^{\cdot -}$ / SO_4^{2-}) of 2.6 V (Wardman, 1989). These radicals are responsible for the effectiveness of the PS ion in oxidative treatments of soils (Osgerby, 2006). Moreover, since iron is a natural constituent of soil, its addition is not necessary for PS activation (Osgerby, 2006).

The possibility of combining PS application with biologic remediation is an attractive strategy. Although the operational conditions in oxidative treatments will have a significant influence on the results (Lemaire et al., 2013b), the impact of that approach in combination with bioremediation processes requires a thorough understanding of the impact of each step on soil geochemistry, biota, and contaminant dynamics (Sutton et al., 2011).

Discrepant results were obtained depending on the dosage of oxidant—the main parameter studied in the oxidative treatments of soil (Ranc et al., 2016). The general tendency in this approach was to apply high quantities of PS, but they produced a wide range of results. In some instances, the effectiveness of the treatment can increase with the dosage of oxidant (Huang et al., 2005). However, other authors reported that PAH degradation ratios with PS were up to 80% and not directly correlated with the oxidant dose (Lemaire et al., 2013a; Mora et al., 2014).

Nevertheless, the dosage of oxidant poses other problems when it is intended to be used in conjunction with bioremediation. Because the addition of PS causes a decrease in the pH and an increase in the salt content, at a high dose the consequent environmental perturbation would limit the efficiency of bioremediation (Lemaire et al., 2013a). An alternative strategy—the one proposed here—is the addition of PS in a series of low doses to minimize the impact on the autochthonous microbial community.

Another key factor in the application of PS is the nature of the salt employed. Most of the researchers use the persulfate sodium salt as the oxidant because it has higher solubility than the potassium counterion. Ammonium persulfate, however, is quite soluble (58.2 g/100 ml H_2O for the NH_4^+ *versus* 55.6 g/100 ml H_2O for the Na^+ salt at 20 °C) (Osgerby, 2006). It was reported that the addition of nutrients to the soil, in the form of nitrogen, phosphorous and carbon compounds, allows the native microbial population to develop and augment. Thus, such addition is translated into an increase of microorganisms capable of metabolizing the pollutant, therefore enhancing the biodegradation rate (Calvo et al., 2009). Then, the use of ammonium persulfate could increase the amount of available nitrogen in the soil, thus potentially improving the growth of bacterial populations. This possibility was thus investigated in the present work.

Soil hydrocarbon biodegradation may be limited by the water available for microbial growth and metabolism. A decrease in moisture content results in a decrease in microbial activity, while rewetting causes a large and rapid increase in activity (Ayotamuno et al., 2006). Generally, optimum activity occurs when the soil moisture is 50%–80% of the field capacity (Calvo et al., 2009). However, when oxidant is added, most of the treatments tested in the laboratory and carried out in batch reactors have been designed under the assumption that the best option is the application of the oxidant in an aqueous solution at a soil:solution ratio varying between 1:1 (Andreottola et al., 2010) and 1:10 (Usman et al., 2012); even though the rational use of water could be considered as a factor to reduce costs and the environmental impact of the treatment.

Hence, attention should be given to the control of the moisture level in the soil to combine the chemical treatment with the biological one. Accordingly, the present experiments assayed the controlled addition of water up to 44.5% and 65% of the field capacity (24.9% and 36.5% MC, respectively). Moreover, working with this moisture content is more representative of the unsaturated zone of soils (Ranc et al., 2016).

The aim of this work was to study the effects of the parameters involved in PS application (*e.g.*, the cation counterion, mode of PS addition, and soil-moisture content) on PAH degradation and its impact on the cultivable autochthonous heterotrophic bacteria populations in order to optimize an ISCO pre-treatment that could be coupled to bioremediation processes. Moreover, due to the moisture content range studied, the conclusions obtained here could be applied to the non-saturated soil zone that has been much less studied in oxidation treatments.

2. Materials and methods

2.1. Soil characteristics

The uncontaminated soil from an area near the city of La Plata, Argentina (34° 50′ S, 58°1 0′ W) that was selected for the study and analyzed in the Laboratory of Soil Science at the University of La Plata had the following physicochemical properties: a clay loam texture, a pH of 6.6, 4.67% organic carbon (Walkley-Black method), 3.89 mg/kg total nitrogen, 4.0 mg/kg of available phosphorus (Bray Kurtz No. 1 method), an electrical conductivity of 3.3 ± 0.3 dS/m (measured on the saturated-paste extract), and 110 ± 1 ppm of Fe (extracted with EDTA and following the EPA method 7950).

2.2. Soil treatment systems

Soil microcosms consisting of 150 g of sieved soil (2-mm mesh) were placed in a glass container of 250 g capacity. They were contaminated with 110 ± 20 mg of phenanthrene per kilogram of dry soil (kg_{DS}). Phenanthrene was delivered in an acetone solution and mixed manually into the soil with a spatula, as reported (Festa et al., 2016).

The treatments applied are shortly described in Table 1. Persulfate salts were dissolved on the minimum amount of water to deliver into soil, maintaining the desired soil-moisture content. In five treatments, the microcosms were maintained at 24.9% (w/w) soil-moisture content (MC). To each of 2 microcosms sodium PS was added in a single application at 8.6 and 43.0 g/kg_{DS} (NaPS1 and NaPS2, respectively), while in another one the oxidant was introduced in successive additions of 5 g/kg_{DS} (NaPSsucc) each up to a total concentration of 19.3 g/kg_{DS} after 28 days (14.9 g/kg_{DS} after 7 days). In addition, two treatments were prepared with ammonium PS, at 38.4 g/kg_{DS} added either all at once (NH4PS2) or in successive increments of 5 g/kg_{DS} (NH4PSsucc) up to a final concentration of 57.7 g/kg_{DS} after 28 days (15.1 g/kg_{DS} after 7 days). As mentioned above, we tested the utilization of NH_4^+, which would also have the ability to stimulate the intrinsic degradation capacities of autochthonous microbiota (Silva-Castro et al., 2016). It should be mentioned that the molar concentrations of PS in sodium and ammonium salts is affected by their molecular weights (238 and 228, respectively), *e.g.* 5 g of sodium PS corresponds to 0.021 mol while 5 g of ammonium PS corresponds to 0.022 mol.

In two treatments, NaPS3 and NaPS4, sodium PS was applied at

Table 1
Experimental conditions of the persulfate (PS) treatments tested.

Treatment	Application	PS added (g/kg_{DS})	doses	Moisture content (% w/w)
Bio1	none	0	–	24.9
NaPS1	single	8.6	1.8	24.9
NaPS2	single	41.7	8.6	24.9
NaPSsucc	successive	14.9 (at 7 days)	3.1	24.9
NH4PS2	single	38.4	8.3	24.9
NH4PSsucc	successive	15.1 (at 7 days)	3.2	24.9
Bio2	none	0	–	36.5
NaPS3	single	11.1	2.3	36.5
NaPS4	single	55.3	11.4	36.5