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Copper and zinc removal from contaminated soils through soil washing process using ethylenediaminedisuccinic acid as a chelating agent: A modeling investigation

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ABSTRACT

This study demonstrated that soil washing using ethylenediaminedisuccinic acid (EDDS) as a chelating agent was efficient at removing copper and zinc from real polluted soils. Only the exchangeable and reducible fractions of Cu and Zn were extracted by EDDS. Intra-particle diffusion was the main rate controlling step in this extraction of heavy metals from the solid matrix. Different contributions were found by applying the Weber and Morris intraparticle diffusion model resulting from the different roles of superficial and intra-particle diffusive processes.The diffusion coefficients of the Cu/EDDS and Zn/EDDS complexes in real contaminated soils were estimated using simplified diffusive models (based on Crank's and Vermeulen's approximations). The relationship between the grain size and diffusion coefficient was also evaluated. In particular, the intraparticle diffusion coefficients increased with increasing the particle size, thus indicating that the smallest granulometric fractions are characterized by a higher percentage of micropores than the largest fractions.

1. Introduction

During the last 20 years, the contamination of soils and sediments with heavy metals (HMs) has become a worldwide concern due to their high toxicity of most species and their ability to accumulate in living tissues [1,2].

In agricultural areas, HMs contamination, even if not related to specific health hazards, compromises the optimal use of the land, may reduces economic output [3], and modifies the existing equilibrium among natural components [4]. In these zones, the remediation interventions are needed that remove the contamination without affecting the original structure and composition of the soil.

In many cases, especially if the pollution is of anthropogenic origin, very high concentrations of HMs may occur in portions of the contaminated areas leading to so-called "hot spots" [5]. The remediation of these hot spots requires specific processes. Soil washing is a promising strategy if the applied extracting agent minimally changes the original solid matrix original characteristics and does not leave toxic residues in the treated soil [6]. Moreover, feasible treatment methods and safe disposal of the washing solution should be available [7,8].

For these reasons, biodegradable organic chelants with low environmental persistence are highly recommended [9]. The most common chelating agents, such as ethylenediaminetetraacetic acid (EDTA), are poorly biodegradable and quite persistent in the environment. An alternative, the [S,S]-stereoisomer of ethylenediaminedisuccinic acid (EDDS), has recently received attention in the literature as it is both safe and environmentally-friendly [10–15]. For example, the use of EDDS for soil reclamation does not

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have any effect on crop yield [16]. Moreover, [S,S]-EDDS can be also produced by some fungi and bacteria [17,18]. Soil washing processes have been investigated for the effect of metal speciation and concentration [19–22]: the effect of soil characteristics, such as particle distribution size, pH, organic matter content, and cation exchange capacity [23–27], and appropriate washing operating conditions, including the EDDS-to-metal ratio, and the solid-to-liquid ratio [10,19,27–30]. The nature of the interaction and the structure of complexes formed between EDDS and HMs has also been studied [21,30].

The effectiveness of extraction for a soil washing process is generally affected by diffusion and kinetic and adsorption mechanisms. Any of these, depending on the operative conditions, can be the rate-limiting step. For diffusive transport phenomena, theoretical descriptions of several mathematical models have been reported for estimating the intra-particle diffusion coefficients of chemicals in solid matrices [31–35].

Nonetheless, very little attention has been focused on the application of these models to micropores and macropores transportation processes for chelating agent/HM complexes in real soils, although these may affect the efficiency of the extraction.

In the present investigation, Crank's [31] and Vermeulen's [36] approximations, due their simplicity, are considered for analyzing the extraction rate data and estimating the diffusion coefficients of the Cu-EDDS and Zn-EDDS complexes in contaminated soil samples.

To the best of authors' knowledge, the application of these two approximated models to the transport of chelating agent/heavy metal complexes in real contaminated soils has received little attention [37,38]. No diffusion coefficient values have been reported for Cu/EDDS and Zn/EDDS complexes in contaminated soil samples: however, the diffusion coefficients of Pb/EDTA and Zn/EDTA complexes have been estimated using different methods than those used in the present study [39,40].

Thus, the aim of this paper is to clarify the role of diffusion of metal/EDDS complexes into a solid structure during the soil washing process. In more detail, the paper investigates whether diffusive phenomena should be considered as key processes affecting the overall performance of soil washing.

The study is carried out at the lab scale, under different operative conditions, on real soil contaminated by copper and zinc. Two different soil samples with similar characteristics were obtained from former agricultural land (Fig. 1) within a highly populated area in Campania Region (Southern Italy). This area is located in a municipality within a larger contaminated region that has been proposed as a Site of Regional Interest (SIR). This territory, located between Naples and Caserta (55 municipalities) has experienced hazardous waste disposal since the 1970s. To further elucidate the seriousness of the problem, it is important to consider that in some particular areas of this region there has been in few years a 300% increase in diseases such as stomach, liver, bronchus, and bladder cancers as well as malformations and birth defects. These incidents are, in some cases, consistent with a lack of remediation of the polluted sites and lingering waste mismanagement [41]. Very recently, the Italian National Institute of Health (ISS) announced "*.observed excesses of children hospitalized in the first year of life for all cancers (particularly non-Hodgkin lymphoma) and excesses of cancers of the central nervous system, the latter also in the range 0–14 years . . .* " [42].

2. Experimental

2.1. Materials

Hydroxylammonium chloride (reagent grade >98% w/w), ammonium acetate (>99% w/w), (S,S)-ethylenediamine-*N*,*N*'-disuccinic acid–trisodium salt solution (35% v/v), hydrogen peroxide

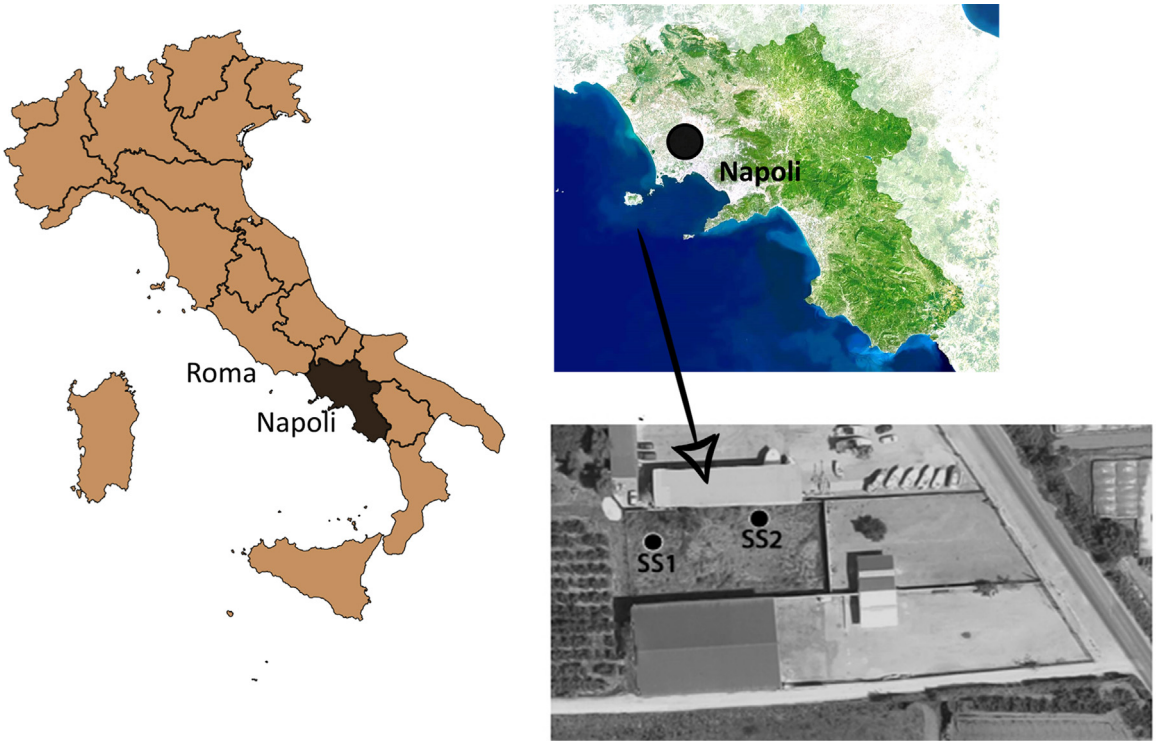

Fig. 1. The sampling points SS_1 and SS_2 (geographic coordinates N 40°96′05″, E 14°11′84″).