



Remediation of highly contaminated soils from an industrial site by employing a combined treatment with exogeneous humic substances and oxidative biomimetic catalysis

Filomena Sannino^{a,*}, Riccardo Spaccini^{a,b}, Davide Savy^a, Alessandro Piccolo^{a,b}

^a Dipartimento di Agraria, Università di Napoli "Federico II", Via Università 100, 80055 Portici, Italy

^b Centro Interdipartimentale di Ricerca sulla Risonanza Magnetica Nucleare per l'Ambiente, l'Agro-Alimentare ed i Nuovi Materiali (CERMANU), Via Università 100, 80055 Portici, Italy

HIGHLIGHTS

- Remediation of two polluted soils from a highly contaminated industrial site in Italy.
- Restoration of soil quality by introducing additional carbon into polluted soil with humic matter amendments.
- Detoxification of contaminants by covalent binding to humic molecules.
- Prevention of environmental transport of pollutants.

ARTICLE INFO

Article history:

Received 3 April 2013

Received in revised form 10 June 2013

Accepted 30 June 2013

Available online xxx

Keywords:

Soil remediation

Oxidative biomimetic catalysis

Humic substances

ABSTRACT

Remediation of two polluted soils from a northern Italian industrial site heavily contaminated with organic contaminants was attempted here by subjecting soils first to addition with an exogenous humic acid (HA), and, then, to an oxidation reaction catalyzed by a water-soluble iron-porphyrin (FeP). An expected decrease of detectable organic pollutants (>50%) was already observed when soils were treated only with the H₂O₂ oxidant. This reduction was substantially enhanced when oxidation was catalyzed by iron-porphyrin (FeP + H₂O₂) and the largest effect was observed for the most highly polluted soil. Even more significant was the decrease in detectable pollutants (70–90%) when soils were first amended with HA and then subjected to the FeP + H₂O₂ treatment. This reduction in extractable pollutants after the combined HA + FeP + H₂O₂ treatment was due to formation of covalent C–C and C–O–C bonds between soil contaminants and amended humic molecules. Moreover, the concomitant detection of condensation products in soil extracts following FeP addition confirmed the occurrence of free-radical coupling reactions catalyzed by FeP. These findings indicate that a combined technique based on the action of both humic matter and a metal-porphyrin catalyst, may become useful to quantitatively reduce the toxicity of heavily contaminated soils and prevent the environmental transport of pollutants.

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1. Introduction

Agricultural and industrial activities may severely pollute soils with toxic chemicals, such as pesticides, fuels, alkanes, dyes, polycyclic and halogenated aromatic hydrocarbons [1,2]. The eco-friendly and relatively inexpensive bioremediation methods are preferably applied to reduce and possibly eliminate soil contamination [3,4]. However, bioremediation processes are hardly applicable on highly contaminated sites due to the simultaneous presence of several pollutants, which are likely to inhibit microbial

activity and consequently pollutants biodegradation. In these cases, bioremediation processes are activated only after a preliminary removal of pollutants by physical or physical–chemical methods [5–7].

Among these methods, soil washing with natural surfactants, such as humic substances (HS), was proved to be very effective in removing most pollutants from a highly contaminated industrial site in Italy [8]. In fact, HS are known to strongly adsorb apolar and medium polar organic contaminants, which are then repartitioned in the humic pseudo-micellar domains [9]. The versatility of humic matter in incorporating environmental contaminants is due to its complex supramolecular conformation which comprises a large number of relatively small molecules with different structure and chemical affinity, which arrange in mostly hydrophobic domains [10–12].

* Corresponding author. Tel.: +39 0812539187; fax: +39 0812539186.
E-mail address: fsannino@unina.it (F. Sannino).

HS are known to facilitate degradation of xenobiotics via either photocatalysis [13–15], or enzymatic oxidation [16], or other abiotic/biotic processes [17,18]. The role of HS in removing organic pollutants was recently found to be significantly enhanced in the presence of biomimetic catalytic systems such as metal-porphyrins [19,20]. These biomimetic catalysts are active in the same oxidation reactions as those catalyzed by peroxidase, ligninase, and monooxygenase enzymes [21–23], since the metal-coordinated tetrapyrrolic ring functions as the redox active site and increases the reactivity of oxygen species in metal-oxo complexes [24–27]. Metal-porphyrins are also efficient catalysts in the photo-oxidation of hydrocarbons, alkanes and alkenes, when oxygen is activated under UV light [28].

A water-soluble iron-porphyrin (FeP), with H_2O_2 as oxygen donor, was proved to be effective by either homogenous or heterogeneous catalysis in increasing the structural rigidity and, hence, molecular size of dissolved HS [29,30]. A similar oligomerization of humic molecules was equally catalyzed by FeP under only solar irradiation, thereby suggesting that dissolved oxygen activate the photo-oxidative coupling of humic components [30,31]. The FeP-catalyzed photo-oxidative polymerization of humic molecules was also found to be effective in situ in soil with consequent reduction of CO_2 emission from soils [32,33] and increased carbon sequestration even in field soils under cropping [34]. Similarly, co-polymerization of multi-halogenated phenols in humic molecules was recently shown to occur under FeP oxidative catalysis [35,36]. Based on these findings, it may be inferred that an in situ addition of FeP biomimetic catalyst to contaminated soils freshly amended with humic matter, may improve inactivation of soil pollutants by their covalent binding into humic molecules.

The aim of this study was to evaluate whether a soil first amended with an exogenous humic acid, and, then, subjected to an oxidation catalyzed by a water-soluble iron-porphyrin may efficiently reduce heavy industrial soil pollution, and hence become a viable remediation technology.

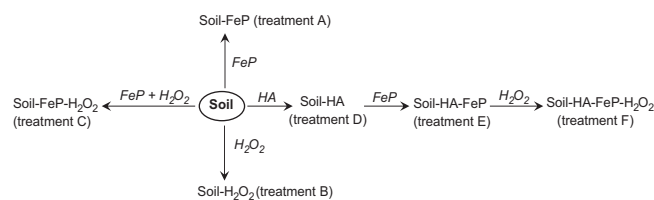
2. Materials and methods

2.1. Soils

Two soil samples (A and B) were collected from the site of ACNA (Aziende Chimiche Nazionali Associate), an industrial area of Cengio (near Savona) in the Northern Italy. The site is extremely polluted due to irregular disposal of organic and inorganic contaminants on surface and lower soil horizons since 1882. The pollution of the area was intensified since 1939 when the manufacture of a range of organic colorants was additionally conducted. In 1999, due to the serious contamination of surrounding soils and waters, the ACNA site was included in the list of national priorities for environmental remediation. Soil samples were air-dried, sieved through 2.00 mm, and then analyzed for the determination of pH and texture according to the official Methods of the

Table 1
Characteristics of soil A and B from the polluted ACNA site.

	Soil A	Soil B
Coarse sand (%)	21.2 ± 0.6	12.8 ± 0.4
Fine sand (%)	35.6 ± 0.8	38.8 ± 0.5
Silt (%)	39.6 ± 0.5	43.6 ± 0.7
Clay (%)	3.6 ± 0.2	4.8 ± 0.3
Total organic carbon (%)	2.8 ± 0.1	2.7 ± 0.2
Nitrogen (%)	1.2 ± 0.1	0.13 ± 0.02
pH	7.4	7.4



Scheme 1. Treatments on the soils of this study.

Italian National Society of Soil Science [37]. The content of carbon and nitrogen was evaluated by Fisons EA 1108 Elemental Analyzer. Their chemical and physical properties are reported in Table 1.

2.2. Biomimetic catalyst

The synthesis and purification of the water-soluble meso-tetra-(2,6-dichloro-3-sulfonatophenyl)-porphyrinate of Fe(III) [Fe(TDCPPS)Cl] used here as biomimetic catalyst (FeP) were previously reported [29].

2.3. Humic substances

A humic acid (HA) was isolated from a North Dakota Leonardite (Mammoth, Chem. Co., Houston, TX), and purified as described earlier [38]. The HA was then suspended in distilled water and titrated to pH 7.0 by an automatic titrator (VIT 909 Videotitrator, Copenhagen) with a 0.1 M NaOH solution under N_2 stream. Titration required 2.66 mequiv of NaOH per g of HA, which represented the HA carboxylic acidity. The resulting sodium-humate was filtered through a Millipore 0.45 μ m, freeze-dried. This HA contained 2.7% of ashes, 56% C, 4% H, 2% N, and, by difference, 38% O or other elements. The relative standard deviation measured for elemental analyses did not exceed 2%. The carbon distribution and both hydrophobicity and aromaticity of this HA, as obtained by ^{13}C -CPMAS-NMR spectroscopy, are shown elsewhere [39].

2.4. Addition of exogenous HA and biomimetic catalyst to polluted soils

A first series of experiments, without HA, were conducted by placing 20 g of each soil sample in Petri glass dishes, and adding the following solutions: (A) 10 mL of a 1.09×10^{-4} M aqueous solution of FeP catalyst; (B) 10 mL of a 1.29 M freshly prepared H_2O_2 solution; (C) both FeP and H_2O_2 solutions, in the order, in the same volumes and concentrations as in the previous two experiments (Scheme 1).

A second series of experiments, with HA, were conducted by first treating 20 g of soil in Petri glass dishes, with 10 mL of a 1 mg mL^{-1} HA aqueous solution (D). The soils were left to air-dry for 10 days, and then added with the following solutions: (E) 10 mL of a 1.09×10^{-4} M aqueous solution of FeP catalyst solution; (F) 10 mL of both FeP catalyst and H_2O_2 solution, in the order, at the same concentration as for the first series of experiments (Scheme 1). In all additions, the final aqueous volume in each Petri glass dish was 20 mL. The treated soils were then incubated at room temperature for 30 days in the dark, in order to prevent any photocatalytic oxidation, and subjected to Soxhlet extractions. All experiments and soxhlet extractions were conducted in triplicate.

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