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ScienceDirect
Chemosphere 72 (2008) 282–289
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Impact of chemical oxidation on soil quality

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Received 29 August 2007; received in revised form 14 January 2008; accepted 15 January 2008

Abstract

Oxidation treatment helps to reduce the polycyclic aromatic hydrocarbon (PAH) load in contaminated soils but it may also have an effect on the soil quality. The impact of permanganate and Fenton oxidation on soil quality is investigated. Soil quality is restricted here to the potential for plant growth. Soil samples were collected from an agricultural field (S1) and a former coking plant (S4). Agricultural soil was spiked with phenanthrene (PHE) and pyrene (PYR) at two concentrations (S2: 700 mg PHE kg^{-1}, S3: 700 mg PHE kg^{-1} and 2100 mg PYR kg^{-1}). Soils were treated with both oxidation processes, and analyzed for PAHs and a set of agronomic parameters. A plant germination and growth test was run with rye-grass on treated soils. Results showed that both treatments produced the expected reduction of PAH concentration (from 64% to 97%). Besides, a significant loss of organic C and N, and strong changes in available nutrients were observed. Permanganate treatment increased the specific surface area and the cation exchange capacity in relation to manganese dioxide precipitation, and produced a rise in pH. Fenton oxidation decreased soil pH and increased the water retention capacity. Plant growth was negatively affected by permanganate, related to lower soil permeability and aeration. Both treatments had an effect on soil properties but Fenton oxidation appeared to be more compatible with revegetation.

Keywords: Potassium permanganate; Fenton oxidation; PAH contaminated soils; Agronomic parameters; *Lolium perenne*

1. Introduction

The choice of appropriate technologies for soil remediation rarely takes into account the impact on soil quality defined as “the capacity of a specific kind of soil to function within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water quality, and support human health and habitation” (Doran and Parkin, 1994). Assessment of soil quality may provide an effective method for evaluating direct and indirect environmental impacts of treatment technologies (Karlen et al., 1997). This is of utmost importance as soils are often re-used as plant support after remediation.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous compounds of particular concern because of their widespread occurrence in the environment (Wilcke, 2000) and their carcinogenic and/or mutagenic potential (White and Claxton, 2004). The most common treatment technologies for PAH removal from soils are thermal desorption and biodegradation (USEPA, 1992). Chemical oxidation has been increasingly regarded as a relevant alternative to conventional treatment technologies. It can be applied to a variety of recalcitrant organic contaminants, including PAHs (Rivas, 2006). Fenton and permanganate oxidation are the mostly used technologies. Fenton’s reaction

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doi:10.1016/j.chemosphere.2008.01.027

operates by the generation of highly oxidative hydroxyl radicals •OH which react with sorbed and aqueous PAHs and lead to oxidised products. PAH oxidation by permanganate is closely dependant of the chemical reactivity of the target compound (Brown et al., 2003). One major advantage of such oxidation technologies is their ability to overcome the limitations imposed by the low aqueous PAH solubility on the biodegradation and/or dissolution rates, since oxidation products would be more polar than parent compounds (Brown et al., 2003; Millioli et al., 2003).

Side-effects of oxidation processes on soil quality have been investigated so far only through the analysis of toxic metabolites. The combination of Fenton oxidation with bioremediation not only significantly improves PAH removal but also reduces soil toxicity as toxic metabolites resulting from modified Fenton reaction may be removed during bioremediation (Palmroth et al., 2006). The effect of hydrogen peroxide on natural soil organic matter (SOM) is well documented as it is commonly used in laboratory procedures to oxidize SOM prior to mineralogical analyses (Leifeld and Kögel-Knabner, 2001; Mikutta et al., 2005). Some authors showed that •OH radicals preferentially attack aromatic compounds (Mikutta et al., 2005) which may account for the enrichment of aliphatic compounds in treated soils (Leifeld and Kögel-Knabner, 2001). Effects on N-containing compounds are less documented: residual nitrogen in treated soils would be mainly water soluble inorganic species (Mikutta et al., 2005). However, information on the effect of oxidation on physical and some chemical soil properties is lacking. This is of particular importance since treated soils should exhibit optimal functions as plant support.

This work was undertaken to assess the effect of Fenton and permanganate oxidation on some ecological functions of soil. A spiked agricultural soil and an industrial soil collected from a coking plant were subjected to either permanganate or Fenton oxidation. Soil properties were assessed before and after treatment measuring the classical physico-chemical soil parameters and running a plant growth-test with rye-grass chosen because of its wide use in site reclamation.

2. Materials and methods

2.1. Soil sampling and analysis

Soil samples were collected from an agricultural field and a former coking plant (North-Eastern France). The agricultural soil was a Cambisol (IUSS Working Group WRB, 2006); sample was collected in the upper horizon, air-dried for 2 d and sieved at 2 mm. Sample was collected at a former coking plant (GISFI experimental station, www.gisfi.prd.fr) in the upper horizon. Large amounts of soil were excavated and homogenized by quartering. Subsamples were collected air-dried at 40 °C, sieved at 2 mm. Soil analyses were performed by the laboratory of soil analyses (Arras, France) according to French standards (AFNOR, 1999): water holding capacity (WHC) (saturated soil compression at 10 kPa for 24 h), permanent wilting point (saturated soil compression at 1.5 MPa for 24 h), particle size distribution, pH, total organic carbon, total N, extractable P (Olsen method), cation exchange capacity (CEC, Metson method), exchangeable bases, nitrate and ammonium (Kjeldahl method), extractable iron and extractable manganese. Specific surface area was measured in the laboratory by N_2 adsorption with a Sorptomatic 1990 (ThermoQuest Instruments).

2.2. Spiking of the agricultural soil

PAH solutions were prepared by dissolving phenanthrene in 40 ml methanol and pyrene in 40 ml acetone. Soil samples of 2 kg received the appropriate solutions to reach concentrations of 700 mg phenanthrene kg^{-1} dry soil (S2), 700 mg phenanthrene and 1400 mg pyrene kg^{-1} dry soil (S3). Control (S1) was the non-spiked agricultural soil. Spiked soils were manually mixed to ensure homogeneity. Solvents were evaporated for 48 h at room temperature under a ventilated hood. Four soil samples presenting a range of PAH concentration from 0 to 3 264 mg 16 USEPA PAHs kg^{-1} dry soil were eventually available: S1–S3 and the coking plant soil sample S4 (Table 1).

2.3. Oxidation processes

All the experimental conditions used were obtained from a previous experiment according to a factorial design (Silva, 2007). The effects of five variables on PAH degradation were evaluated: pH, reaction time, exposure (or not) to ultraviolet radiation, hydrogen peroxide concentration and

Table 1
Concentrations of the 16 USEPA PAHs in the agricultural soil S1, the spiked soil samples S2 and S3, and the soil sampled at a former coking plant S4

PAH	S1	S2	S3	S4
		mg kg^{-1} dry soil		
Naphthalene	nd	nd	nd	nd
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	490 ± 56
Fluorene	nd	nd	nd	60 ± 7
Phenanthrene	nd	701 ± 1	701 ± 1	332 ± 4
Anthracene	nd	nd	nd	129 ± 16
Fluoranthene	nd	nd	nd	664 ± 35
Pyrene	nd	nd	1406 ± 3	371 ± 117
Benzo(*a*)anthracene	nd	nd	nd	277 ± 3
Chrysene	nd	nd	nd	221 ± 13
Benzo(*b*)fluoranthene	nd	nd	nd	136 ± 14
Benzo(*k*)fluoranthene	nd	nd	nd	8.7 ± 0.2
Benzo(*a*)pyrene	nd	nd	nd	142 ± 9
Indeno(1,2,3-*c*-*d*)pyrene	nd	nd	nd	66 ± 7
Dibenzo(*a*,*h*)anthracene	nd	nd	nd	64 ± 2
Benzo(*g*,*h*,*i*)perylene	nd	nd	nd	303 ± 37
Total		701 ± 1	2107 ± 4	3264 ± 320

(nd = not detected).
Values are given as mean ± standard error (3 replicates).