



Effect of pre-heating on the chemical oxidation efficiency: Implications for the PAH availability measurement in contaminated soils



Coralie Biache^{a,b,*}, Catherine Lorgeoux^{c,d}, Sitraka Andriatsihoarana^{a,b,c,d,e}, Stéfán Colombano^e, Pierre Faure^{a,b}

^a Université de Lorraine, LIEC, UMR7360, Vandœuvre-lès-Nancy 54506, France

^b CNRS, LIEC, UMR7360, Vandœuvre-lès-Nancy 54506, France

^c Université de Lorraine, GeoRessources, UMR7359, Vandœuvre-lès-Nancy 54506, France

^d CNRS, GeoRessources, UMR7359, Vandœuvre-lès-Nancy 54506, France

^e BRGM, Orléans 45060, France

HIGHLIGHTS

- KMnO₄, H₂O₂ and Fenton-like treatments were applied on PAH-contaminated soils.
- Soils were heated prior the oxidation in order to increase the PAH availability.
- KMnO₄ was efficient to degrade PAHs even in samples presenting low PAH-availability.
- H₂O₂-based treatments were sensitive to PAH availability

ARTICLE INFO

Article history:

Received 2 September 2014

Received in revised form

15 December 2014

Accepted 21 December 2014

Available online 24 December 2014

Keywords:

Hydrogen peroxide

Potassium permanganate

Fenton-like

Polycyclic aromatic hydrocarbon

Contaminant availability

ABSTRACT

Three chemical oxidation treatments (KMnO₄, H₂O₂ and Fenton-like) were applied on three PAH-contaminated soils presenting different properties to determine the potential use of these treatments to evaluate the available PAH fraction. In order to increase the available fraction, a pre-heating (100 °C under N₂ for one week) was also applied on the samples prior oxidant addition. PAH and extractable organic matter contents were determined before and after treatment applications. KMnO₄ was efficient to degrade PAHs in all the soil samples and the pre-heating slightly improved its efficiency. H₂O₂ and Fenton-like treatments presented low efficiency to degrade PAH in the soil presenting poor PAH availability, however, the PAH degradation rates were improved with the pre-heating. Consequently H₂O₂-based treatments (including Fenton-like) are highly sensitive to contaminant availability and seem to be valid methods to estimate the available PAH fraction in contaminated soils.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The European Environment Agency (EEA) inventoried about 1.5 millions of contaminated sites in Europe including 200,000 sites contaminated by polycyclic aromatic compounds (PACs) comprising polycyclic aromatic hydrocarbons (PAHs) [1]. These sites are mostly former coking plant, gas plant and wood treating facilities. In France these sites account for almost 22% of the inventoried contaminated sites [2]. Due to the PAH recalcitrance and their toxic and

carcinogenic properties that place them in the US-EPA pollutant priority list [3], applications of remediation treatments are necessary to rehabilitate these sites. One of the main factors determining the efficiency of these remediation treatments is the contaminant availability [4–6]. Several methods are commonly used to estimate the (bio)available fraction of the contamination. Mild extractions [7,8], cyclodextrine extraction [9,10], Tenax resin extraction [4], passive samplers [11,12], biosensors [13] and microbial incubations [14,15] can be cited. Another method was investigated by Cuypers et al. [16] implying the application of chemical oxidant. Such reagents (e.g., O₃, KMnO₄, H₂O₂, persulfate) are commonly used to treat contaminated matrixes and they can be activated by catalyst addition [17–25]. The oxidant action will be different according to the type of reagents and their oxidation potentials.

* Corresponding author at: LIEC, Boulevard des Aiguillettes, B.P. 70239, 54506 Vandœuvre-lès-Nancy Cedex, France. Tel.: +33 3 83 68 47 40.

E-mail address: coralie.biache@yahoo.fr (C. Biache).

For instance hydrogen peroxide is one of the most common oxidant (oxidation potential c.a. 1.8 V; [26]). Its application, associated with ferrous ions, leads to the formation of OH radicals which are strong and non-selective oxidant agents (oxidation potential c.a. 2.7 V; [27,28]). Ferrous ions can be introduced in solution and the mixture with H_2O_2 is called Fenton's reagent. The catalytic potential of iron mineral can also be used, in this case the process is referred to as Fenton-like oxidation [21]. In aqueous system sodium permanganate and potassium permanganate generate MnO_4^- ions presenting an oxidation potential of 1.7 V [17]. Despite this relatively low value, MnO_4^- are able to break organic compounds containing carbon-carbon double bonds, aldehyde and hydroxyl groups and are therefore, considered as strong oxidant agents [29].

Cuyppers et al. [16] validated persulfate oxidation as a method for the bioavailability estimation by comparing the PAH fraction of a contaminated soil chemically degraded to the PAHs biodegraded during batch experiment. Therefore chemical oxidants could be used as alternative ways to determine the available fraction of the contamination.

Other studies show the strong connection between chemical oxidation efficiency and contaminant availability. Usman et al. [24] studied the Fenton-like treatment applied on former coking plant soils and on their solvent extractable organic matter (EOM) mixed with sand. The treatment efficiency shows major differences with more than 90% of PAH removal for the EOM/sand mixture whereas oxidation has only negligible effect on the soil PAHs. These results highlight the major constraint of the chemical treatments caused by contamination low availability. The use of solvent extraction to improve PAH availability was explored in another study, where magnetite-activated persulfate treatments were applied on the same soils, with/without a prior solvent extraction [23]. Results demonstrate that the extraction enhances the PAH degradation by magnetite-activated persulfate oxidation by increasing their availability toward the reagents with a modification of the EOM dispersion (including PAHs) on the soil constituents. Although these studies gave new information on chemical oxidation processes and the key role of the contaminant chemo-availability (toward the chemical agent), the field application of solvent extraction to enhance the chemical treatment efficiency seems difficult to implement. Another more practical technique improving the chemo-availability of organic contaminants consists in heating the contaminated matrices at moderate temperatures (60–150 °C) [30]. This technique was applied on the same aged coking plant soil and has proven to be capable to enhance the oxidation efficiency (Fenton-like) for PAH contaminated soils presenting low PAH availability [31,32].

The purpose of the present study was to determine if chemical treatment efficiencies can be used as indicator of contaminant availability and to test the effect of pre-heating on the PAH chemical degradation according to (i) the soil properties and (ii) the type of treatments. In order to fulfill these objectives, three PAH contaminated soils, originating from different industrial activities (coking, gasification and wood treatment) and presenting various characteristics (EOM and total organic carbon (TOC) contents, PAH concentrations and distributions) were selected. Several oxidants (H_2O_2 , Fenton-like, KMnO_4) were applied with/without pre-heating used to enhance the PAH chemo-availability.

2. Materials and methods

2.1. Soil samples

The selected soils presented PAH contaminations and originated from the use or transformation of coal or its by-products. Soils were sampled in the former coking plant of Neuves-Maisons (France), in

a former gas plant located near Rennes (France) and in an active wood-treating facility located in Midi-Pyrénées (France).

After being collected, the samples were stored at -18°C . They were freeze-dried, sieved at 2 mm and the undersize was crushed at 500 μm .

2.2. Thermal treatment

To modify the PAH availability, fractions of soil samples were placed in 500 mL-Schott bottles which were hermetically closed under N_2 , to prevent air-oxidation, and placed in an oven at 100°C for one week.

2.3. Chemical oxidations

Each soil (5 g), raw and pre-heated, was placed in 250 mL-Schott bottles. Four reagents were added, (i) 100 mL of deionized (DI) water, as reference; (ii) 14.5 mL of H_2O_2 (30% wt) adjusted to 100 mL with DI water; (iii) Fenton-like reagent with the same procedure as H_2O_2 with addition of magnetite (500 mg); (iv) 100 mL of KMnO_4 solution (16.7 g/L). The bottles were agitated (200 rpm) in the dark for one week. The pre-heated samples were also collected after 1 and 24 h to follow the reaction kinetics.

2.4. Organic matter extraction

OM extractions were carried out on 1.5 g of each sample with an accelerated solvent extractor (Dionex ASE 350). Copper powder (2 g) and sodium sulfate (2 g) were added to the extraction cells to remove the molecular sulfur and the residual water, respectively. The extractions were performed with dichloromethane (DCM) at 100°C and 100 bars for 10 min. After adjusting the volume at 20 mL, aliquots of the solvent extracts (5 mL) were placed in pre-weighed vials. The EOM content was determined by weighing the vials after solvent evaporation under a gentle N_2 flow.

2.5. PAH quantification

Quantification of the 16 listed PAHs (Table S1) was carried out using internal calibration. An internal PAH standard mix (20 μL at 16 $\mu\text{g}/\text{mL}$) was added to the EOM (80 μL) before being injected in a gas chromatograph coupled with a mass spectrometer (GC-MS). Analytical conditions and calibration details were reported in the supplementary data file. All results were expressed as a mean value of three experiments and relative standard deviation (RSD) of the three replicates was less than 5%.

2.6. TOC content measurement

The TOC content determination was performed with a total carbon analyser TOC-V CSH (Shimadzu) associated with a solid sample module SSM-5000A (Shimadzu). The catalytic combustion was performed at 900°C after carbonate removal with hydrochloric acid (10% wt).

2.7. Radiocarbon analysis

The $\Delta^{14}\text{C}$ activity was measured to determine recent organic carbon proportion in the soil samples [33]. The soils were previously treated with hydrochloric acid (1 M) to remove the mineral carbon (carbonates). Radiocarbon analyses were performed by Poznan radiocarbon laboratory (Poland) and the results were given in percentage of modern carbon (pMC).

Download English Version:

<https://daneshyari.com/en/article/576111>

Download Persian Version:

<https://daneshyari.com/article/576111>

[Daneshyari.com](https://daneshyari.com)