Research paper

Development of new remediation technologies for contaminated soils based on the application of zero-valent iron nanoparticles and bioremediation with compost ☆

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A B S T R A C T

This study aimed to develop new techniques for the remediation of contaminated soils based on the application of zero-valent iron nanoparticles (nZVI) and bioremediation with compost from organic wastes and a mixed technique of both. An assessment of the effectiveness of remediation in two soils contaminated with hydrocarbons and heavy metals was carried out, with the aim of looking for positive synergies by combining the two techniques, and demonstrating their viability on an industrial scale. The application of nZVI for *in situ* immobilization of As and Cr in two different soils (Soil I from a contaminated industrial site and Soil II, contaminated artificially) showed a decrease in the concentration of As in Soil I and Soil II, as well as a decrease in Cr concentration for Soil I and Soil II in the leachate of both soils. The addition of compost and nanoparticles under uncontrolled environmental conditions in biopiles was able to produce a decrease in the concentration of aliphatic hydrocarbons of up to 60% in the two soils. Especially, degradation and transformation of longer chains occurred. A significant reduction of ecotoxicity was observed throughout the process in the biopile of soil II, not reaching the LC50 even with 100% of the sample after the treatment, in both earthworm and seeds growth tests.

1. Introduction

The ceasing of industrial activity has left behind a large amount of contaminated sites on the periphery of urban areas (brownfields) that are characterized by soils with high concentrations of organic and inorganic compounds (mixed pollution). Mixed pollution generates problems to determine the pollution nature and, consequently, makes the selection of the technologies that must be applied for the removal of contaminants difficult. Each polluted site has its own characteristics related to the typology of pollutants, the concentration levels of these, hydrogeological characteristics of the environment, biogeochemical soil properties, etc.

The soil natural heterogeneity adds to this complexity. Soil properties such as texture, degree of structure development, water retention capacity and/or chemical properties can be determinants for the diffusion of contaminants, and more importantly, for their degree of attachment to the soil mineral and organic matrix. This can be positive when it results in reduced diffusion and high bio-geo-chemical stabilization of pollutants in soils, but at the same time limiting when the goal is removing soil contamination. For instance, clayey soils rich in high-reactive silicates and/or containing pH-modifiers such as carbonates can retain easily degradable organic pollutants in primary and secondary organo-mineral complexes, hindering their biological decomposition within the soil matrix.

In this framework, contaminants in soils and sediments can be found in six different ways [1]: as particulate contaminants, as liquid films, adsorbed, absorbed, dissolved in the interstitial pore water, or as solid phases in the pores. For each case, the behavior of the contaminant is different so its hazardousness must be

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evaluated on the basis of its mobility and availability, which is determined by different chemical and mineralogical procedures. In the case of heavy metal pollution in soils, which poses a worldwide challenge, their mobility can be evaluated extracting the water-soluble fraction of the metal. This fraction measurement represents an approximation to the amount of metals that plants can absorb from the soil under normal conditions [2]. The availability of a metal depends, as that of organic pollutants, on its chemical speciation and on a number of soil parameters such as pH, organic matter concentration, clay mineral carbonates, etc. For instance, the availability of any exchangeable cation is conditioned by the associated minerals that form the exchange complex. Thus, As, in its oxidized form, especially at acid-neutral pH, is chemically adsorbed to oxides of iron and aluminum, aluminosilicates and, to a lesser extent, sheet silicates. In sodium soils, arsenic is more mobile and is released from the solid phase to soil dissolution, such as arsenate anion. In reducing environments, As is in the form of arsenite anion, which is still absorbed by the clay fraction with more force than the anion arsenate. This results in As (III) being manifestly more toxic than As (V), since it forms very stable complexes with the SH groups of the enzymes. The oxidative capacity of manganese oxides is sufficient to oxidize the arsenite to arsenate. As far as Cr is concerned, it is found in the natural environment, especially in tri- and pentavalent forms. The trivalent form gives rise to very stable complexes with organic and inorganic ligands containing oxygen or nitrogen atoms. In the soil, this metal can be found to several depths. In general, normal soil conditions favor the Cr (III) form, which remains quite immobile, being retained on the surface of oxides and silicates, where it forms stable chemical bonds even at acid pH. At pH above 5, $Cr(OH)_3$ is precipitated as an hydroxide. In higher pH media, Cr (III) can be oxidized to chromate anion, CrO_4^{2-}, which is the toxic form of Cr. The presence of Mn oxides favors this oxidation. The Cr (VI) species is more mobile than Cr (III), especially in the presence of organic matter. The organic matter acts as reducing agent, and, in addition, it complexed, which favors the retention of the Cr (III) produced in the reaction [3].

Organic pollutants are also widespread in brownfields and other polluted sites in industrial and peripheral areas worldwide. They occur as byproducts and residues or spills of the chemical, metallurgical and other industrial activities, and include a wide range of molecules containing C and at least one C−H group. Many of these are the result of liberation of human-made organic components to the environment. On average, 260 Tg of organic compounds are manufactured annually only in the US. Oil byproducts are the most significant source of hydrocarbons into the environment, usually associated with the use of oil-derived fuels [4].

One class of organic pollutants which has gained great attention in environmental studies is polycyclic aromatic hydrocarbon (PAH). PAHs have high resonance energies as a consequence of their dense clouds of pi electrons surrounding the aromatic rings, which make them persistent compounds in the environment and recalcitrant to degradation [5]. This molecular structure is characterized by their hydrophobicity so that they display decreasing solubility in water with increasing molecular mass. The environmental fate of PAHs depends largely on the environment to which they are exposed. The phase or state of a PAH is determined by its vapor pressure and room temperature. Experiments have shown that, at 25 °C, four- and five-ring PAHs are distributed between the solid phase and steam, while PAHs with six and more rings are almost exclusively in the solid phase [6]. PAHs with high molecular weights (from four benzene rings) are more likely to be absorbed to the soil organic matter, and therefore their availability is reduced, but this also makes them less susceptible to remediation [7]. The fate and transport of PAHs is led by physical, chemical and biological processes that are influenced by the nature of the

subsurface environment. Hence, several techniques have been used, with varying results, to achieve acceptable degradation of these recalcitrant compounds (e.g., chemical degradation, biodegradation, phytodegradation and combined degradation methods).

Soil bioremediation is based on the biological degradation of organic pollutants, ideally until their final transformation to CO_2, inorganic compounds and/or other organic compounds with reduced toxicity. Microorganisms able to degrade hydrocarbons in soils are bacteria, fungi and algae, bacteria being those with the highest and fastest degradation rates [8,9]. Average contents of these microorganisms in polluted soils are usually higher than in non-polluted soils [10]. The success of bioremediation techniques depends on the environmental conditions, number and type of organisms, and the type and structure of the pollutants [8]. Bioremediation techniques are usually based on the stimulation of the natural ability of soil microorganisms to degrade organic pollutants by favoring their activity. This is generally done by granting adequate physical–chemical conditions (nutrients and water availability, aerobic conditions, right pH and red-ox characteristics) [11] and/or by adding exogenous microbial populations especially competent for biodegradation of the targeted pollutants. The addition of organic amendments such as compost is a frequent strategy in this sense and has been used in many sites and contexts [12–14]. In addition, the pre-incubation of small quantities of the polluted soil in contact with this amendment favors the development of the native microbial populations able to degrade pollutants present in the soil. This is known as *assisted* bioremediation including biostimulation.

Currently the most widely used techniques for soil remediation are based on the application of different physical and chemical treatments. Lack of knowledge to properly assess new approaches and technologies tend to please the technologies that have been already proven successful in previous cases, and therefore the classical approach "dig and dump" is still hegemonic. At the same time, there is an inertia to extract the contaminated soil and carry out external treatments, which requires the processing of large amounts of contaminated soil resulting in high costs and making the control of the treatments difficult.

The synergistic use of nZVI and bioremediation is a new strategy for restoring contaminated sites by the *onsite* application of two combined advanced technologies that can contribute to the implementation of recovery alternatives that reduce the volume of waste generated in decontamination processes and therefore reduce the industrial impact on the environment.

Iron nanoparticles perform like strong reducing agents. Their action mechanism involves oxidation–reduction reactions (redox), so that in contact with the medium they are oxidized rapidly and donate their electrons to pollutants, thus reducing them. The pollutants become more stable, less mobile and/or less toxic products. Among the advantages associated with the use of nZVI for soil decontamination, there is the prospect of a notable reduction in the ratio of kg of product per volume of soil to be treated, thanks to the large surface area provided by nanomaterials regarding macroscopic materials. The granular zero valent iron has been used for years with success, especially in permeable reactive barriers (PRBs) for the treatment of chlorinated hydrocarbons (ethanes and ethenes), metals and metalloids (arsenic, chromium and uranium), nitroaromatics, and treatment of perchlorates with limited results [15].

There is a dearth of studies about the decontamination potential of nZVI in soils [16]. The treatment of the metals by nZVI is produced via immobilization [17]. This strategy prevents its transport through the layers of soil, rivers and groundwater. So far, the studies about the immobilization of metals by nZVI in soils have been conducted in "in vitro" conditions. Some of the most important trials have demonstrated the immobilization of Pb and Zn in