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PhD Thesis

**Chemical washing of contaminated soils and  
photocatalytic treatments  
of spent soil washing effluent**

by

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# Abstract

This dissertation has been addressed to study the reclamation of heavy metal contaminated soils by soil washing, and to investigate the feasibility of photocatalytic processes for the treatment of the spent soil washing solution (SSWS). Indeed, the collected SSWS, containing the extracted metals and chelating agents, represents one of the main drawbacks of the washing technique, as it has to be submitted to further treatments for a complete detoxification before being discharged into the environment.

The soil washing using EDDS as chelating agent has been demonstrated to be an efficient soil remediation technique to remove Cu and Zn from real polluted soils. Only Cu and Zn present as exchangeable and reducible fractions have been extracted by EDDS. The intra-particle diffusion was the main rate controlling step in the extraction of heavy metals from the solid matrix. Different contributions have been found by applying the Weber and Morris intra-particle diffusion model due to 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 have been estimated using simplified diffusive models.

The simultaneous removal of EDDS and metals (Cu, Fe and Zn) from both synthetic solutions and real contaminated soil washing mixtures at neutral pH has been investigated to assess the possibility of applying TiO<sub>2</sub> based photocatalytic processes for the treatment of SSWS and identify the sequence of photocatalytic processes required to optimally decontaminate the liquid wastes. The photocatalytic tests have demonstrated that the sequence of treatment constituted by two steps, TiO<sub>2</sub>-photocatalysis with oxygen followed by TiO<sub>2</sub>-sacrificial photocatalysis, is required to completely detoxify the SSWS. In particular, the results show that Fe and Zn are mainly removed by precipitation as insoluble hydroxides during the first step whereas the second step is necessary to reduce cupric ions to zero-valent Cu, which precipitates from the solution.

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# Introduction

As noted by several authors over the last 20 years, heavy metals (HMs) contamination of soils and sediments has become a worldwide concern. The concern for the presence of HMs is due not only to their toxicity but also to their lipid solubility. HMs tend to concentrate in the fatty tissue and be excreted very slowly causing the phenomenon of "biological magnification", or the tendency to concentrate in organisms from one trophic level to another, along the food chain. The soils are the main target of HMs released into the environment by human activities and their removal cannot be achieved by biological degradation as naturally occurs for organic compounds.

In the agricultural sector, HMs contamination limits the optimal use of large areas of land, causing serious economic damage [1] and altering the existing balance of natural components [2].

The concentration of HMs in soil can persist for a very long time: after their release, however, they can change their chemical forms (speciation) and bioavailability.

The European Environment Agency (EEA) estimated that there are 3 million potentially contaminated sites in the EU. In 9% of these cases contamination has already been ascertained and therefore it requires remediation. Furthermore it is estimated that the sites requiring an intervention may increase by 50%, by 2025.

Contaminated agricultural areas require remedial interventions which are able to remove pollutants without affecting the original structure and composition of the soil. Generally, the best way to achieve this result is thorough phytoremediation, but this technique might not be feasible, because of the depth and the degree of the contamination. If the pollution is of anthropogenic origin, HMs can reach very high concentrations in parts of the contaminated area, -called **hot spots** [3]. Remedial decontamination of hot spots requires more specific approaches rather than phyto-based systems, because these techniques are only appropriate in case of low levels of contamination [4].

The remediation of HMs contaminated soils is therefore an important challenge that has to be faced with appropriate tools. Washing processes, in all their possible variants, represent a promising alternative, if the applied washing agent is able to minimize the alteration of the soil's original characteristics, and does not leave toxic residues in the treated soil [4].

The Soil Washing is a chemical-physical technique which provides the transfer of the contaminants from the solid matrix to the aqueous phase. It is a real washing in a closed system, of the excavated soil, conducted using a water solution containing surfactants, biosurfactants, organic solvents, chelating agents, acids or bases, i.e. a washing agent able to desorb from the solid matrix the pollutant, so that it turns in solution or suspension.

The technique is successfully applicable to different classes of pollutants, such as semi-volatile organic compounds, fuels, HMs and also volatile organic compounds and pesticides.

The volatile organic contaminants are usually easily removable and can demand also the addition of surfactants in the wash water. The removal efficiencies of inorganic compounds can be very high and depends on the type of extractant added to the washing solution. In the case of HMs extractant agents of different nature can be used and they differ each other for costs and yields. In particular they can be used in acid solutions (HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>), to complexing agents such as citric acid, ammonium acetate, Nitrilotriacetic acid (NTA), Ethylenediaminetetraacetic acid (EDTA) and Ethylenediaminedisuccinic acid (EDDS) [5].

The feasible treatment and safe disposal of the exhausted washing agent also have to be carefully considered. In recent decades, many studies have been carried out on different chelating agents and they have shown that aminopolycarboxylate chelating agents (APC) [6], and especially EDTA, are used in the majority of the applications. Unfortunately, EDTA is persistent in the environment and not biodegradable, thus the actual tendency is to use the S,S-stereoisomeric form of EDDS, an isomer of EDTA, which is easily biodegradable[7].

Several studies concerning EDDS were carried out with activated sludges aimed at verifying the biodegradability of free EDDS in wastewater treatment plants, considering the extensive application of APCs in many consumer products and industrial processes. Therefore their consistent presence in wastewaters is also observed. Obtained results claim the almost complete biodegradability of [S,S]-EDDS, which is the only stereoisomer used for soil washing applications nowadays [7].

Concisely, the process of soil washing is carried out in successive stages. The main steps are:

- pre-treatment designed to classify the contaminated soil in different particle size fractions;
- washing and extraction of the contaminants based on the intensive mixing of soil pretreated with the extractant, in order to transfer the HMs from the solid phase to the liquid phase;
- phase separation, liquid/solid extraction;
- post-treatment of the soil;
- repetition of the treatment cycle, to increase the efficiency of extraction (Optional);
- purification and recovery of the extractant agents, whose reintroduction within subsequent extraction cycles is required in case of a very expensive chelating agent is used for the extraction of HMs.

Factors that affect the efficiency of the soil washing process beyond the choice of the chelating agent include the metal speciation and concentration, the characteristics of the soil (e.g. grain size, pH, organic matter, and cation exchange capacity) and the conditions of the washing process (e.g. EDDS to metal ratio and solid to liquid ratio) [6].

To be able to predict the efficiency of the soil washing process, it is crucial to identify the correct operating conditions to adopt. Multiple studies have formulated empirical models to predict extraction efficiency, but few of them have investigated the impact of the various mechanisms that can affect removal efficiency (diffusion, kinetic and adsorption mechanisms) [8,9]. Each mechanism can result in different efficiency, it depends on the type of soil and operating conditions. As for the diffusive transport, there are mathematical models appropriate to estimate the intra-particle diffusion coefficient in the solid matrix<sub>7</sub>. However, less attention has been paid to the application of such models for the transport of complex APC-Me in in macro and micro pores.

One of the main disadvantages of soil washing is the production of spent soil washing solution (SSWS) that contains the contaminants extracted from soil. As a result, an appropriate treatment must be chosen for the decontamination of the effluents before discharging them-

The treatment of SSWS containing APCs (aminopolycarboxylates) has been investigated in several studies: conventional technologies, such as adsorption or precipitation, are not much efficient due

to the high thermodynamic stability of the Me-APC complexes. For these reasons, the applicability of reverse osmosis, electrochemical processes, precipitation, in presence of high concentrations of EDTA and low concentration of metals or protonation of EDTA, followed by an exchange of metals, has been widely evaluated [10–13].

Most previous studies [14,15] involve the treatment of solutions containing EDTA, but few of them address treatment of EDDS SSWS. However, no one investigated the applicability of photocatalytic processes.

The photocatalytic processes allows to increase the velocity of a chemical reaction by activating specific compounds defined "photocatalyst", through the use of solar energy. These compounds, irradiated by light at a suitable wavelength, determine the formation of oxidizing species capable of decomposing organic and inorganic substances [16,17].

The photocatalysts are semiconductors, materials characterized by an intermediate resistivity between conductors and insulators. The semiconductor, absorbing a quantity of light energy ( $h\nu$ ) greater than or equal to the correspondent in the band gap ( $E_g$ ), generates a transfer of electrons ( $e^-$ ) from the valence band to the conduction band. It involves the consequent formation of electronic holes ( $h^+$ ) in the band valence. The components of the photogenerated couple,  $e^-$  and  $h^+$ , are respectively able to reduce and oxidize a substance adsorbed on the surface of the photocatalyst.

Among the most common photocatalysts there are some metal oxides, such as  $TiO_2$  (Titanium Dioxide),  $ZnO$  (Zinc Oxide),  $SnO_2$  (Tin Dioxide), however not all are efficient and stable over time[18].

In a photocatalytic process, regardless of condition in which is developed (gas phase, organic liquids or aqueous solutions), five independent stages can be distinguished:

1. transfer of the reagents from the fluid phase to the catalyst surface;
2. adsorption of at least one of the reagents;
3. redox reaction, in the adsorbed phase, between the catalyst and the adsorbed reagents;
4. products desorption;

5. removal of the products from the solid-fluid interface and diffusion in solution.

The oxides of the metal semiconductors are characterized by a high reductant power of the photogenerated electrons and a high oxidizing power on the corresponding hole.

Consequently, in the aqueous phase processes and in the presence of oxygen and organic compounds, the electrons are able to reduce the dissolved oxygen, generating the superoxide radical  $O_2^{\bullet-}$ , while the positive hole can react with water or with hydroxyl ions adsorbed and can produce radical  $OH^{\bullet}$ , or it can directly oxidize and decompose the organic substance.

The photocatalytic process of oxidation in organic matters using a photocatalyst (mostly  $TiO_2$ ) is also possible in absence of oxygen if some species are able to capture the electron of the conduction band of the semiconductor are provided (sacrificial photocatalysis). These species, therefore, have to be capable of being reduced. This process is extremely interesting from the environmental point of view. If oxygen is replaced with metal ions ( $Me^+$ ) dissolved in solution, these capture photogenerated electrons ( $e^-$ ) thereby reducing them oxidation state while, at the same time, the organic (D) is oxidized reacting with the electronic holes ( $h^+$ ) or with  $OH$  radicals generated this way [19,20].

Sometimes, after the reduction, the  $Me^+$  ions precipitate as  $Me(0)$ , which allows its separation and the recovery of the solution. The organic compounds act in this case as sacrificial agents: their oxidation enables the reduction of the metals and determines the precipitation.

In the SSWS the EDDS can form several stable mono-, bis- and hydroxy- complexes with HMs (e.g. at pH values close to 7.0, these are:  $[CuEDDS]^{2-}$ ,  $[ZnEDDS]^{2-}$ ,  $[FeEDDS]^-$  and  $[Fe(OH)EDDS]^{2-}$  [21]).

These stable complexes increase the dissolution of the metals, even at neutral pHs, and prevent their removal from water through precipitation, mainly as hydroxy species. In addition,  $Me-APC$  complexes are photosensitive and decompose in sunlight by charge transfer from metal to ligand, which can lead to metal reduction and ligand radical formation [22].

For example, the  $Fe(III)-EDDS$  complexes were found to be the most photosensitive among the  $Me-APC$  complexes. Photochemically driven reactions of this complex may lead to production of oxidative species (e.g. hydroxyl radicals) [23].

In this way, Fe(III)-EDDS complexes may operate as “homogeneous photo-Fenton systems” and can result in the precipitation of metals like hydroxides at a pH of around 7, thanks to the oxidative degradation of EDDS. Another option for treatment of effluents is heterogeneous TiO<sub>2</sub>-photocatalysis, at acidic pH. Cupric ions chelated with EDDS can be also photo-reduced to zero-valent copper, which can then be efficiently removed from the solution (a system known as “sacrificial photocatalysis”).

Specifically, the aims of this thesis are:

- 1) to evaluate the applicability of soil washing procedures for the decontamination of a soil contaminated by Cu and Zn;
- 2) to assess the possibility of applying photocatalytic processes for the treatment of SSWS containing HMs and EDDS;
- 3) to identify the sequence of photocatalytic processes required to optimally decontaminate the SSWS, thus make it suitable for being recycled or discharged into the municipal sewer;
- 4) to assess the use of a solar reactor to treat SSWS including assessment of the ecotoxicity of solutions before and after solar radiation and an assessment of the related costs of treatment.

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# Chapter 1 Copper and zinc removal from contaminated soils through soil washing process using ethylenediaminedisuccinic acid as chelating agent: a modeling investigation

The soil washing using EDDS as chelating agent was demonstrated to be an efficient soil remediation technique to remove copper and zinc from real polluted soils. Only Cu and Zn present as exchangeable and reducible fractions were extracted by EDDS. The intra-particle diffusion was the main rate controlling step in the extraction of heavy metals from the solid matrix. Different contributions were found by applying the Weber and Morris intraparticle diffusion model due to 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 (Crank's and the Vermeulen's approximations). The dependence between grain size and diffusion coefficient was also evaluated. In particular, the intraparticle diffusion coefficients increased at increasing the particle size thus indicating that the smallest granulometric fractions were characterized by higher percentage micropores than the biggest ones.

## 1.1 Introduction

During last 20 years heavy metals (HMs) contamination of soils and sediments has become a worldwide concern because of the high toxicity of most species and because of their capacity of being magnificated as consequence of accumulation in living tissues [1,2].

In agriculture vocated areas, HMs contamination, when not related to health hazard, compromises the optimal use of extended zones, causing important damages to the economy [3], and altering the existing equilibrium among natural components [4]. In these zones the recourse to remediation interventions able to remove the contamination without affecting the original structure and composition of the soil represents an imperative exigency.

Especially if the pollution is of anthropogenic origin, in fact, HMs can attain very high concentrations in more or less extended portions of the contaminated areas, which are called "hot spots" [5]. The remediation of "hot spots" requires specific processes. Among them soil washing represents a promising alternative if the applied extracting agent is able to minimize the alteration of the solid matrix original characteristics, and does

not leave toxic residues in the treated soil [6]. Moreover a feasible treatment and a safe disposal of the washing solution should be available [7,8].

For these reasons the use of biodegradable, low environmentally persistent organic chelants, such as [S,S]-stereoisomer of ethylenediaminedisuccinic acid (EDDS) is highly recommended [9], and is receiving increasing attention in the scientific literature [10–15]. For example, the use of EDDS for soil reclamation does not involve effects on crop yield [64]. Moreover, [S,S]-EDDS can be also produced by some fungi and bacteria [66–67].

For soil washing processes, the effect of metal speciation and concentration has been investigated [16–19], together with the effect of soil characteristics, such as particle distribution size, pH, organic matter content and cation exchange capacity [20–24], and the washing operative conditions, including EDDS to metal ratio, and solid to liquid ratio [10,16,24–27]. The nature of the interaction and the structure of complexes formed between EDDS and HMs have been studied too [18,28].

The effectiveness of extraction for a soil washing process is generally affected by diffusion, kinetic and adsorption mechanisms, each of them, depending on the operative conditions, can be the rate-limiting step. As regards the diffusive transport phenomena, theoretical descriptions of several mathematical models, more or less detailed, for the estimation of intra-particle diffusion coefficients of chemicals in solid matrices have been reported [48–51, 60].

Nonetheless very little attention has been focused to the application of these models to micro and macro pores transportation processes of chelating agent/HM complexes in real soils, which may affect the efficiency of the extraction.

In the present investigation, Crank's [48] and Vermeulen's [56] approximations, due their simplicity to use, are taken into account to analyze the extraction rate data and estimate the diffusion coefficients of the complexes Cu-EDDS and Zn-EDDS in the contaminated soil samples.

The application of these two approximated models to the transport of chelating agent/heavy metal complexes in real contaminated soils has been poorly investigated [53, 62]. No values have been reported for the diffusion coefficients of the complexes Cu/EDDS and Zn/EDDS in contaminated soil samples. Just some numerical values are found in literature for the diffusion coefficients of Pb/EDTA and Zn/EDTA complexes [61,63], estimated using methods different from those used in the present study.

The aim of this chapter is thus to better clarify the role of Metal/EDDS complexes diffusion into the solid structure during the soil washing process. More in details the chapter intends to investigate whether diffusive phenomena have to be considered as key processes affecting the overall performance of the soil washing treatment.

The study is carried out at lab scale, under different operative conditions, on a real soil contaminated by copper and zinc, using two different soil samples having similar characteristic. They are obtained from a formerly agricultural area (Figure 1.1) place of illegal toxic waste dumping in the past.

## 1.2 Experimental

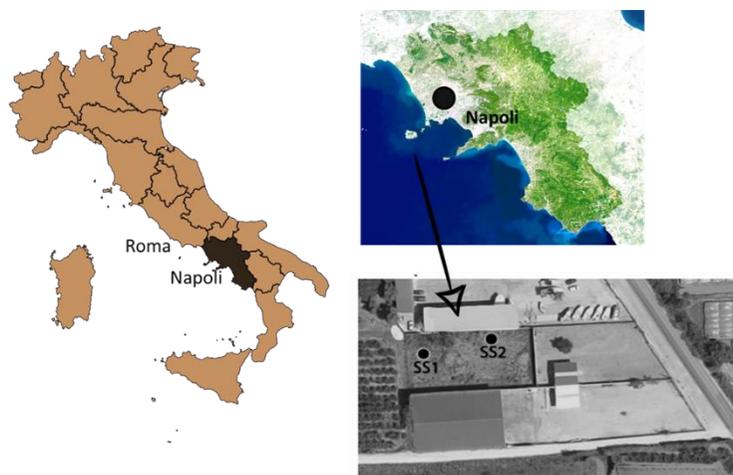
### 1.2.1 Materials

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 solution (30 %

v/v), acetic acid (ACS reagent >97% v/v), nitric acid (ACS reagent >67% v/v), from Sigma–Aldrich were used as reagents. Only Ultra-pure water was used for analytical preparations and dilution.

### 1.2.2 Soil sampling

The soil used was collected in Giugliano in Campania (South of Italy) within a very big area proposed, for the contamination, as a Site of Regional Interest (SIR) [29]. This area was subject to illegal deposit of waste. Two different soil samples were used, indicated as SS<sub>1</sub> and SS<sub>2</sub>. The two sampling points were chosen at a mutual distance of 20 meters, in order to have similar characteristics for the two samples, except for the metal content (Figure 1). The samples were manually collected from the top 20 cm of the soil, stored in hermetic containers, dried at 40 °C, and afterwards preserved at room temperature.



**Figure 1.1** – The sampling points SS<sub>1</sub> and SS<sub>2</sub> (geographic coordinates N 40°96'05", E 14°11'84").

### 1.2.3 Analytical procedures

Grain size analysis, using sieves of different size (20, 10, 5, 2, 1, 0.5, 0.3, 0.15 and 0.075 mm) was performed according to ASTM method D 422-63 [30].

The specific gravity analysis was carried out according to Bowles [31]. Only the grain sizes smaller of 2.0 mm were used in the analytical determinations. The HMs concentration in the soil sampled was determined according to the EPA method 3051 [32]. The metal distribution in soil sample was estimated by a multi-step sequential extraction procedure [33]. The procedure was based on a first extraction with in 40 mL of acetic acid (0.11 M) (*step 1*); afterwards 40 mL of hydroxylammonium chloride solution (0.5 M) were added to the soil residue from "*step 1*" and acidification by the addition of a 2 M HNO<sub>3</sub> solution (*step 2*). Progressively in the oxidation (*step 3*) 20 mL of hydrogen peroxide (8.8 M) and 50 mL of ammonium acetate (1.0 M) were used. The sequence of the extractions was related to the exchangeable phase, reducible and the oxidizable phases, and residual phase respectively. The steps and the soil extracted fractions of metal are detailed elsewhere [17].

Metal concentrations were determined through Atomic Absorption Spectrometry (AAS), using Varian Model 55B SpectrAA (F-AAS) equipped with flame (acetylene/air) with a deuterium background correction, GBC Avanta AAS with graphite furnace (GF-AAS) or Atomic Fluorescence Spectrometer AFS-8220.

SEM images were acquired with the following tool: SEM EDX FEI – Ispsect S, Column E-SEM W. Source: 200 V – 30 Kv, filament: tungsten equipped with a Everhart – Thornley detector (ETD). Pores characterisation of soil samples was carried out applying both mercury intrusion and gas adsorption porosimetry. The mercury porosimetric analysis was carried out by Micromeritics AutoPore IV apparatus.

Sorption/desorption isotherms were obtained using N<sub>2</sub> at 77 K as adsorbate in an Autosorb-1, (Quantachrome) apparatus. Before analysis, the samples were degassed at 383 K for 12 h under vacuum conditions. The surface area was evaluated from the BET equation while the surface of micropores was calculated from the t-plot method of Lippens and de Boer.

The pH of soil was evaluated in solution at 1:2 soil to water ratio (EPA Method 9045C, [34]). All pH measurements were carried out with WTW pH/oxi340i pH-meter. Electrical conductivity was determined according to Violante and Adamo [35] using a conductivity meter (Eutech Instruments, COND 6+). The organic matter was measured through Loss On Ignition (L.O.I.) index [36, 37]. The Chapman [38] method was used to estimate the cation exchange capacity (CEC). The CHNS content in the samples was determined using a Perkin-Elmer Series II 2400 CHNS/O Elementary Analyzer. All analyses were performed out in triplicate.

#### 1.2.4 Soil washing procedure

The soil washing experiments were carried out in polyethylene bottles (50 mL). Most of the runs were carried out using a sole fraction of soil with grain size smaller of 2-mm at liquid-to-solid ratio (L/S) to 10:1 and with different concentrations of chelating agent (0.36 mM, 0.72 mM, 3.6 mM and 7.2 mM). Some additional runs were performed on different fractions collected after sieving the soil (75 µm, 75 – 1.5·10<sup>2</sup> µm, 1.5·10<sup>2</sup> – 5·10<sup>2</sup> µm, 5·10<sup>2</sup> – 2·10<sup>3</sup> µm), at L/S of 10:1 and EDDS initial concentration equal to 3.6 mM.

The sample were shaken by means of a mechanical shaker (Edmund Bühler, Kombischüttler KL2) at 190 rpm for different contact times at room temperature. Following the shaking, the samples were centrifuged using an IEC Centra GP8R centrifuge at 4800 rpm for 15 min and then filtered with 0.45 µm regenerated cellulose filters. The concentration of extracts metals from soil was determined trough the determination of metals in the washing solution. All experiments were conducted in triplicate.

#### 1.2.5 Models adopted for data analysis

The Crank's and the Vermeulen's approximations were considered. For both approximations, it is assumed to operate under infinite solution volume conditions, that is the volume of the external solution is much higher than the exchanger quantity.

##### *Crank's approximation*

The total amount of diffusing substance, entering or leaving a particle of radius  $a$ , is given by [48]:

$$\frac{q_t}{q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{\left(-Dn^2\pi^2\frac{t}{a^2}\right)} \quad (\text{for spherical particles}) \quad 1.1$$

$$\frac{q_t}{q_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2\alpha_n^2} e^{\left(-D\alpha_n^2 t\right)} \quad (\text{for cylindrical particles}) \quad 1.2$$

where  $q_\infty$  and  $\alpha_n$  indicate respectively the amount of metal extracted per soil unit mass at equilibrium and the positive roots of  $J_0(a\alpha_n) = 0$  with  $J_0(x)$  being the Bessel function of the first kind of zero order and  $D$  is the "apparent" diffusion coefficient.

For small contact times (generally  $\frac{q_t}{q_\infty} < 0.3$ , [48]) the equations (1.1) and (1.2) become respectively [52,53]:

$$\frac{q_t}{q_\infty} = 6 \left( \frac{Dt}{\pi a^2} \right)^{0.5} - 3 \frac{Dt}{a^2} \quad (\text{for spherical particles}) \quad 1.3$$

and

$$\frac{q_t}{q_\infty} = 4 \left( \frac{Dt}{\pi a^2} \right)^{0.5} - \frac{Dt}{a^2} \quad (\text{for cylindrical particles}) \quad 1.4$$

The Matlab Software (routine 'ode45'), which is based on the Runge–Kutta method with adaptive step-size, was used to numerically solve eqs. 3 and 4 and to calculate the concentrations of copper and zinc at different contact times.

### *Vermeulen's approximation*

For moderate and large contact times ( $\frac{q_t}{q_\infty} > 0.3$ ), instead of eqs. 3-4, Vermeulen's approximation can be used [56]:

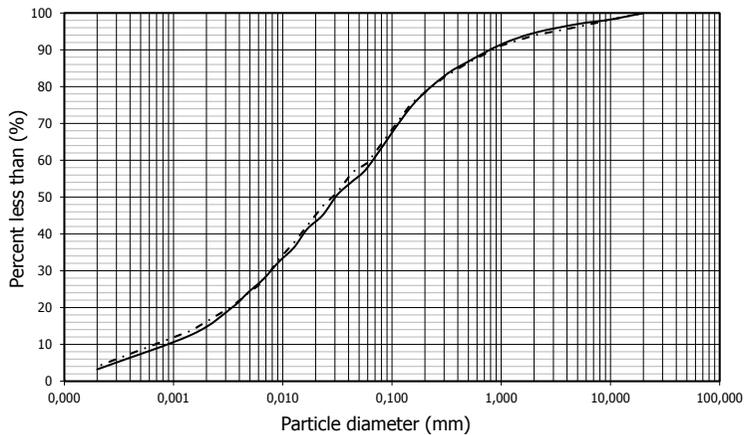
$$\frac{q_t}{q_\infty} = \left[ 1 - e^{-\pi^2 \frac{Dt}{a^2}} \right]^{0.5} \quad 1.5$$

This model is widely used in literature mainly, but not only, for isotopic exchange systems with spherical particles [51,57,58].

## 1.3 Results and discussion

### 1.3.1 *Soil characterization*

The grain size distribution, reported in Figure 1.2, allowed to characterize the composition of soil samples. On the basis of these preliminary results, the soil resulted a loam, useful for plant growth, confirming the agricultural vocation of the area [39].



**Figure 1.2** – Grain size distribution SS1; SS2.

The two samples had similar physical and chemical characteristics (Table 1.1), indicating the same origin of the soil, even if SS<sub>1</sub> had a higher content of copper and zinc, most probably as consequence of the induced anthropogenic confined contamination. Such a result guarantees that the efficiency of the washing process cannot be dependent on soil characteristics, and that the extraction kinetics are likely to follow the same trend for the two samples, whenever the operative parameters of the process remain unchanged.

	SS <sub>1</sub>	SS <sub>2</sub>
pH	6.97	6.74
CSC [meq/100gr]	35.37	38.67
LOI [%]	7.19	6.53
C [%]	3.96	2.94
H [%]	2.47	1.87
N [%]	0.42	0.29
S [%]	0.43	0.23
Specific gravity [g/cm <sup>3</sup> ]	2.42	2.44
Electrical conductivity [dS/m]	0.17	0.15
K [mg/Kg]	1.81·10 <sup>5</sup>	1.87·10 <sup>5</sup>
Na [mg/Kg]	3.13·10 <sup>4</sup>	3.31·10 <sup>4</sup>
Mg [mg/Kg]	2.26·10 <sup>4</sup>	2.39·10 <sup>4</sup>
Ca [mg/Kg]	4.12·10 <sup>5</sup>	3.98·10 <sup>5</sup>
Cu [mg/Kg]	2.54·10 <sup>2</sup>	67.63
Zn [mg/Kg]	2.13·10 <sup>2</sup>	90.02
Fe [mg/Kg]	1.33·10 <sup>4</sup>	1.42·10 <sup>4</sup>
Mn [mg/Kg]	6.28·10 <sup>2</sup>	5.97·10 <sup>2</sup>
BET [m <sup>2</sup> /g]	5.98	6.03

**Table 1.1** - Soil characterization.

SEM analysis confirmed the similarities of the two samples, allowing a more detailed knowledge of the microscopic structure of the soil, useful to understand the effect of diffusion processes. Figures 1.3a–f clearly indicate that the samples soil appear as an heterogeneous phase multi-aggregated material. In particular, Figure 1.3a shows that the particle sizes, for the sample monitored (SS<sub>1</sub>), ranged from 180 μm to 1–2 μm. The particle reported in Figure 1.3b (size 13 μm) is an almost spherical agglomerated of minutes grains of less than 1 μm in size (Figure 1.3d), overlapped together, but other smaller particles have irregular shapes (Figure 1.3c). The particle has macro and mesopores of 0.4 – 2.5·10<sup>-2</sup> μm in diameters and because the high heterogeneity and particular morphology of the material (existence of interconnection of openings and macrovoids, Figures 1.3c and 1.3d), it may be assumed that the natural crushing of larger particles occurs by breaking mainly at interstices and macrovoids (Figure 1.3f) generating smaller particulate matter having larger area percentage of micropores (Figure 1.3e).

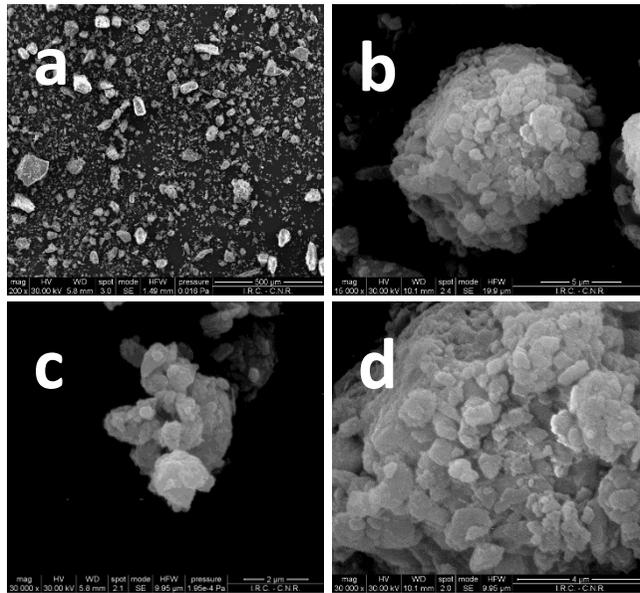


Figure 1.3 – SEM images of SS<sub>1</sub> sample.

The presence of macroporosity in the soil sampled was confirmed by mercury intrusion porosimetry. The incremental intrusion vs. pore diameter curve shows that the pore size distributions are centered at 3–4 µm and 0.4–0.5 µm for the fractions with particle diameters < 75 µm and  $5 \cdot 10^2 - 2 \cdot 10^3$  µm respectively (Figure 1.4b).

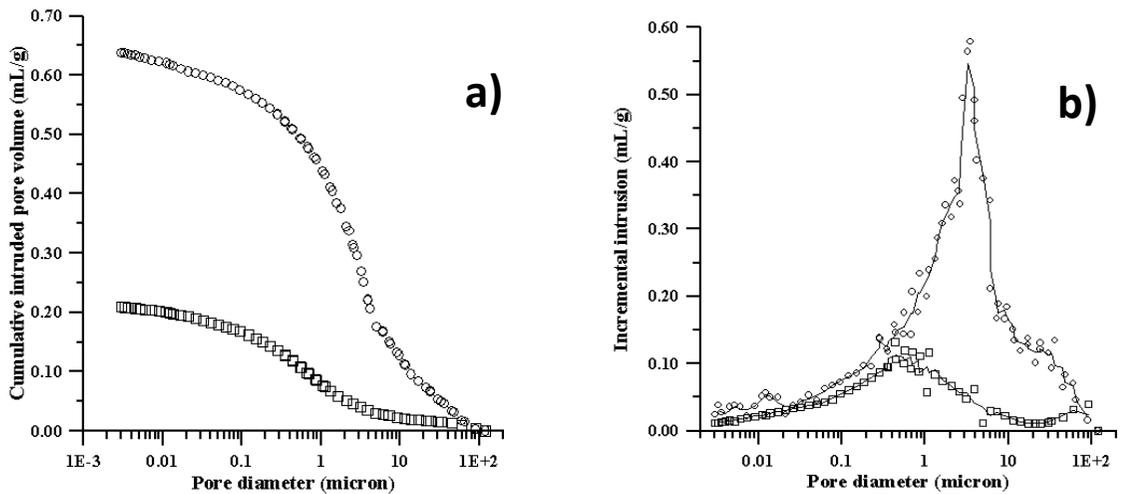
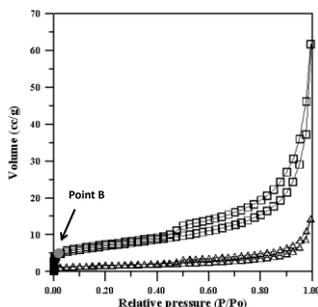


Figure 1.4 – Cumulative intruded Hg volume vs. pore diameter curves for SS<sub>1</sub> sample  
 a); incremental intrusion volume vs. pore diameter curves  
 (b): (○) particle diameter < 75 µm; (□) particle diameter range  $5 \cdot 10^2 - 2 \cdot 10^3$  µm.

The peak centered at 3–4 µm may be ascribed to the presence of interaggregate pores originating from the packing of the very fine particles of the soil, as shown by SEM analysis (Fig. 1.2c) and reported in literature [40].

Moreover, the pore-size distribution related to the fraction containing particles with diameters smaller than  $75\ \mu\text{m}$  (empty circles) is not monomodal, with additional maxima appearing in the distribution function, in particular in the range  $3\cdot 10^{-3} - 2\cdot 10^{-2}\ \mu\text{m}$ . On the other hand, for the same fraction, the cumulative intruded mercury volume vs. pore diameter curve (Figure 1.4a) can be divided in two distinct parts: a first region corresponding to the filling of pores with diameters ranging from  $1\ \mu\text{m}$  to  $10\ \mu\text{m}$  and a second one related to the filling of small pores with diameters of about  $1\cdot 10^{-2}\ \mu\text{m}$  and its inflection point is displaced to the fine pores zone.

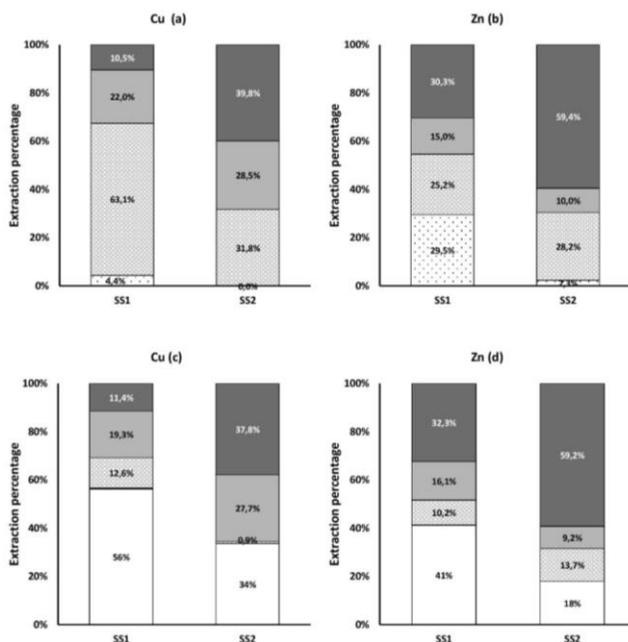


**Figure 1.5** – Adsorption-desorption isotherms of  $\text{N}_2$  at 77 K. (□) particle diameter  $< 75\ \mu\text{m}$ ; (△) particle diameter range  $5\cdot 10^2 - 2\cdot 10^3\ \mu\text{m}$  ( $\text{SS}_1$  sample).

Figure 1.5 reports the adsorption-desorption isotherms of the sample  $\text{SS}_1$  obtained by nitrogen adsorption porosimetry for soil fractions with particle diameters  $< 75\ \mu\text{m}$  and  $5\cdot 10^2 - 2\cdot 10^3\ \mu\text{m}$ . The initial part corresponds to type II isotherms of the IUPAC classification, typical of macroporous materials. Nevertheless, the isotherms show a little microporosity feature indicated by the presence of a well defined point “B”, the beginning of the linear middle section of the isotherm (grey circle in Figure 1.5), for low values of the relative pressure. The point “B” is often taken to indicate the stage at which monolayer coverage is complete. In the low relative pressure region the isotherms differ for the amount of  $\text{N}_2$  adsorbed up to the point “B” thus indicating a higher microporous volume in the soil sample with particle diameter  $< 75\ \mu\text{m}$ , in agreement with the results from mercury intrusion porosimetry. As expected, the value of BET surface of the same sample,  $24.9\ \text{m}^2/\text{g}$ , is significantly higher than that one measured for the soil with particle diameter in the range  $5\cdot 10^2 - 2\cdot 10^3\ \mu\text{m}$  (Table 1.1). The values of microporous area obtained from the t-plot show the same trend as BET surface, namely  $3.94\ \text{m}^2/\text{g}$  for the fine soil sample and  $0.87\ \text{m}^2/\text{g}$  for the coarse one. After the point “B” the hysteresis loop, typical of type IV isotherm of the IUPAC classification with unlimited adsorption at high relative pressure region, is associated with capillary condensation indicating the presence of a mesoporous volume. The shape of the hysteresis loop was type H3 of the IUPAC classification typical of aggregated particles forming plates and giving rise to pores in the form of rift or wedges as evidenced also by SEM micrographs (Fig. 1.3). Similar characteristics in the SEM and BET investigations were observed for  $\text{SS}_2$  sample.

### 1.3.2 Washing results

The distribution of copper and zinc in the two samples before and after soil washing with EDDS, estimated by sequential extraction procedure, is reported in Figure 1.6.



**Figure 1.6** – Sequential extraction of Cu and Zn in soil samples before (a,b) and after the soil washing (c,d). Soil washing conditions: S/L ratio = 1:10, [EDDS]<sub>0</sub> = 7.24 mM, treatment time = 96 hr, T = 20 °C, pH = 7.8. (□) Exchangeable and weak acid soluble fraction, (▒) Reducible fraction, (▓) Oxidizable fraction, (■) Residual fraction, (◻) Extracted by EDDS.

As already noted, the samples showed some differences in the initial distributions of copper and zinc, confirming the effect of larger anthropogenic contamination on SS<sub>1</sub> sample. The latter, in fact, had a higher content of the available fraction (sum of the exchangeable, the reducible and the oxidizable one) of both Cu and Zn, although it is worth noting that the concentration of zinc related to the oxidizable fraction was quite similar in two samples. Comparing the distribution of the metals in the two samples before and after the washing process it can be easily observed that only the fractions related to the exchangeable and reducible fraction were affected by the extraction. The amount of Cu and Zn associated with the oxidizable and the residual fractions, instead, remained almost unchanged, for both samples. For example, even in case of almost complete removal of Cu in the exchangeable and reducible fractions, the oxidizable fraction (mono- and zero-valent copper) was not removed. This result can be tentatively explained considering that in presence of soil humic matter, under anoxic or sub-oxic conditions, di-valent copper (Cu<sup>II</sup>), can be partially reduced to mono-valent (Cu<sup>I</sup>), one and further to zero-valent copper (Cu<sup>0</sup>) [41].

Regarding to Cu<sup>I</sup> species, similarly to EDTA [42] - a structural isomer of EDDS - Cu(I)-EDDS chelates do not form being very unstable complexes. On the contrary there are no evidences on the capacity of the organic matter in soil to reduce bivalent zinc ions. On the other hand, copper and zinc zero-valent cannot be chelated with EDDS.

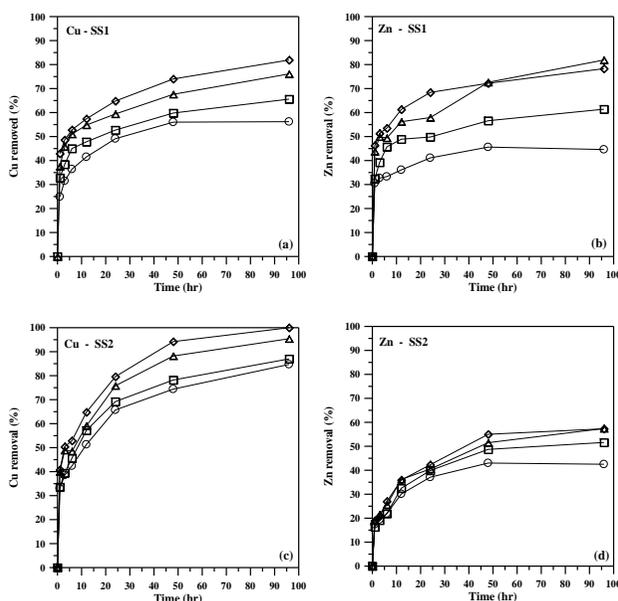
On the basis of the obtained results and taking into account the previous considerations, it can be assessed that only copper and zinc present in exchangeable and reducible fractions were effectively removed by EDDS.

The extraction kinetics of copper and zinc from two contaminated soils are shown in Figs. 1.7a-d at fixed solid-to-liquid ratio (S:L, 1:10) and varying initial EDDS concentrations (0.36 – 7.2 mM). As expected the extraction efficiency increased with increasing the initial concentration of the chelating agent from 0.36 mM to 7.2 mM. Under the adopted experimental conditions, after 96 hr of treatment, the highest Cu extraction

efficiencies were 82.0% for SS<sub>1</sub> and 100 % for SS<sub>2</sub>, while the highest Zn extraction efficiencies were 80.9% for SS<sub>1</sub> and 57.4% for SS<sub>2</sub>.

The better extraction efficiency of copper respect to zinc may be essentially ascribed to the higher stability (higher logK) of Cu-EDDS complexes respect to Zn-EDDS ones [43]. The recovery percentage of both metal was not substantially affected by L:S ratio-dependent variations within the range of liquid-to-solid ratio of 5:1 – 20:1 (data not shown).

For all tested experimental conditions the extraction process increased with the time, attaining an asymptotic value at around 96 hours. More in details the extraction rate was extremely high during the first 2-3 hours, and thereafter tended to decrease, remaining almost constant up to 10-15 hours, and decreasing one more up to the end of the test.



**Figure 1.7** – Metal removal percentage respect to exchangeable + reducible fractions as function of time at 1:10 of S:L ratio. T=20 °C, pH=7.8, with respect to EDDS (mM): ○ 0.36, □ 0.72, △ 3.6, ◇ 7.2.

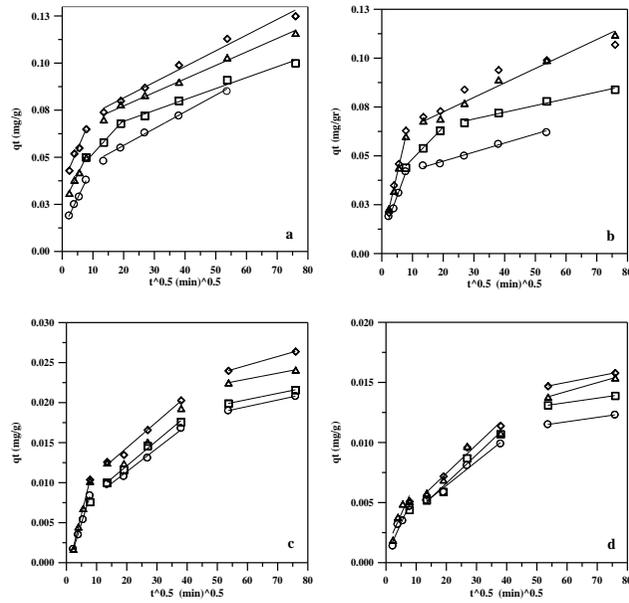
The results collected from the soil washing of samples SS<sub>1</sub> and SS<sub>2</sub> showed that, under the adopted experimental conditions, contact times of 24–36 hr resulted the best compromise for the extraction of copper and zinc, since longer contact times provided minor additional benefits.

### 1.3.3 Diffusion models

The extraction rate of metals from soils by organic molecules may be controlled by mass transfer phenomena or chemical reaction processes. Whether the extraction process develops under an intra-particle diffusive regime (rate-limiting step), a linear dependence of the extraction capacity for each metal on square root of the contact time is obtained [44–46]:

$$q_t = k_D \cdot t^{0.5} + c \quad 1.6$$

where  $q_t$  is the amount of metal per unit of soil mass extracted at time  $t$ ,  $k_D$  the rate constant of intra-particle diffusion,  $t$  the contact time and  $c$  is a constant.



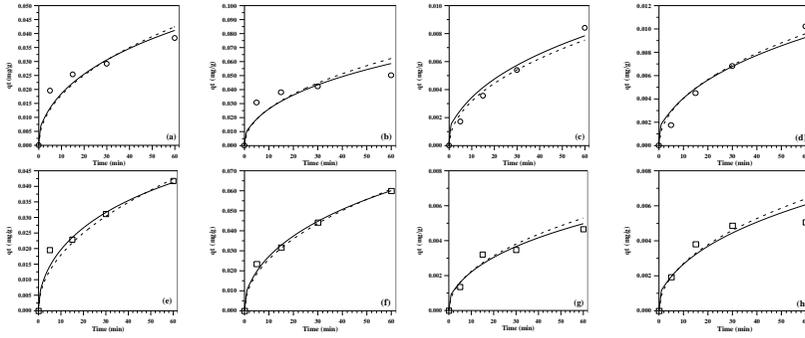
**Figure 1.8** – Intra-particle diffusion plots for copper (a,c) and zinc (b,d) during the soil washing of SS<sub>1</sub> (a,b) and SS<sub>2</sub> (c,d) at fixed S:L (1:1:10) and different initial EDDS concentrations. EDDS (mM): ○ 0.36, □ 0.72, △ 3.6, ◇ 7.2.

The mass Cu and Zn extracted at any time  $t$  with respect to the soil mass versus  $t^{1/2}$  is reported in Figures 1.8a-d at different initial EDDS concentrations for SS<sub>1</sub> and SS<sub>2</sub> soils respectively.

The Weber plots indicate that, after the initial minutes of soil washing, where the convective diffusion in the solution and/or the external exchange are presumably the dominant processes, multi straight lines fit the experimental data. The multi-linearity observed indicates that the diffusive process develops in pores of progressively smaller sizes. The first segment of the plot may be ascribed to boundary layer diffusion effects such as external film resistance and superficial diffusion whereas the other linear segments are related to further curve portions depict the different processes of the intra-particle diffusion (macropore and micropore) [47].

Moreover, under the adopted experimental conditions, an increase in initial concentration of the chelating agent did not result into a corresponding appreciable increase of the slope of the plot thus indicating that the rate of intra-particle diffusive process is not dependent upon the initial EDDS solution concentration.

The comparison between the experimental data for SS<sub>1</sub> and SS<sub>2</sub> samples and the curves calculated from the diffusion model according to Crank's approximation with the assumption of spherical or cylindrical particles is reported in Figures 1.9a-h for contact times less than 1 hour and for two different initial EDDS concentrations.



**Figure 1.9** – Crank's model, comparison between experimental (Cu: ○, Zn: □) and calculated (lines) results ( $\bar{\alpha} = 23 \mu\text{m}$ ; S:L 1:10). Continuous curve for spherical particles, dashed curve for cylindrical particles [EDDS]<sub>0</sub> 0.36 mM, Cu extraction (SS<sub>1</sub>, (a); SS<sub>2</sub>, (c)); [EDDS]<sub>0</sub> 3.6 mM, Cu extraction (SS<sub>1</sub>, (b); SS<sub>2</sub>, (d)); [EDDS]<sub>0</sub> 0.36 mM, Zn extraction (SS<sub>1</sub>, (e); SS<sub>2</sub>, (g)), [EDDS]<sub>0</sub> 3.6 mM, Zn extraction (SS<sub>1</sub>, (f); SS<sub>2</sub>, (h)).

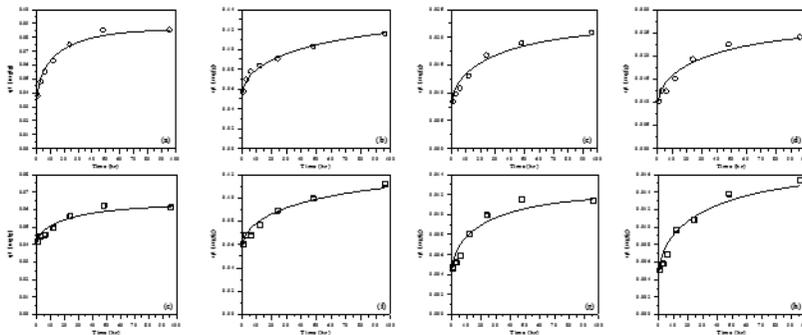
It is found that the fitting of data is almost satisfactory for all experimental cases if assuming the spherical particles either cylindrical, as demonstrated also by the coefficient of correlation ( $R^2$ ) and the percentage standard deviation ( $\sigma\%$ ) reported in Table 1.2. The percentage standard deviation is defined as:

$$\sigma\% = 100 \cdot \frac{1}{\bar{q}_{exp}} \cdot \sqrt{\frac{\sum_N [q_{t,cal} - q_{t,exp}]^2}{N}}$$

where  $q_{t,exp}$  and  $q_{t,cal}$  are the experimental and calculated  $q_t$  values respectively,  $\bar{q}_{exp}$  is the average measured concentration and  $N$  the number of data points.

The mean values of intraparticle diffusion coefficients ( $\bar{D}$ ) are quite similar for copper-EDDS and zinc-EDDS chelates for both sampled soils. Moreover, the calculated values for the effective diffusion coefficients are comparable with those reported in the literature for different organic substances in soils and sediments [54,55].

The diffusion coefficients evaluated using the Vermeulen's approximation are reported in Table 1.3 along with the coefficient of correlation and the percentage standard deviation, whereas the model was fitted to the experimental results (Figs. 1.10a-h).



**Figure 1.10** – Vermeulen's model, comparison between experimental (Cu: ○, Zn: □) and calculated (lines) results. S:L 1:10. [EDDS]<sub>0</sub> 0.36 mM, Cu extraction (SS<sub>1</sub>, (a); SS<sub>2</sub>, (c)); [EDDS]<sub>0</sub> 3.6 mM, Cu extraction (SS<sub>1</sub>, (b); SS<sub>2</sub>, (d)) [EDDS]<sub>0</sub> 0.36 mM, Zn extraction (SS<sub>1</sub>, (e); SS<sub>2</sub>, (g)); [EDDS]<sub>0</sub> 3.6 mM, Zn extraction (SS<sub>1</sub>, (f); SS<sub>2</sub>, (h))

Crank's Model (cylindrical particles)												
Metal	Cu						Zn					
Soil	SS <sub>1</sub>			SS <sub>2</sub>			SS <sub>1</sub>			SS <sub>2</sub>		
EDDS (mM)	0.36	3.6	7.2	0.36	3.6	7.2	0.36	3.6	7.2	0.36	3.6	7.2
$D$ (m <sup>2</sup> ·s <sup>-1</sup> )	$8.13 \cdot 10^{-15}$	$7.20 \cdot 10^{-15}$	$1.06 \cdot 10^{-14}$	$4.01 \cdot 10^{-15}$	$4.47 \cdot 10^{-15}$	$4.13 \cdot 10^{-15}$	$1.56 \cdot 10^{-14}$	$8.65 \cdot 10^{-15}$	$1.02 \cdot 10^{-14}$	$6.23 \cdot 10^{-15}$	$4.88 \cdot 10^{-15}$	$7.06 \cdot 10^{-15}$
$\sigma$ (%)	9	13	15	7	8	10	7	4	2	8	11	6
R <sup>2</sup>	0.91	0.80	0.89	0.97	0.97	0.91	0.95	0.99	0.99	0.95	0.91	0.96
$\bar{D}$ (m <sup>2</sup> ·s <sup>-1</sup> )	$8.64 \cdot 10^{-15} \pm 1.45 \cdot 10^{-15}$			$4.20 \cdot 10^{-15} \pm 2.7 \cdot 10^{-16}$			$1.15 \cdot 10^{-14} \pm 4.10 \cdot 10^{-15}$			$6.06 \cdot 10^{-15} \pm 1.18 \cdot 10^{-15}$		
Crank's Model (spherical particles)												
Metal	Cu						Zn					
Soil	SS <sub>1</sub>			SS <sub>2</sub>			SS <sub>1</sub>			SS <sub>2</sub>		
EDDS (mM)	0.36	3.6	7.2	0.36	3.6	7.2	0.36	3.6	7.2	0.36	3.6	7.2
$D$ (m <sup>2</sup> ·s <sup>-1</sup> )	$4.03 \cdot 10^{-15}$	$3.50 \cdot 10^{-15}$	$5.52 \cdot 10^{-15}$	$1.95 \cdot 10^{-15}$	$2.03 \cdot 10^{-15}$	$2.25 \cdot 10^{-15}$	$9.03 \cdot 10^{-15}$	$4.55 \cdot 10^{-15}$	$5.50 \cdot 10^{-15}$	$2.87 \cdot 10^{-15}$	$2.33 \cdot 10^{-15}$	$3.26 \cdot 10^{-15}$
$\sigma$ (%)	8	12	14	7	8	10	6	3	3	7	10	6
R <sup>2</sup>	0.93	0.83	0.86	0.97	0.96	0.92	0.97	0.99	0.99	0.96	0.92	0.96
$\bar{D}$ (m <sup>2</sup> ·s <sup>-1</sup> )	$4.35 \cdot 10^{-15} \pm 1.17 \cdot 10^{-15}$			$2.08 \cdot 10^{-15} \pm 1.70 \cdot 10^{-16}$			$6.36 \cdot 10^{-15} \pm 2.67 \cdot 10^{-15}$			$2.82 \cdot 10^{-15} \pm 4.90 \cdot 10^{-16}$		

**Table 1.2** - Best estimated values of pore diffusivities based on Crank's approximation for Cu/EDDS and Zn/EDDS species for SS<sub>1</sub> and SS<sub>2</sub> samples.

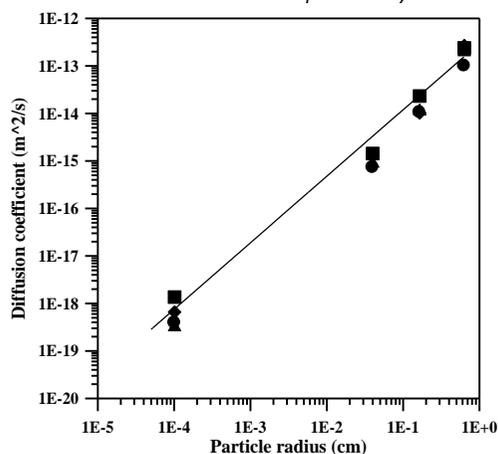
Vermeulen's Model								
Cu								
Soil	SS <sub>1</sub>				SS <sub>2</sub>			
EDDS (mM)	0.36	0.72	3.6	7.2	0.36	0.72	3.6	7.2
$D$ (m <sup>2</sup> ·s <sup>-1</sup> )	2.65·10 <sup>-16</sup>	2.01·10 <sup>-16</sup>	1.67·10 <sup>-16</sup>	1.50·10 <sup>-16</sup>	2.42·10 <sup>-16</sup>	2.61·10 <sup>-16</sup>	2.15·10 <sup>-16</sup>	3.32·10 <sup>-16</sup>
$\sigma$ (%)	8	3	3	2	6	5	7	9
R <sup>2</sup>	0.95	0.98	0.98	0.98	0.97	0.98	0.96	0.93
$\bar{D}$ (m <sup>2</sup> ·s <sup>-1</sup> )	1.96·10 <sup>-16</sup> ± 6.90·10 <sup>-17</sup>				2.62·10 <sup>-16</sup> ± 7.00·10 <sup>-17</sup>			
Zn								
Soil	SS <sub>1</sub>				SS <sub>2</sub>			
EDDS (mM)	0.36	0.72	3.6	7.2	0.36	0.72	3.6	7.2
$D$ (m <sup>2</sup> ·s <sup>-1</sup> )	3.32·10 <sup>-16</sup>	2.98·10 <sup>-16</sup>	1.76·10 <sup>-16</sup>	2.67·10 <sup>-16</sup>	3.25·10 <sup>-16</sup>	3.32·10 <sup>-16</sup>	2.38·10 <sup>-16</sup>	2.80·10 <sup>-16</sup>
$\sigma$ (%)	9	5	6	4	9	9	7	8
R <sup>2</sup>	0.93	0.97	0.97	0.98	0.93	0.94	0.96	0.95
$\bar{D}$ (m <sup>2</sup> ·s <sup>-1</sup> )	2.68·10 <sup>-16</sup> ± 9.20·10 <sup>-17</sup>				2.94·10 <sup>-16</sup> ± 3.80·10 <sup>-17</sup>			

**Table 1.3** - Best estimated values of pore diffusivities based on Vermeulen's approximation for Cu/EDDS and Zn/EDDS species for SS<sub>1</sub> and SS<sub>2</sub> samples.

The results indicate that the diffusion model according to Vermeulen's approximation was found to be very suitable for predicting copper and zinc extraction for contact times higher than 1 hour. The average values estimated for the pore diffusion coefficient are about one order of magnitude smaller than those estimated using Crank's approximation according to the fact that, for more prolonged contact times, even the effects of diffusive processes in smaller pores are taken into account.

With the aim to evaluate the dependence of pore diffusivity on the particle size of the soil sampled, the intraparticle diffusion coefficients for the extraction of copper and zinc using an initial EDDS concentration of 3.6 mM and a solid-to-liquid ratio equal to 1:10 were estimated for different sieved granulometric fractions using the optimization procedure, previously described, assuming the Vermeulen's approximation. The results indicated that the intraparticle diffusion coefficient of Cu-EDDS and Zn-EDDS chelates increases at increasing soil particle mesh size, ranging from 10<sup>-18</sup> – 10<sup>-19</sup> m<sup>2</sup>·s<sup>-1</sup> for particle diameters smaller than 30 µm to 10<sup>-13</sup> m<sup>2</sup>·s<sup>-1</sup> for diameters higher than 5 mm thus indicating that the smallest granulometric fractions are characterized by higher percentage micropores than the biggest size particles, as it has been suggested by SEM analysis and evidenced by BET analysis.

The best estimated values of pore diffusivity against the mean particle radius were very well fitted by the non-linear relationship ( $D = 3 \cdot 10^{-13} \cdot R_p^{1.4}$ ) proposed by Badruzzaman for intraparticle diffusion processes of arsenic into porous iron oxides [59] (Fig. 1.11).



**Figure 1.11** – Intraparticle diffusivity coefficient vs mean particle radius. Continuous curve: literature data [59]. [EDDS]<sub>0</sub> = 3.6 mM, S:L 1:10. Cu (SS<sub>1</sub> ●, SS<sub>2</sub> ■); Zn (SS<sub>1</sub> ▲, SS<sub>2</sub> ◆)

## 1.4 Conclusions

The present investigation demonstrated the removal effectiveness of copper and zinc from polluted soils through a soil washing process using EDDS as chelating agent and evidenced that the intra-particle diffusion was the main rate controlling step in the extraction of heavy metals from the solid matrix. The soil washing process allows to efficiently extract the Cu and Zn exchangeable and reducible fractions only. The Weber plots exhibited multi-linearity thus indicating that the diffusive process develops in pores of progressively smaller sizes. The diffusion coefficients of the Cu/EDDS and Zn/EDDS complexes in real contaminated soils were calculated using the Crank's approximation (for short contact times, < 1 hr) and Vermeulen's approximation (for long contact times, > 1 hr). Both models gave a good fit of the experimental data and the best calculated pore diffusion coefficients are consistent with those reported in the literature. The "apparent" diffusion coefficients of Cu-EDDS and Zn-EDDS species increase at raising particle size, ranging from  $10^{-18}$  –  $10^{-19}$   $m^2 \cdot s^{-1}$  for particle diameters smaller than 30  $\mu m$  to  $10^{-13}$   $m^2 \cdot s^{-1}$  for diameters higher than 5 mm. The results collected suggest that the soil washing with chelating agents, under the adopted experimental conditions, is limited by the intra-particle diffusion process and, because of the very small pore sizes of the sampled soils, it represents a promising alternative to soil remediation, as the two heavy metals could not be available for the removal using less intense techniques.

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# Chapter 2 Simulated solar photocatalytic processes for the simultaneous removal of EDDS, Cu(II), Fe(III) and Zn(II) in synthetic and real contaminated soil washing solutions.

Metal contamination of natural soil is a global problem. In many cases the contamination is due to anthropogenic activities, and, sometimes, it comes from illegal waste disposal due to uncontrolled industrial development. One of the ways of solving metal soil contamination is by soil washing using a chelating biodegradable agent (EDDS). However, the resulting liquid wastes that contain the extracted metals and chelating agents have to be submitted to further treatments for a complete detoxification before being discharged into the environment. The simultaneous removal of EDDS and three metals (Cu, Fe and Zn) from both synthetic waters (home prepared) and real contaminated soil washing mixtures at neutral pH has been investigated, a lab-scale, considering four artificial solar driven photocatalytic technologies (TiO<sub>2</sub>/hν/N<sub>2</sub>, TiO<sub>2</sub>/hν/Air, Fe(III)-EDDS/hν/Air and Fe(III)-EDDS/hν/H<sub>2</sub>O<sub>2</sub>/Air). The soils were sampled in the Province of Naples (South of Italy) in a zone infamously known for its high incidence of cancer mortality.

The results indicate that both the type and the sequence of photocatalytic technologies that need to be apply should be chosen prudently considering both the nature and the content of the soil washing solutions.

## 2.1 Introduction

The metal contamination of natural soils is a worldwide concern because of the negative effect that metals could have on living beings [1]. In order to face the problem, several remediation techniques, based on physical, chemical, and even biological processes, have been proposed [2,3]. Among these techniques, soil washing certainly plays a primary role because of its proven efficiency for various soil characteristics and metal types [4,5]. As is well known, soil washing is an off-site treatment that includes the removal of contaminants from the solid phase, using an appropriate washing solution, and a subsequent treatment of the liquid phase containing the extracted metals, for its complete detoxification [6]. Although in the past 20 years many compounds have been tested as washing agents [4,5], the most frequently used ones today are those belonging to aminopolycarboxylate chelants groups (APCs) [2,7,8]. Most of the studies concerning the use of APCs processes have been carried out on aqueous solutions containing ethylenediaminetetraacetic acid (EDTA) because of its easy availability and relatively low cost [9,10]. Unfortunately, EDTA is quite persistent in the environment as it is poorly biodegradable [8]. Therefore, more and more often ethylenediaminedisuccinic acid (EDDS) is proposed as a safe and environmentally friendly replacement for EDTA in soil washing processes [11-13].

Although the *S,S*-stereoisomeric form of EDDS is considered to be easily biodegradable, the biodegradability of the complexes formed between *S,S*-EDDS and the heavy metals extracted during the washing process is still under discussion [14]. This is why it is extremely important to find an appropriate technique for exhausted EDDS washing solution detoxification. In this context it is necessary to consider that exhausted solutions cannot generally be treated using conventional physical methods, such as filtration, flocculation, precipitation or adsorption [15,16].

Although, the use of soil washing for the remediation of metal polluted soils has been largely applied, little attention has been posed to the treatment of the exhausted washing solution through photochemical processes. The present chapter aims to focus the attention on this latter aspect, investigating the applicability and the convenience of solar photo-catalysis for the simultaneous removal of the washing agent and the targeted metals extracted from a real contaminated soil.

In aqueous solution, EDDS forms several stable mono-, bis- and hydroxy- complexes with copper, iron and zinc (Table 2.1), which relative concentrations are affected to a great extent by the pH of the solution.

The predominant complexes at pH values close to 7.0, are:  $[CuEDDS]^{2-}$ ,  $[ZnEDDS]^{2-}$ ,  $[FeEDDS]^{-}$  and  $[Fe(OH)EDDS]^{2-}$  as reported by Orama et al. [17].

Cu(II)	Log K	Fe(III)	Log K
$Cu^{2+} + EDDS^{4-} \rightleftharpoons [CuEDDS]^{2-}$	18.6	$Fe^{3+} + EDDS^{4-} \rightleftharpoons [FeEDDS]^{-}$	20.6
$[CuEDDS]^{2-} + H^{+} \rightleftharpoons [CuHEDDS]^{-}$	3.6	$[Fe(OH)EDDS]^{2-} + H^{+} \rightleftharpoons [FeEDDS]^{-}$	7.9
$[CuHEDDS]^{-} + H^{+} \rightleftharpoons CuH_2EDDS$	2.3	$[Fe(OH)_2EDDS]^{3-} \rightleftharpoons [Fe(OH)EDDS]^{2-} + HO^{-}$	9.9
$[Cu(OH)EDDS]^{3-} + H^{+} \rightleftharpoons [CuEDDS]^{2-} + H_2O$	11.1		
$[CuEDDS]^{2-} + Cu^{2+} \rightleftharpoons Cu_2EDDS$	2.4		
$[CuEDDS]^{2-} + [HEDDS]^{3-} \rightleftharpoons [CuEDDS(HEDDS)]^{5-}$	2.5		
$[CuEDDS(HEDDS)]^{5-} + H^{+} \rightleftharpoons [Cu(HEDDS)_2]^{4-}$	7.1		
Zn(II)	Log K	EDDS	pK <sub>a</sub>
$Zn^{2+} + EDDS^{4-} \rightleftharpoons [ZnEDDS]^{2-}$	13.6	$H_4EDDS \rightleftharpoons H_3EDDS^{-} + H^{+}$	2.4
$[ZnEDDS]^{2-} + H^{+} \rightleftharpoons [ZnHEDDS]^{-}$	3.7	$H_3EDDS^{-} \rightleftharpoons H_2EDDS^{2-} + H^{+}$	3.9
$[ZnHEDDS]^{-} + 2H^{+} \rightleftharpoons [ZnH_3EDDS]^{+}$	5.9	$H_2EDDS^{2-} \rightleftharpoons HEDDS^{3-} + H^{+}$	6.8
$[Zn(OH)EDDS]^{3-} + H^{+} \rightleftharpoons [ZnEDDS]^{2-} + H_2O$	11.3	$HEDDS^{3-} \rightleftharpoons EDDS^{4-} + H^{+}$	9.8
$[ZnHEDDS]^{-} + HEDDS^{3-} \rightleftharpoons [Zn(HEDDS)_2]^{4-}$	5.5		

**Table 2.1:** Stability constants (Log K) for the Cu(II), Fe(III) and Zn(II) ion complexes of EDDS [17] and acidity constants (pK<sub>a</sub>) for EDDS (T=20°C) [14].

These stable complexes enhance the dissolution of the metals, even at neutral pHs and prevent their removal from water through precipitation, mainly as hydroxy species.

On the other hand, it has been reported that some metal-aminopolycarboxylic complexes are photosensitive to sunlight irradiation, and their photodecomposition, which results from the charge transfer from metal to ligand, may lead to metal reduction and ligand radical formation [18].

Among the complexes formed between aminocarboxylic ligands and metals, the Fe(III) ones have proved to be the most photosensitive. In particular, Fe(III)-EDDS complexes undergo fast photochemical reactions through a ligand to metal charge transfer (LMCT) process, which leads to the formation of oxidative species,

such as hydroxyl radicals [19]. In other words, Fe(III)-EDDS complexes, working like “homogeneous photo-Fenton systems” but at neutral pHs, may enhance the oxidative degradation of organic ligands and promote the precipitation of some metal ions present in the solution as metal hydroxides.

In some cases, an alternative route may be followed using heterogeneous TiO<sub>2</sub>-photocatalysis. For example, it has recently been shown that, at acidic pH, cupric ions, chelated with EDDS, are photoreduced to zero-valent copper, which is then efficiently removed from the solution [20]. This system is an example of “sacrificial photocatalysis” because it uses EDDS as a sacrificial agent, since it is a scavenger for the photogenerated holes.

The possibility of simultaneously removing EDDS and three metals (Cu, Fe and Zn) from synthetic water (home prepared) and real contaminated soil washing mixtures, for pH conditions close to neutrality, has been explored, in the present investigation, by means of artificial solar-driven homogeneous and heterogeneous photocatalytic processes. The sampled soils were taken from the Province of Naples (Southern Italy) in one of the areas with the highest levels of solar irradiation in Europe with a solar radiation per unit area equal to an average daily sum of close to 5 kWh×m<sup>-2</sup>×day<sup>-1</sup> [21]. The place is well known because of the high incidence of cancer mortality that exceeds both the Italian national and European average number [22-24]. This area, in fact, has been used, for many years by Criminal Organizations for illegal disposal of industrial waste, and it is actually characterized by high level of pollution due to toxic heavy metals [25]. Because of the mentioned characteristics of the photochemical processes, the applicability of the proposed processes in this specific area appears to be particularly appropriate. It has to be mentioned, of course, that the applicability of the proposed process is subordinated to the realization of a suitable pretreatment of the washing solution able to remove the residual turbidity without leaving residues of metals used for coagulation processes.

## 2.2 Experimental

### 2.2.1 Materials

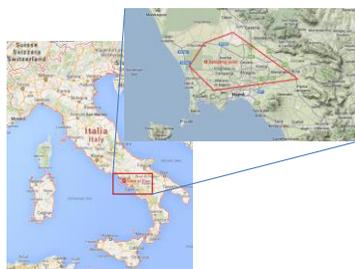
Copper(II) sulphate (reagentPlus® >99% w/w), copper(II) perchlorate hexahydrate (98% w/w), copper(II) carbonate basic (reagent grade >98% w/w), zinc(II) chloride (reagent grade >98% w/w), Fe(III) perchlorate hydrate (low chloride content < 0.005%), (S,S)-Ethylenediamine-*N,N'*-disuccinic acid-trisodium salt solution (35% in H<sub>2</sub>O), titanium(IV) oxide pure crystalline anatase powder (99.8% w/w), nitric acid (ACS reagent >67% v/v), hydrogen peroxide (ACS reagent 30% wt% in H<sub>2</sub>O), perchloric acid (ACS reagent 70%) and sulfuric acid (ACS reagent 95-98% v/v) were purchased from Sigma Aldrich and used as received.

### 2.2.2 Titanium oxide characterization

BET specific surface area of TiO<sub>2</sub> used (9.5 m<sup>2</sup>×g<sup>-1</sup>) was measured by single point BET method using a Micrometrics Flw Sorb 2020 apparatus. A Laser Light Scattering particle size analyzer (Malvern Instruments Mastersizer 2000) was used to measure the particle size distribution of the commercial TiO<sub>2</sub> (LLS particle size range 0.16 – 1.78 μm, LLS average particle size 0.50 ± 5.3×10<sup>-2</sup> μm).

### 2.2.3 Soil sampling

The soils samples used in the present investigation were taken in Giugliano in Campania, in the province of Naples (Southern Italy), in the center of a large geographic area interested by illegal disposal of hazardous waste and therefore known as the “Triangle of Death” (Figure 2.1). This region covers an area of 1076 km<sup>2</sup> and has 57 municipalities: 33 of them are located in the province of Naples and 24 municipalities are in the province of Caserta, which totalize about 2.5 million of people living in a potential health risk [58].



**Figure 2.1.** Map of the province of Naples in which the sampling point are highlighted (geographic coordinates N 40° 96' 05", E 14° 11' 84").

Two soil samples (SS) were taken at a distance of 10 m from each other, named SS<sub>A</sub> and SS<sub>B</sub>. The samples were collected manually from the top 20 cm of the soil, over an area of about 1 square meter, and then stored in hermetic containers. Immediately after collection, the samples were dried at 40 °C in an oven (Argolab, TCN115), sieved at 2 mm, and kept at room temperature. Only the fraction of soil that was smaller than 2 mm, which was assumed to be the most contaminated [26], was used in all the experiments and analytical determinations.

The grain size was determined according to ASTM protocol [27]. The determination of the organic matter in the soil was carried out as loss-on-ignition (LOI), heating the soil samples before at 105 °C and successively at 550 °C in a muffle furnace. The pH of the sampled soils was evaluated through U.S. EPA Method [28]. Main soil characteristics were: pH 7.48, LOI 7.35%, clay 14.3%, silt 39.8% and sand 45.9% for SS<sub>A</sub> sample and pH 7.53, LOI 7.82%, clay 19.1%, silt 37.2% and sand 43.7% for SS<sub>B</sub> sample.

#### 2.2.4 Analysis of the metals in the soil

Total concentration of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn was determined in SS after wet digestion, according to the EPA method 3051 [29], which corresponds to the pseudo total extraction procedure. In particular, 2 g of a dried sieved sediment sample was subjected to digestion in a microwave oven (Milestone START D). The temperature was raised to 175 °C in less than 5.5 minutes, and kept between 170-180 °C for at least 10 minutes. A nitric acid solution and a hydrogen peroxide solution were used, in 10 mL HNO<sub>3</sub> to mL H<sub>2</sub>O<sub>2</sub> ratio, as the extraction reagents. After cooling, the digestate was filtered and diluted by adding up to 50 mL of distilled water.

Metal concentration was determined through Atomic Absorption Spectrometry (AAS), using a Varian Model 55B SpectrAA (F-AAS) equipped with a flame (acetylene/air), with a deuterium background correction or a GBC Avanta AAS with a graphite furnace (GF-AAS). AAS standards for Cd, Cr, Cu, Fe, Pb, Zn (Carlo Erba, Reagenti), Mn and Ni (Fluka Reagents) were used in digestion and analysis as part of the EPA protocol. All the measurements were conducted in triplicate using analytical grade chemicals and ultrapure water.

#### 2.2.5 Soil washing procedure

Soil washing experiments were performed in 50 mL polyethylene bottles. Ethylenediamine-N,N'-disuccinic acid was used as the chelating agent. The tests were carried out at a natural pH (7.5) fixing the liquid-to-solid ratio (L/S) to 10:1 and the EDDS washing solution concentration to 0.36 mM, which corresponds to a mean ratio between EDDS and the sum of the total concentrations of Cd, Cr, Cu, Ni, Pb and Zn in the soils ( $\overline{MR}$ ) close to 0.6, that is under EDDS-deficiency conditions as proposed by Yan et al. [30].

The soil-solution ratio of 1:10 (w/v) was chosen following the literature findings [7,31-33]. The pH was measured by means of a pH-meter (Orion 420A<sup>+</sup>, Thermo).

The samples were stirred in a mechanical shaker (Edmund Bühler, Kombischüttler KL2) at 190 rpm for 96 hrs at ambient temperature. Moreover, soil washing with only water was carried out for the blank sample. All the experimental tests were conducted in triplicate.

#### *2.2.6 Metal analysis in the soil washing solution*

After washing, the samples were centrifuged at 4800 rpm for 15 min using an IEC Centra GP8R centrifuge and filtered at 0.45  $\mu$ m. The filtered washing solution samples were transferred to polyethylene containers for metal determination through AAS.

All the measurements were carried out in triplicate using analytical grade chemicals and ultrapure water.

#### *2.2.7 Photocatalytic procedures*

All the experiments were performed in an annular cylindrical glass jacketed batch reactor (280 ml) thermostated at 25 °C and equipped with a high-pressure UV lamp (UV 12F-Helios Italquartz, nominal power 125 W) mainly emitting at 305, 313 and 366 nm (manufacturer's data). The photon flow of the lamp at 305 was  $8.08 \cdot 10^{-7}$  einsteins $\times$ s<sup>-1</sup>, determined through hydrogen peroxide photolytic experiments [34], at 313 nm was  $1.39 \cdot 10^{-6}$  einsteins $\times$ s<sup>-1</sup> determined by valerephenone actinometry [52] and at 366 nm was  $4.52 \cdot 10^{-6}$  einsteins $\times$ s<sup>-1</sup> measured using a UV radiometer (Delta Ohm HD 9021).

The apparatus has been reported elsewhere [36]. The aqueous solutions, containing EDDS, and eventually a proper TiO<sub>2</sub> load, were purged with oxygen or nitrogen (flow 0.2 L $\times$ min<sup>-1</sup>) before and during the photolytic experiments. A load of TiO<sub>2</sub> equal to 100 mg $\times$ L<sup>-1</sup> was chosen for the experimental investigation, as good compromise, on the basis of the previous investigations [20]. The Cu(II), Fe(III) and Zn(II) starting concentrations used for the synthetic mixtures (synthetic) were chosen very similar to those measured for the same metals but present in the real soil washing solutions. The samples, collected at different reaction times up to 120 or 180 minutes, were filtered through regenerated cellulose filters (pore diameter 0.45  $\mu$ m, Teknokroma) before the chemical analysis.

#### *2.2.8 EDDS analysis*

The EDDS analyses were performed using a modified version of a previously reported colorimetric method [14]. After adjusting the pH to 2.0, the sample (3.3 mL) and a suitable amount of the reagent solution, containing cupric sulphate (2 mM), were added to a volumetric flask (5.0 mL). Cu(II)-EDDS, a blue complex, was formed and its concentration was quantified through spectrophotometric analysis at 670 nm (ATI-Unicam UV/Vis spectrophotometer).

## 2.3 Results and discussion

### *2.3.1 Metal contents in the soil*

The analytical determinations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn elements contained in the soil samples are reported in Table 2.2.

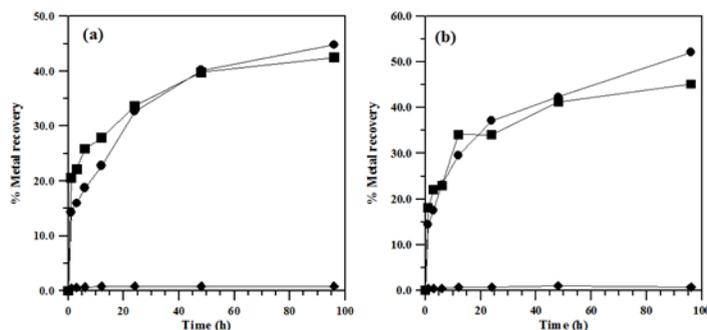
Sample	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
SS <sub>A</sub>	0.53	40.3	1.9×10 <sup>2</sup>	1.2×10 <sup>5</sup>	5.4×10 <sup>2</sup>	7.6	32.2	1.7×10 <sup>2</sup>
	±	±	±	±	±	±	±	±
SS <sub>B</sub>	0.10	8.0	10.4	9.4×10 <sup>2</sup>	38.1	0.49	2.6	12.0
	±	±	±	±	±	±	±	±
Mean values for soils <sup>(a)</sup>	0.28	16.8	1.4×10 <sup>2</sup>	1.1×10 <sup>5</sup>	5.3×10 <sup>2</sup>	8.9	21.1	1.7×10 <sup>2</sup>
	1.4×10 <sup>-2</sup>	2.5	10.3	1.4×10 <sup>3</sup>	26.5	1.0	0.3	2.0
Mean values for soils <sup>(a)</sup>	0.35	5.0×10 <sup>-2</sup>	51	2.8×10 <sup>5</sup>	1.5×10 <sup>3</sup>	2.5×10 <sup>2</sup>	1.0×10 <sup>2</sup>	1.5×10 <sup>2</sup>
<b>Detection Limits</b>								
F-AAS	5.0·10 <sup>-2</sup>	0.5	0.2	0.25	0.1	0.3	1.0	5.0×10 <sup>-2</sup>
GF-AAS	5.0·10 <sup>-4</sup>	5.0·10 <sup>-3</sup>	5.0·10 <sup>-3</sup>	5.0·10 <sup>-3</sup>	1.0·10 <sup>-3</sup>	5.0·10 <sup>-3</sup>	5.0·10 <sup>-3</sup>	2.0·10 <sup>-4</sup>

**Table 2.2:** Metal concentrations in the soil samples (SS<sub>i</sub>). SS<sub>A</sub>, SS<sub>B</sub>: samples A and B respectively. <sup>(a)</sup> mean concentration of metals in soils elsewhere reported [28].

Of all the analyzed metal species, copper and zinc, along with iron and manganese, were found to be present in the soil samples at the highest concentration levels. However, the measured concentrations of Fe and Mn were lower than the average values for unpolluted soils, whereas the Cu and Zn levels were much higher than those usually reported [37]. On the basis of these preliminary results, an attempt was made to remove the copper and zinc from the soils through the soil washing process.

### 2.3.2 Metal recovery from the soils through EDDS extraction

Figures 2.2a,b show the removal percentage of copper, zinc and iron from the two polluted soils using EDDS as the chelating agent for different extraction times. The starting metal concentrations present in the soil samples have been reported elsewhere (Table 2.2). The metal removal efficiency, respect to the mobile fraction, from both samples was very similar. In particular, the Cu removal was 45% and 52% for SS<sub>A</sub> and SS<sub>B</sub> respectively, whereas the percentage removal for Zn was close to 45% for both samples. The removal of iron, which is naturally present in the soils, was lower than 1%, because of the soil washing with EDDS-to-metal molar ratios less than unity, as confirmed by Tsang [30].



**Figure 2.2:** Metal recovery percentage by means of EDDS solutions from soils at varying time: (a) SS<sub>A</sub>, (b) SS<sub>B</sub>. (●) Cu, (◆) Fe, (■) Zn. pH=7.8, T=25°C. EDDS-to-metal molar ratio: 0.53 for SS<sub>A</sub>, 0.66 for SS<sub>B</sub>.

Moreover, the experiments evidenced a marked increase in removal of both Cu and Zn within 24 hrs, which then slowed down until 96 hrs was reached. Most of the Fe extraction took place within 12 hrs. Additional extractions, which are carried out for prolonged treatment times (192 hrs) resulted in a further recovery of

less than 10% for both Cu and Zn (data not shown). These results suggested choosing a contact time of 96 hrs as a acceptable time compromise for the preparation of the soil washing solutions for the photocatalytic treatments in order to remove copper, iron and zinc from the soils.

The removals efficiency achieved for Cu was similar to that found in previous investigations carried out using EDDS with a low chelating agent/metal ratio, whereas the removal of Zn was higher than the literature results obtained on natural soils [39].

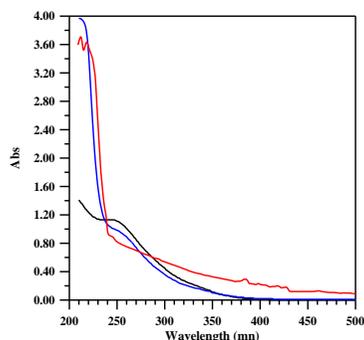
pH	$\overline{MR}^a$	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
7.8	0	$< 5.0 \cdot 10^{-4}$	$< 5.0 \cdot 10^{-3}$	0.07 $\pm$ $5.8 \cdot 10^{-3}$	2.51 $\pm$ 0.66	$< 1.0$	$< 0.5$	$< 5.0 \cdot 10^{-3}$	$< 5.0 \cdot 10^{-2}$
7.8	0.59	$< 5.0 \cdot 10^{-4}$	$< 0.5$	6.84 $\pm$ 0.48	3.55 $\pm$ 0.54	$< 1.0$	$< 0.5$	$< 0.05$	6.20 $\pm$ 0.4

**Table 2.3:** Metals concentrations (ppm) in the soil-washing solutions. pH=7.8, T=25 °C.  $\overline{MR}$  = EDDS-to-metal molar average ratio

The average analytical concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn elements contained in the soil-washing solutions (SW) from both the polluted soil samples (SSA and SSB) after 96 hrs of contact time are reported in Table 2.3. The collected results indicated that the SW solutions, in which EDDS was used as the chelating agent, instead of only distilled water, mainly contained copper, iron and zinc at concentration levels that required one or more post-treatment processes, before being discharged into the environment.

### 2.3.3 UV-Vis light absorption spectra of the synthetic and real soil washing solutions

The UV/Vis absorption spectra of the synthetic and soil washing solutions were recorded and are compared in Figure 2.3.



**Figure 2.3:** Absorption spectra of a synthetic solution (—), a real soil washing solution with EDDS (—) and a real soil washing solution without EDDS (—). Synthetic solution:  $[EDDS]_0 = 3.6 \cdot 10^{-1}$  mM,  $[Cu(II)]_0 = 8.0 \cdot 10^{-2}$  mM,  $[Fe(III)]_0 = 0.10$  mM,  $[Zn(II)]_0 = 8.0 \cdot 10^{-2}$  mM. pH=7.5. Real soil washing solution without EDDS:  $[Cu(II)]_0 \sim 1.0 \cdot 10^{-3}$  mM,  $[Fe(III)]_0 \sim 4.5 \cdot 10^{-2}$  mM,  $[Zn(II)]_0 < 7.6 \cdot 10^{-4}$  mM. pH=7.8. Real soil washing solution with EDDS:  $[EDDS]_0 \sim 3.6 \cdot 10^{-1}$  mM,  $[Cu(II)]_0 \sim 8.0 \cdot 10^{-2}$  mM,  $[Fe(III)]_0 \sim 7.0 \cdot 10^{-2}$  mM,  $[Zn(II)]_0 \sim 8.0 \cdot 10^{-2}$  mM. pH 7.8.

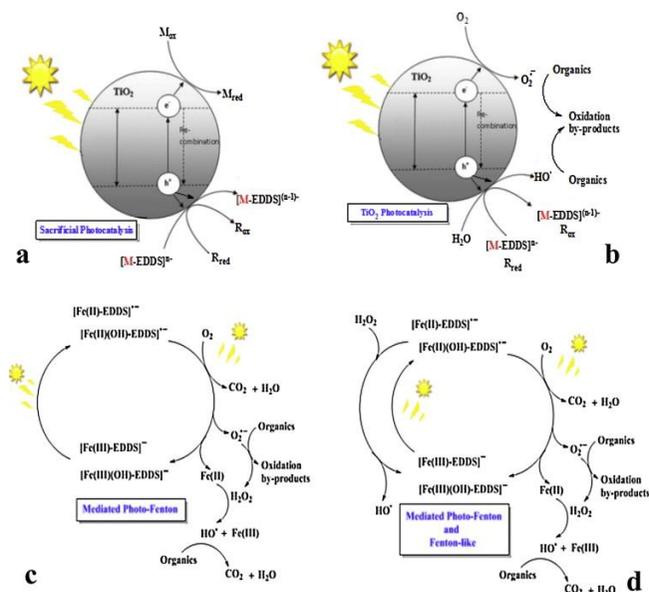
The spectra of three samples showed a decrease in the total absorbance as the wavelength increased. However, the real solutions, the one without EDDS and with a low metal content (red) and the other one with EDDS (blue), showed a total absorption in the 210 nm to 230 nm wavelength much higher than the synthetic mixture (black). These results suggest that both soil washing solutions contain a relatively high fraction of hydrophilic terrestrial Dissolved Natural Organic Matter (DNOM) released from the soil during the washing process [40]. The DNOM fraction is characterized by very high molecular weights and generally possesses

phenolic, ketonic and carboxylic groups able to complex soluble metal ions [41]. In particular, depending on the experimental conditions, some metal/DNOM complexes, such as Fe(III)/DNOM, undergo a rapid photochemical reaction under sunlight irradiation and generate reactive oxidant species (ROS) [42].

### 2.3.4 Photocatalytic treatments

The simultaneous removal of EDDS and the Cu(II), Fe(III) and Zn(II) species has been attempted with four different photocatalytic systems:  $\text{TiO}_2/\text{h}\nu/\text{N}_2$ ,  $\text{TiO}_2/\text{h}\nu/\text{Air}$ , Fe(III)-EDDS/h $\nu$ /Air and Fe(III)-EDDS/h $\nu$ /H<sub>2</sub>O<sub>2</sub>/Air (schemes 2.1a-d).

The mechanism representations of two  $\text{TiO}_2$  heterogeneous photocatalytic systems that were adopted are depicted in the schemes 2.1a,b. The common first step is the formation of charge carriers by a photon. The formed photo-holes ( $h^+$ ) and photoelectrons ( $e^-$ ) can move to the surface of the semiconductor in the presence of light energy, thus starting redox reactions with chemicals, eventually adsorbed on the solid surface. The excited electrons and holes in the absence of suitable electron and hole scavengers, tend to recombine very quickly, and to dissipate the energy as heat. In particular, scheme 2.1a represents the system based on sacrificial photocatalysis in which, under deaerated conditions, metal ions with a more negative reduction potential than that of the conduction band ( $e^-$ ) can be reduced to a zero-valent state. Metal-EDDS complexes or their derivatives can simultaneously be oxidized through a scavenging reaction with the positive holes ( $h^+$ ). Under aerated conditions (scheme 2.1b), oxygen acts as an electron acceptor, and can generate superoxide ion, which is a powerful oxidative species. However, the great oxidation power of the positive holes can enable a one-electron oxidation step with water molecules to produce hydroxyl radicals.



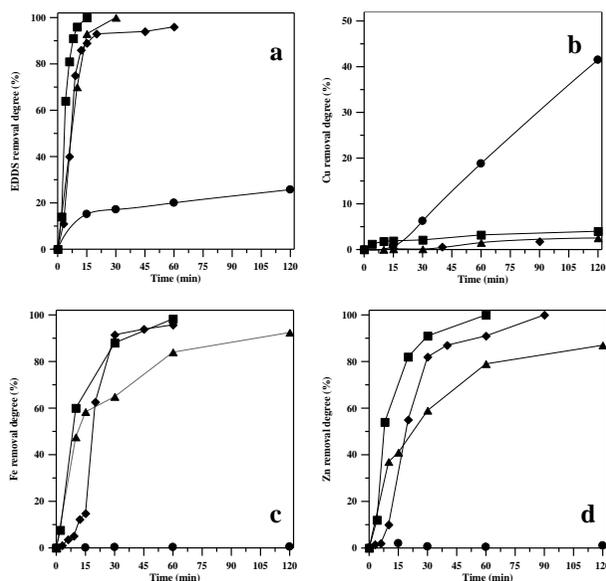
**Scheme 2.1:** Homogeneous and heterogeneous photocatalytic system mechanisms.  $\text{TiO}_2/\text{h}\nu/\text{N}_2$  (a),  $\text{TiO}_2/\text{h}\nu/\text{Air}$  (b), Fe(III)-EDDS/h $\nu$ /Air (c) and Fe(III)-EDDS/h $\nu$ /H<sub>2</sub>O<sub>2</sub>/Air (d)

The homogeneous photocatalytic processes are shown in schemes 2.1c,d. Scheme 2.1c depicts a simplified mechanism of the Fe(III)-EDDS complex mediated photo-Fenton process. Oxidant species, such as  $\text{HO}^\bullet$ ,  $\text{O}_2^{\bullet-}$ ,  $\text{HO}_2^\bullet$  and  $\text{H}_2\text{O}_2$ , are formed during the photolysis of the iron(III)-EDDS complexes under aerated conditions [43,44].

The last process (scheme 2.1d) differs from the previous one for the adding of hydrogen peroxide which can promote additional Fenton-like reactions [45].

### 2.3.4.1 Photocatalytic treatments of the synthetic aqueous solutions

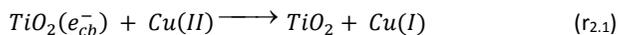
The removal degrees of EDDS and the soluble copper, iron and zinc species from synthetic aqueous solutions by means of heterogeneous or homogeneous photocatalytic treatments are reported in Figures 2.4a-d. Preliminary runs, carried out in the dark, in the presence of  $100 \text{ mg} \times \text{L}^{-1}$  of  $\text{TiO}_2$ , showed no adsorption of EDDS or of the investigated metallic species on the solid surface (data not shown).

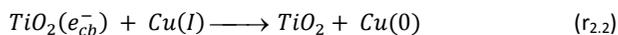


**Figure 2.4:** Removal of EDDS (a), Cu (b), Fe (c) and Zn (d) from the synthetic aqueous solutions by means of  $\text{TiO}_2/\text{h}\nu/\text{N}_2$  (●),  $\text{TiO}_2/\text{h}\nu/\text{Air}$  (▲),  $\text{Fe(III)-EDDS}/\text{h}\nu/\text{Air}$  (◆) and  $\text{Fe(III)-EDDS}/\text{h}\nu/\text{H}_2\text{O}_2/\text{Air}$  (■).  $[\text{EDDS}]_0 = 3.6 \times 10^{-1} \text{ mM}$ ,  $[\text{Cu(II)}]_0 = 8.0 \times 10^{-2} \text{ mM}$ ,  $[\text{Fe(III)}]_0 = 1.0 \times 10^{-1} \text{ mM}$ ,  $[\text{Zn(II)}]_0 = 8.0 \times 10^{-2} \text{ mM}$ .  $\text{TiO}_2$  initial load:  $100 \text{ mg} \times \text{L}^{-1}$ ,  $[\text{H}_2\text{O}_2]_0 = 5.0 \text{ mM}$  (when added to the reacting solution),  $\text{pH} = 7.5$ ,  $T = 25 \text{ }^\circ\text{C}$ .

As far as the EDDS species (Fig. 2.4a), is concerned a marked difference can be observed for the removal degrees achieved by means of the  $\text{TiO}_2/\text{h}\nu/\text{N}_2$  system and those obtained through  $\text{TiO}_2/\text{h}\nu/\text{Air}$  or  $\text{Fe(III)-EDDS}/\text{h}\nu/\text{Air}$  or  $\text{Fe(III)-EDDS}/\text{h}\nu/\text{H}_2\text{O}_2/\text{Air}$  processes. In fact, in the first case, under deaerated conditions, a maximum removal degree (25.7%) was reached after 120 minutes of treatment whereas complete or almost complete removal of the organic chelant was achieved for the photocatalytic aerated systems within 30 minutes of the reaction time. The high efficiency of EDDS abatement for the  $\text{TiO}_2/\text{h}\nu/\text{Air}$ ,  $\text{Fe(III)-EDDS}/\text{h}\nu/\text{Air}$  and  $\text{Fe(III)-EDDS}/\text{h}\nu/\text{H}_2\text{O}_2/\text{Air}$  processes could be ascribed to the generation of hydroxyl radicals (schemes 2.1b-c), which are powerful oxidizing species that are capable of rapidly destroying a very large number of organic molecules. Instead, when the  $\text{TiO}_2/\text{h}\nu/\text{N}_2$  system is adopted, EDDS is mainly removed, as previously reported [20] through the reaction with the photogenerated holes (scheme 2.1a).

However, the  $\text{TiO}_2/\text{h}\nu/\text{N}_2$  system has proved to be the only one capable of removing soluble copper species (full circles, Fig. 2.4b). In fact, under deaerated conditions, cupric ions are reduced to zero-valent copper through the reactions with the photoelectrons:





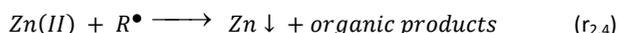
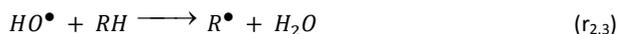
The negligible Cu removal recorded for the TiO<sub>2</sub>/hv/Air, Fe(III)-EDDS/hv/Air and Fe(III)-EDDS/hv/H<sub>2</sub>O<sub>2</sub>/Air processes, even for prolonged reaction times in which EDDS is completely destroyed, prove that, under the adopted conditions, copper did not precipitate as Cu(OH)<sub>2</sub> in spite of its low K<sub>ps</sub> value (4.8×10<sup>-20</sup> M<sup>3</sup> - T 25 °C, [46]).

Iron cannot be removed from the solution by means of photoreduction using the TiO<sub>2</sub>/hv/N<sub>2</sub> system (full circles, Fig. 2.4c), whereas almost complete removal degrees were achieved when the aerated photocatalytic processes, there are able to efficiently destroy the Fe(III)/EDDS or Fe(III)/EDDS-like complexes, were adopted. The high Fe removals are thus ascribed to the precipitation of Fe(OH)<sub>3</sub> (K<sub>ps</sub> = 1.6×10<sup>-39</sup> M<sup>4</sup> - T 25 °C [46]).

It was not possible to remove the soluble zinc species through sacrificial photocatalysis (full circles, Fig. 2.4d), in agreement with literature findings [47], because the direct reduction of Zn(II) to the corresponding zero-valent state, by means of photogenerated titania electrons, is thermodynamically prevented [48].

On the other hand, progressively increasing Zn removal degrees were achieved by moving from the TiO<sub>2</sub>/hv/Air system (full triangles) to the Fe(III)-EDDS/hv/O<sub>2</sub> (full diamonds) process and then to the hv/H<sub>2</sub>O<sub>2</sub> one (full squares). The K<sub>ps</sub> value of Zn(OH)<sub>2</sub> (3.0×10<sup>-16</sup> M<sup>3</sup> - T 25 °C, [46]) is too high, compared with the one reported above for Cu(OH)<sub>2</sub>, to allow precipitation under the same adopted experimental conditions.

Literature findings suggest a zinc reduction through the formation of organic radical intermediates, which are normally highly reducing [49], and which are generated by the HO• species attack to EDDS and its oxidation by-products [50,51]:



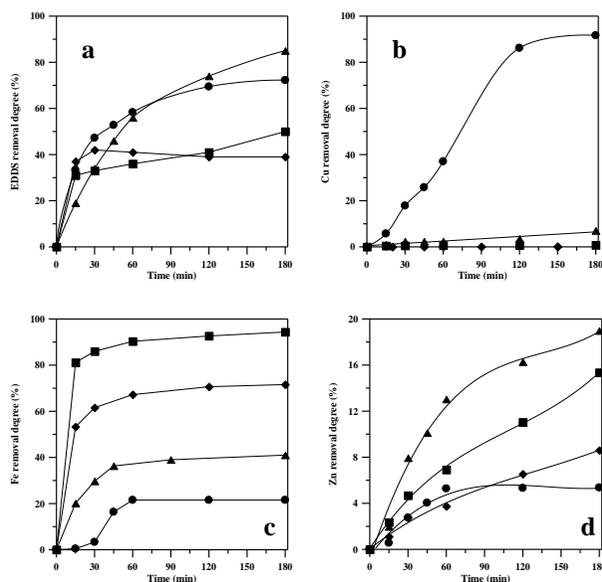
#### 2.3.4.2 Photocatalytic treatments of the real soil washing solutions

An experimental investigation, similar to that described for the synthetic solutions in the previous paragraph, was carried out on real soil washing solutions (SW), containing EDDS, copper, iron and zinc soluble species at comparable concentration levels (listed in Table 2.3) to those present in the synthetic solutions. The collected results for the real SW solutions are reported in Figures 2.5a-d.

The most efficient removal processes for EDDS were TiO<sub>2</sub>/hv/N<sub>2</sub> and TiO<sub>2</sub>/hv/Air (full triangles and circles, Fig. 2.5a). It is worth nothing that for the TiO<sub>2</sub>/hv/N<sub>2</sub> system, the EDDS removal profile presents asymptotic behavior, as it is closely dependent on the concentration of the Cu(II) species in the solution. Electron-hole recombination is promoted for very high degrees of cupric ion removal, thus discouraging the oxidation of EDDS with the photogenerated positive holes. Lower removal degrees were achieved with the Fe(III)-EDDS/hv/Air and Fe(III)-EDDS/hv/H<sub>2</sub>O<sub>2</sub>/Air techniques, probably due to the presence of the less photoactive or non-photoactive and more stable Fe(III)-L complexes that could be generated, during the HO• mediated oxidation of both EDDS and DNOM, between the ferric ions and the organic natural species present in the soil washing waters. It has been reported that some carboxylic acids, such as oxalic, malonic and formic acids, that normally form during the photoassisted Fenton and Fenton-like processes of organic substrates, are capable of forming stable Fe(III) complexes, which, under particular experimental conditions, can exhibit poor organic matter degradation efficiencies whereas Fe(III)-acetate complexes are even non-photoactive [52,53].

As observed for the synthetic solutions, the  $\text{TiO}_2/\text{h}\nu/\text{N}_2$  system was the only effective one for  $\text{Cu}(\text{II})$  removal (full circles, Fig. 2.5b).

As far as the soluble iron species are concerned, the removal degrees, after 180 minutes of treatment, were 21.5%, 41%, 71.6% and 94.4% for  $\text{TiO}_2/\text{h}\nu/\text{N}_2$ ,  $\text{TiO}_2/\text{h}\nu/\text{Air}$ ,  $\text{Fe}(\text{III})\text{-EDDS}/\text{h}\nu/\text{Air}$  and  $\text{Fe}(\text{III})\text{-EDDS}/\text{h}\nu/\text{H}_2\text{O}_2/\text{Air}$  respectively (Fig. 2.5c). Low removal degrees were achieved for zinc soluble species, even for prolonged reaction times (Fig. 2.5d). Of all the investigated photocatalytic systems, the best results were obtained using  $\text{Fe}(\text{III})\text{-EDDS}/\text{TiO}_2/\text{h}\nu/\text{Air}$  (19%,  $t=180$  min) and  $\text{Fe}(\text{III})\text{-EDDS}/\text{h}\nu/\text{H}_2\text{O}_2/\text{Air}$  (15.3%,  $t=180$  min) as they are able to generate organic radical intermediates which can reduce the  $\text{Zn}(\text{II})$  ions to zero-valent state.



**Figure 2.5:** Removal of EDDS (a), Cu (b), Fe (c) and Zn (d) from the real soil washing solutions through  $\text{TiO}_2/\text{h}\nu/\text{N}_2$  (●),  $\text{TiO}_2/\text{h}\nu/\text{Air}$  (▲),  $\text{Fe}(\text{III})\text{-EDDS}/\text{h}\nu/\text{Air}$  (◆) and  $\text{Fe}(\text{III})\text{-EDDS}/\text{h}\nu/\text{H}_2\text{O}_2/\text{Air}$  (■).  $[\text{EDDS}]_0 = 3.6 \times 10^{-1}$  mM,  $[\text{Cu}(\text{II})]_0 \sim 8.0 \times 10^{-2}$  mM,  $[\text{Fe}(\text{III})]_0 \sim 7.0 \times 10^{-2}$  mM,  $[\text{Zn}(\text{II})]_0 \sim 8.0 \times 10^{-2}$  mM,  $\text{TiO}_2$  initial load:  $100 \text{ mg} \times \text{L}^{-1}$ ,  $[\text{H}_2\text{O}_2]_0$  5.0 mM (when added to the reacting solution), pH 7.8, T 25 °C.

### 2.3.4.3 Synthetic solutions vs real soil washing mixtures

A comparison between the sets of data collected in Table 2.4 indicates that the removal degrees achieved for the synthetic solutions, being equal photocatalytic process, were higher than the real ones, with the sole exception of  $\text{TiO}_2/\text{h}\nu/\text{N}_2$  process.

For real soil washing solutions, the efficiency of the treatments for the  $\text{TiO}_2/\text{h}\nu/\text{Air}$ ,  $\text{Fe}(\text{III})\text{-EDDS}/\text{h}\nu/\text{Air}$  and  $\text{Fe}(\text{III})\text{-EDDS}/\text{h}\nu/\text{H}_2\text{O}_2/\text{Air}$  processes, which are mainly based on the production of hydroxyl radicals, is probably reduced by DNOM, which acts as an  $\text{HO}^\bullet$  radical scavenger [54]. A different explanation can be given for the sacrificial photocatalysis ( $\text{TiO}_2/\text{h}\nu/\text{N}_2$ ) where EDDS is mainly removed through the reaction with positive holes, since there is no oxygen in the system. In this case, DNOM could enhance the removal degree of EDDS and acts as a “photosensitizer” for the generation of reactive radical organic species, capable of attacking the metal-EDDS complexes [55].

However, in the case of soil washing solutions, an efficient EDDS removal can be obtained for very prolonged treatment times (> 3 hrs) through any of the investigated processes. Copper is only removed through the  $\text{TiO}_2/\text{h}\nu/\text{N}_2$  process, whereas the best technologies for  $\text{Fe}(\text{III})$  removal has proved to be  $\text{Fe}(\text{III})\text{-EDDS}/\text{h}\nu/\text{H}_2\text{O}_2/\text{Air}$ .

EDDS/hv/H<sub>2</sub>O<sub>2</sub>/Air. With regard to the Zn(II) removal, the best processes have been TiO<sub>2</sub>/hv/Air and Fe(III)-EDDS/hv/ H<sub>2</sub>O<sub>2</sub>/Air although with a lower efficiency.

		REMOVAL DEGREE							
		EDDS (%)		Copper (%)		Iron (%)		Zinc (%)	
Treatment time (min)		30	120	30	120	30	120	30	120
SYNTHETIC	TiO <sub>2</sub> /hv/N <sub>2</sub>	17	26	6	41	< 1	< 1	1	1
	TiO <sub>2</sub> /hv/Air	100	100	< 1	2.5	65	92	59	87
	Fe(III)-EDDS/hv/Air	93	100	< 1	2	91	100	82	100
	Fe(III)-EDDS/hv/H <sub>2</sub> O <sub>2</sub> /Air	100	100	2	4	88	100	91	100
REAL	TiO <sub>2</sub> /hv/N <sub>2</sub>	47	69	18	86	3	21	3	5
	TiO <sub>2</sub> /hv/Air	34	74	2	3	30	40	8	16
	Fe(III)-EDDS/hv/Air	42	39	< 1	< 1	61	71	3	6
	Fe(III)-EDDS/hv/H <sub>2</sub> O <sub>2</sub> /Air	33	41	0.5	1	86	93	4	11

**Table 2.4:** Removal degrees (%) of EDDS, Cu(II), Fe(III) and Zn(II) species after 30 and 120 minutes of treatments with different photocatalytic processes for synthetic and real waters. TiO<sub>2</sub> initial load: 100 mg×L<sup>-1</sup>, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>=5.0 mM, T=25 °C. Synthetic waters: [EDDS]<sub>0</sub>=3.6×10<sup>-1</sup> mM, [Cu(II)]<sub>0</sub>=8.0×10<sup>-2</sup> mM, [Fe(III)]<sub>0</sub>=1.0×10<sup>-1</sup> mM, [Zn(II)]<sub>0</sub>=8.0×10<sup>-2</sup> mM. Real waters: [EDDS]<sub>0</sub>=3.6×10<sup>-1</sup> mM, [Cu(II)]<sub>0</sub> ~ 8.0×10<sup>-2</sup> mM, [Fe(III)]<sub>0</sub> ~ 7.0×10<sup>-2</sup> mM, [Zn(II)]<sub>0</sub> ~ 8.0×10<sup>-2</sup> mM.

### 2.3.5 Electrical energy determination

Since the investigated photocatalytic processes are energy-intensive operations, and electric energy can represent an important fraction of the operating costs, simple figures-of-merit based on electric energy consumption could be useful and informative. The most appropriate figure-of-merit for the present investigation is the electrical energy-per-order (*EE/O*), which is defined as the number of kWh of electrical energy required to reduce the concentration of a pollutant by one order of magnitude (90%) in 1 m<sup>3</sup> of contaminated water [56]. The *EE/O* (kWh×m<sup>-3</sup>×order<sup>-1</sup>) for a batch reactor can be calculated using the following equation:

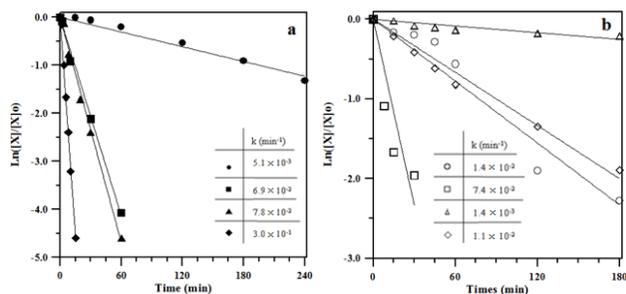
$$EE/O = \frac{1000}{V} \times \frac{P}{k} \times \frac{\ln 10}{60} = 38.4 \times \frac{P}{V \times k}$$

where *P* is the lamp power (kW), *V* the volume of the solution in the reactor (L), *k* the pseudo-first-order rate constant (min<sup>-1</sup>) for the abatement of the pollutant concentration. Values of *EE/O* not higher than 2.5 are considered suitable for practical applications with lamps [57], otherwise, where possible, the natural solar radiation is highly recommended.

In the present study, an attempt was made to estimate the *EE/O* for those processes that have proved to be more effective in the removal of EDDS, copper, iron and zinc in synthetic and real water.

For this purpose, the pseudo-first order kinetic rate constants (*k*) were calculated by plotting the neperian logarithm of the normalized concentration of each species to be removed (Ln([X]/[X]<sub>0</sub>) against the reaction times (Figs. 2.6a,b). In each case, the decay of EDDS, Cu(II), Fe(III) and Zn(II) was found to follow first-order

reaction kinetics within a range of treatment times of 240 min and 180 min for synthetic and real water respectively.



**Figure 2.6:** Linear profiles of  $\ln([X]/[X]_0)$  vs time and the corresponding pseudo-first order kinetic constants for the most efficient photocatalytic processes: (a) synthetic solutions, (b) real water. Removal: (●, ○) Cu(II) by  $\text{TiO}_2/\text{hv}/\text{N}_2$ ; (■, □) Fe(III) by Fe(III)-EDDS/hv/ $\text{H}_2\text{O}_2$ /Air; (▲, △) Zn(II) by Fe(III)-EDDS/hv/ $\text{H}_2\text{O}_2$ /Air; (△, △) Zn(II) by  $\text{TiO}_2/\text{hv}/\text{Air}$ ; (◆, ◇) EDDS by Fe(III)-EDDS/hv/ $\text{H}_2\text{O}_2$ /Air; (◇) EDDS by  $\text{TiO}_2/\text{hv}/\text{Air}$ .

Once the  $k$ -values are known, the  $EE/O$  can be obtained using the previous equation with  $P$  and  $V$  equal to 125 W and 0.250 L, respectively (Table 2.5).

SYNTHETIC WATERS			REAL WATERS		
Species	Process	$EE/O^a$ ( $\text{kWh} \times \text{m}^{-3} \times \text{order}^{-1}$ )	Species	Process	$EE/O^a$ ( $\text{kWh} \times \text{m}^{-3} \times \text{order}^{-1}$ )
Cu	$\text{TiO}_2/\text{hv}/\text{N}_2$	$3.75 \times 10^3$	Cu	$\text{TiO}_2/\text{hv}/\text{N}_2$	$1.40 \times 10^3$
Fe	Fe(III)- EDDS/hv/ $\text{H}_2\text{O}_2$ /Air	$2.79 \times 10^2$	Fe	Fe(III)- EDDS/hv/ $\text{H}_2\text{O}_2$ /Air	$2.58 \times 10^2$
Zn	Fe(III)- EDDS/hv/ $\text{H}_2\text{O}_2$ /Air	$2.46 \times 10^2$	Zn	$\text{TiO}_2/\text{hv}/\text{Air}$	$1.37 \times 10^4$
EDDS	Fe(III)- EDDS/hv/ $\text{H}_2\text{O}_2$ /Air	64	EDDS	$\text{TiO}_2/\text{hv}/\text{Air}$	$1.73 \times 10^3$

**Table 2.5:** The  $EE/O$  for the photocatalytic processes. <sup>a</sup> the cost factor for hydrogen peroxide has been considered negligible.

The very high numerical values of  $EE/O$  indicate that using artificial radiation for soil washing decontamination, through the investigated photocatalytic processes, at industrial scale would be unfeasible economically, and encourage further investigations on the use of solar radiation, in the sense that electric energy consumption could be avoided if the lamps were replaced by solar collectors and sunlight.

## 2.4 Conclusions

The results demonstrate that for the removal of EDDS and copper, zinc and iron metals from synthetic solutions and real soil washing mixtures a different photocatalytic treatment is necessary.

For the field scale, prior the photocatalytic processes, consideration must be given to the real washing solution, because treatments aimed to remove the residual turbidity are required.

The EDDS removal degrees, obtained using  $\text{TiO}_2/\text{hv}/\text{N}_2$  or  $\text{TiO}_2/\text{hv}/\text{Air}$  processes on the real solutions ( $[\text{EDDS}]_0 \sim 0.36 \text{ mM}$ ,  $\text{TiO}_2$  load =  $100 \text{ mg} \times \text{L}^{-1}$ ), are close to 70–80 % after 3 hrs of treatment, while shorter

reaction times (10 minutes) are necessary to reach the same percentage conversion degrees for synthetic contaminated water with  $\text{TiO}_2/\text{h}\nu/\text{Air}$ ,  $\text{Fe(III)-EDDS}/\text{h}\nu/\text{Air}$  and  $\text{Fe(III)-EDDS}/\text{h}\nu/\text{H}_2\text{O}_2/\text{Air}$  processes. Of all the investigated metal species, only cupric ions can be removed by photoreduction to zero-valent copper through the  $\text{TiO}_2/\text{h}\nu/\text{N}_2$  process for both synthetic and real aqueous solutions. The results indicate that both the type and the sequence of photocatalytic technologies that need to be applied to simultaneously remove EDDS and metals, such as copper, iron and zinc, from soil washing mixtures, should be chosen prudently on the basis of the nature and the content of the soil washing solutions. Before directly exploiting natural sunlight by carrying out the photocatalytic experiments under outdoor conditions, further investigations, using artificial solar radiation on real soil washing waters are strongly recommended in order to choose the best sequence of photocatalytic steps in order to achieve the concentration limits established in the national regulations

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# Chapter 3      Solar photocatalytic processes for treatment of soil washing wastewater

Contaminated soil is a growing problem in the last decades. The most common technique used to remove contaminants like metals from the soil is the soil washing process. However it produces a final effluent containing the chelating agent used (ethylenediaminedisuccinic acid, EDDS) and the extracted metals (Cu, Fe and Zn) at concentration levels higher than discharge limits allowed by Italian law. This requires the development of a further step in the treatment of the effluent before discharge to sewers or its reuse if possible. In the present study, with the soil remediation aim, it was done soil washing tests through two sequential paths, besides diverse artificial sunlight-driven photocatalytic treatments were used to remove Cu, Zn, Fe and EDDS from soil washing effluent. The metal concentrations after the additional treatment were within Italian regulatory limits for discharge in public sewers. The combined TiO<sub>2</sub>-photocatalytic processes applied were enough to decontaminate the effluents permitting their recycling in soil washing treatment. Ecotoxicological assessment using different living organisms was carried out to assess the impact of the proposed two-step photocatalytic process of soil washing solution on effluent ecotoxicity.

## 3.1 Introduction

Heavy metal pollution of soils and sediments is a global concern due to the negative impact that such metals have on living organisms [1]. Hence, different remediation techniques based on physical, chemical, and even biological processes have been proposed to remove metals from contaminated soils [2]. Among the chemical techniques, the soil washing using chelating organic agents is one of the most promising “ex-situ” processes [3], even though the extracting agents can persist in the environment at unacceptable levels. Recently the attention has been focused on soil washing processes adopting more readily biodegradable substances, such as (S,S)-Ethylenediamine-N,N'-disuccinic (EDDS), for heavy metals removal from polluted soils [4]. The main disadvantage of such processes is the subsequent need to remove the heavy metals extracted from contaminated soil and the residual chelating agent from the washing effluent before any reuse and/or discharge into the aquatic environment. Normally, adsorption or precipitation processes are ineffective for treating these effluents due to the presence of the chelating agent which inhibits the separation of the heavy metals from the liquid phase [5].

Among the investigated processes for treating soil washing effluents [6–10], solar driven photocatalytic systems are of interest due to their simplicity and low cost [11]. Previous studies carried out on synthetic [12] and real soil washing solutions [12,13] using exclusively UV-A lamps as radiation source, showed the possibility to remove metals, such as Cu and Zn, and chelating agent from soil washing effluents through different photocatalytic treatments, or by the adoption of an appropriate combination of photocatalytic and

physical processes (adsorption on activated carbon). This study proposes, for the first time, an integrated approach based on soil washing process and a sequence of TiO<sub>2</sub> photocatalysis to treat its effluent. This allows the simultaneous decrease of unwanted metals and chelating agent concentrations in the soil washing effluent to acceptable values so it can be reused in the soil washing process and/or discharged to municipal sewers

## 3.2 Experimental

### 3.2.1 Materials

(S,S)-ethylenediamine-N,N'-disuccinic acid-trisodium salt (EDDS) solution (35%), titanium(IV) oxide (pure crystalline anatase phase, average size 25-70 nm, 99.8% w/w) and perchloric acid (ACS reagent 70%) were purchased from Sigma-Aldrich and used as received.

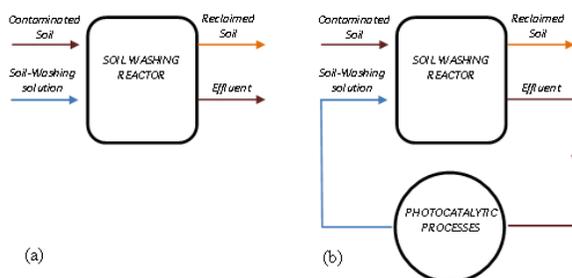
### 3.2.2 Soil sampling

Soil samples were manually collected from the top 20cm over an area of about 1m<sup>2</sup>, stored in hermetic containers and sieved before use (2.0mm), from a site located in the province of Naples (Italy), within a very big area proposed, for the contamination, as a Site of Regional Interest (SIR) [14,15]. This region has been used for decades by criminal organizations as a dumping ground for toxic waste. It is also known for its high cancer mortality incidence, which exceeds average Italian and European values [14] and which is related to the presence of heavy metals [15]. Moreover this area is characterized by some of the highest levels of solar irradiation in Europe.

### 3.2.3 Soil washing procedure

The EDDS (chelating agent) initial concentration was 0.36mM, as suggested by Yan et al. [16]. The tests (triplicates, standard deviation ~ 8%) were carried out at circumneutral pH (7.5-7.9), fixing the liquid-to-solid ratio (L/S) at 10:1. The samples were stirred in a mechanical shaker (Edmund Bühler, Kombischüttler KL2) at 190 rpm for different contact times at room temperature. Blank tests (without EDDS) were carried out using bi-distilled water.

Firstly the aim was to improve the Cu and Zn removal efficiency, then to test the possibility of reusing the soil washing solution after photocatalytic treatment. Two different plant configurations were adopted (Fig. 3.1a and 3.1b). The configuration, reported in Fig. 3.1a, was applied for long duration washing (96 h or 192 h) without any further treatment. Whereas in the configuration represented in Fig. 3.1b, two washing cycles of 96 h each were done, but the first washing effluent was treated and then reused for the second washing cycle when more EDDS was added.



**Figure 3.1** - Soil washing using different approaches: (a) no effluent reuse and (b) with photocatalytically treated effluent reuse.

### 3.2.4 Photocatalytic procedure

The photocatalysis was conducted using a Hg-vapor lamp (UV 12F-Helios Italquartz, nominal power 125 W) and a polychromatic Na-lamp (Helios Italquartz, model Na 15F, nominal power of 150 W) in an annular cylindrical glass jacketed batch reactor [17].

#### *Hg-lamp as UV-A source*

The reactor is characterized by a volume, height and diameter respectively of 280 ml, 40 cm and 6.5cm. The photocatalytic experiments were performed at 25°C. The high-pressure UV lamp mainly emits at 305, 313 and 366 nm (manufacturer's data).

The photon flow of the lamp at 305 nm was  $1.07 \cdot 10^{-6} \text{ E} \cdot \text{s}^{-1}$ , determined through  $\text{H}_2\text{O}_2$  photolytic experiments [18], at 313 nm was  $1.62 \cdot 10^{-6} \text{ E} \cdot \text{s}^{-1}$  determined by valerephenone actinometry [19] and at 366 nm was  $5.13 \cdot 10^{-6} \text{ E} \cdot \text{s}^{-1}$  measured using a UV radiometer (Delta Ohm HD 9021).

#### *Na-lamp as artificial solar radiation*

The same reactor was used with a polychromatic sodium lamp that emits in the wavelength range between 350-800 nm. The photon fluxes of the Na-lamp, measured by UVA radiometer (DELTA OHM, model HD2102.1), were  $2.72 \text{ W} \cdot \text{m}^{-2}$  (350-400 nm) and  $2.02 \cdot 10^3 \text{ W} \cdot \text{m}^{-2}$  (400-800 nm). In the case of Hg-lamp, the process began with Cu and EDDS total removal, and Zn and Fe partial removal, through a "sacrificial"  $\text{TiO}_2$ -photocatalysis, followed by two different photocatalytic steps, such as  $\text{TiO}_2$ -photocatalysis and assisted photo-Fenton. These last two steps were carried out under oxygenated conditions for organic substances and residual metals, especially Fe, removal. Eventually, an alkalization step could be added to further increase the efficiency of removal of metal ions. On the other hand, when the Na-lamp was used, the sequence was started with the  $\text{TiO}_2$ -photocatalysis under oxygenated conditions, lowering Fe, Zn and EDDS concentrations, followed by a sacrificial  $\text{TiO}_2$ -photocatalysis (under an inert atmosphere) for the removal of residual metals, particularly Cu, and also organic substances.

All photocatalytic tests were performed in triplicate and only the average values were reported. In repeated tests, the metals concentrations standard deviations were below 6%.

### 3.2.5 Analytical procedures

The metal concentrations were determined by Atomic Absorption Spectrometry (AAS), using a Varian Model 55B SpectraAA (F-AAS) or GBC Avanta AAS with a graphite furnace (GF-AAS). For the soil the EPA method 3051 [20] was followed. The soil pH was measured according to EPA Method 9045C [21]. Organic matter was evaluated using the Loss On Ignition (LOI) index [22]. Elemental analysis was performed using a Perkin-Elmer Series II 2400 CHNS/O Elementary Analyzer. The EDDS analysis were performed using a modified colorimetric method [23] previously reported by Vandevivere et al. [24]. Total organic carbon analyses were performed using a TOC analyzer (Shimadzu 5000A). All the analysis were carried out in triplicate.

### 3.2.6 Ecotoxicity assessment

Ecotoxicological tests were carried out to evaluate the ecotoxicity of the soil washing wastewater before and after exposure to the solar photocatalytic process. The assessments were performed on a seed (*Lepidium*

sativum) [25] and on three different target organisms: a bacterium (*Vibrio fischeri*) [26], a green microalga (*Pseudokirchneriella subcapitata*) [27] and a crustacean (*Daphnia magna*) [28].

The bioluminescence inhibition assay was performed using marine bacteria of the species *Vibrio fischeri* NRRL-B-11177 (formerly known as *Photobacterium phosphoreum*). This test evaluates the acute toxicity of a sample using the inhibition of the luminescence naturally emitted by the bacterium as an endpoint. The luminescence was measured with a Microtox luminometer (Model 500, AZUR Environmental). The light emission drop was measured after 5, 15 and 30 minutes contact times with the test samples. The temperature during the exposure was 15°C [26]. Tests were carried out at least in duplicate with a control solution. The data were statistically processed by the instrument software and the result was expressed as percentage of bioluminescence inhibition (% IB).

The algal growth inhibition test using *Pseudokirchneriella subcapitata* was carried out according to published protocol [27]. The growth of the algae exposed to the sample was compared with the growth of the algae in a negative control. The cell density in the cultures was measured after 72 h in a Bürker cell counting chamber. The specific growth rate of *P. subcapitata* in each replicate culture was calculated from the logarithmic increase in cell density in the intervals from 0 to 72 h using the following equation:

$$\psi = \frac{\ln N_n - \ln N_0}{t_n - t_0}$$

where  $N_0$  is the cell concentration at  $t=0$ ,  $N_n$  the final cell concentration after 72 h of exposure,  $t_0$  the start measurement time, and  $t_n$  the last measurement time (hours from the start). The cell growth inhibition percentage (% I) was calculated as the difference between the rate of growth of the control and of the test sample, expressed as the mean ( $\pm$  standard deviation) of the replicates for  $p \leq 0.05$ .

Use of *Daphnia magna* allowed evaluation of the toxicity of the samples using crustacean immobilization as a readout [28]. Tests were conducted in quadruplicate in the dark. The test readout used was the number of immobile individuals in each replica, after 24 h and 48 h of exposure, compared to the number of individuals initially exposed. Each assay was considered valid only if the immobilization in the control solution was less than or equal to 10%.

The phytoassay used evaluated the possible toxicity of a sample by comparing the germination and root elongation of seeds (*Lepidium sativum*) placed in contact with the sample with those obtained for seeds placed in controlled conditions [25]. Germination and growth experiments were carried out in aqueous solutions at controlled pH in triplicate. Bioassays took 72 h and after this period, the germinated seeds were counted and the root length was measured. The growth index was calculated by multiplying the number of germinated seed (G1) and length of roots (L1), both exposed to sample, and then divided by the factor obtained from the multiplication of the number of germinated seeds (Gc) and length of root (Lc), from seed exposed to control medium.

## 3.3 Results and discussion

### 3.3.1 Soil characterization

The soil characteristics are reported in Table 3.1. The pH was close to neutrality and the LOI index is 7.19%. The metals concentrations were lower than the Italian regulatory limits except for Cu and Zn [30].

The soil contamination of Cu and Zn is highly diffuse because these elements are present in several common pesticides and fertilizers [31]. The United States Environmental Protection Agency classifies them as toxic and

as priority pollutants. Therefore, in the soil washing experiments, the aim was to remove Cu and Zn. As suggested by Yan and co-workers [16] the soil washing tests were carried out with a molar ratio of EDDS/(Cu+Zn) equal to 0.6.

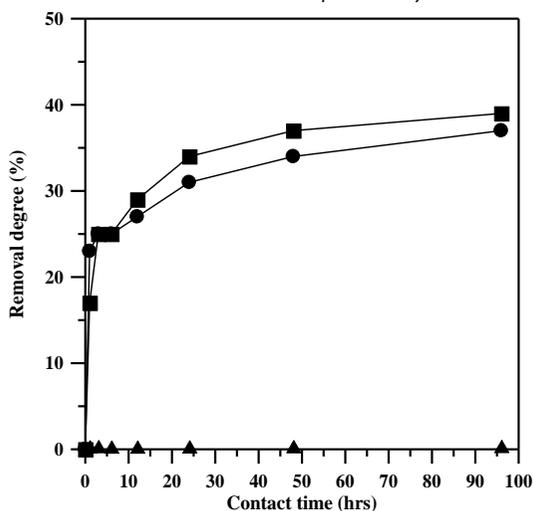
	Soil	<sup>a</sup> Italy	Mean values found on the soil sample
pH	7.1		
L.O.I.	7.19 ± 0.15		
C	3.96 ± 0.21		
[%]	H	2.47 ± 0.18	
	N	0.42 ± 0.09	
	S	0.43 ± 0.12	
	Mg	2.1·10 <sup>4</sup> ± 1.0·10 <sup>2</sup>	
	Ca	4.4·10 <sup>5</sup> ± 8.2·10 <sup>2</sup>	
	Cu	2.2·10 <sup>2</sup> ± 39.2	1.2·10 <sup>2</sup> 51
	Pb	24.37 ± 2.3	1.0·10 <sup>2</sup> 1.0·10 <sup>2</sup>
	Cr	33.17 ± 1.1	1.5·10 <sup>2</sup> 5.0·10 <sup>2</sup>
ppm	Ni	8.27 ± 0.8	1.2·10 <sup>2</sup> 2.5·10 <sup>2</sup>
	Zn	1.8·10 <sup>2</sup> ± 11.8	1.5·10 <sup>2</sup> 1.5·10 <sup>2</sup>
	Cd	0.40 ± 0.1	2 0.35
	Fe	1.4·10 <sup>4</sup> ± 3.2·10 <sup>2</sup>	2.78·10 <sup>5</sup>
	Mn	5.1·10 <sup>2</sup> ± 72.1	1.5·10 <sup>3</sup>

**Table 3.1** Comparison between the collected soil parameters and the Italian regulatory limits.[30]

### 3.3.2 Soil washing in one cycle

The results at different extraction times are presented in Fig. 3.2. During the first 24 h of soil washing, the Cu and Zn extraction reached 33.1% and 33.2%, and after 96 hr approximately 39.9% and 37.7% respectively. The Fe removal was up to 1 %, as previously reported [12].

Final concentrations of Cu and Zn in the soil after the washing procedure were 136 ppm and 114 ppm, respectively. These concentrations do not meet the Italian regulatory limits. Thus, a second washing step was required so has been proposed to reuse of the effluent produced on the first washing after its treatment by photolysis.

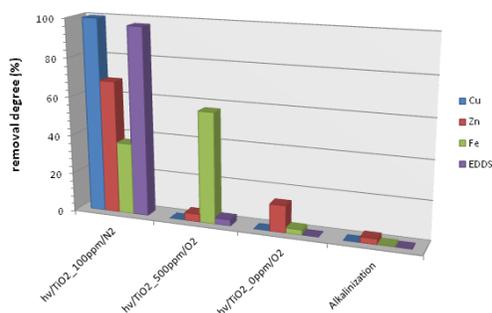


**Figure 3.2** Cu (●), Zn (■) and Fe (▲) removal through EDDS soil washing at varying time.  $[EDDS]_0=0.36\text{mM}$ ; L/S ratio=10;  $RSD_{\text{max}}<8.11$ .

### 3.3.3 Combined photocatalytic processes for soil washing effluents

#### 3.3.3.1 UV-A radiation source

On the basis of previously reported findings [12], an optimal sequence of combined photocatalytic processes, that ensures the highest efficiency of Cu, Zn, Fe and EDDS removal, was established: “sacrificial”  $\text{TiO}_2$ -photocatalysis (step 1),  $\text{TiO}_2$ -photocatalysis (step 2) and assisted photo-Fenton (step 3). The final removal percentage for Cu, Zn, Fe and EDDS is reported in Fig. 3.3. During the 1<sup>st</sup> step, Cu and EDDS were completely removed, whereas a lower percentage removal was achieved for Zn (68%) and Fe (37%). Additional heterogeneous (2<sup>nd</sup> step) and homogeneous (3<sup>rd</sup> step) photocatalytic treatments and the alkalization process were able to remove residual Fe and Zn.

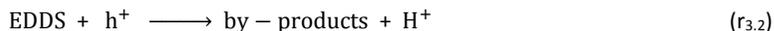


**Figure 3.3** - Cu, Zn, Fe and EDDS removal from soil washing effluents using three sequential photocatalytic steps by Hg-lamp irradiation.  $[EDDS]_0=0.36\text{ mM}$ ,  $\text{pH}=7.8$  (not regulated).  $\text{TiO}_2_{100\text{ppm}}/\text{N}_2/\text{hv}$ :  $t_r=16\text{ h}$ .  $\text{TiO}_2_{500\text{ppm}}/\text{O}_2/\text{hv}$ :  $t_r=6\text{h}$ .  $\text{TiO}_2_{0\text{ppm}}/\text{O}_2/\text{hv}$ :  $t_r=8\text{h}$ .  $[\text{Cu}]_0 = 8.9 \pm 1.7\text{ ppm}$ ;  $[\text{Zn}]_0 = 6.7 \pm 1.3\text{ ppm}$ ;  $[\text{Fe}]_0 = 7.8 \pm 4.6\text{ ppm}$ .  $RSD_{\text{max}} < 4.43$ .

Cu elimination during the first step is due to the reduction of cupric ions to zero-valent copper by photogenerated electrons:



and its precipitation as  $\text{Cu(OH)}_2$  ( $K_{ps}=4.8 \cdot 10^{-20} \text{ M}^3 - T=25 \text{ }^\circ\text{C}$ , leading to EDDS destruction by the reaction with positive holes:



The sequence was able to remove all the metals, and in the end the waste had concentrations within the Italian legal limits as is shown in Table 3.2.

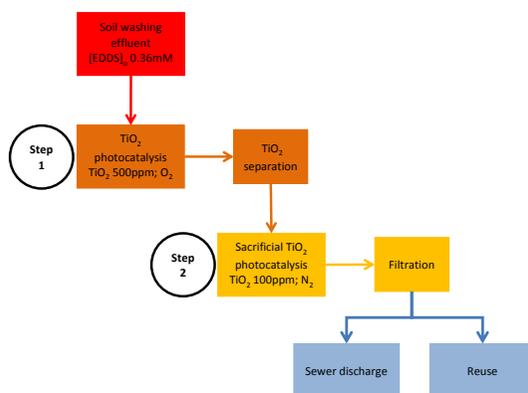
	Cu (mg·L <sup>-1</sup> )	Fe (mg·L <sup>-1</sup> )	Zn (mg·L <sup>-1</sup> )
<sup>a</sup> Italy	0.4	4.0	1.0
Before treatment	7.8	10.5	5.7
After treatment	<0.05	0.09	0.8

**Table 3.2** Regulatory limits of metal ion concentrations for Italy and the concentrations achieved in these experiments before and after the photocatalytic processes. <sup>a</sup>[30]

The use of UV-A artificial radiation for soil washing effluent decontamination allowing its reuse is not economically viable for industrial scale-up due to the high energy consumption needed to reach the desired degree of pollutant removal [12]. Therefore, another set of experiments was carried out using an artificial solar light irradiation (Na-lamp), source more similar to sunlight, to evaluate the system behavior.

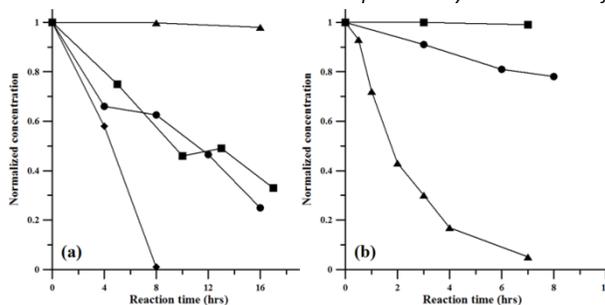
### 3.3.3.2 Artificial solar light irradiation

In this case the sequence changed since previously results [12] suggested that better results are achieved by starting with  $\text{TiO}_2$ -photocatalysis in the presence of  $\text{O}_2$ , followed by a sacrificial  $\text{TiO}_2$ -photocatalysis. In this way, firstly the Fe, Zn and EDDS concentrations are reduced, and secondly residual metals, particularly Cu, and also organic substances are removed (Fig. 3.4).



**Figure 3.4** Photocatalytic processes carried out using Na-lamp as radiation source. Step 1: EDDS, Fe and Zn removal; Step 2: EDDS and Cu removal

Results (data not shown) exploring the effect of the  $\text{TiO}_2$  load used on the efficiency of Fe and Zn removal during the Step 1 ( $\text{TiO}_2$ -photocatalysis/ $\text{O}_2$ ) showed that 500 ppm provided a good compromise between the optimal photocatalyst load and treatment time, whereas a 100 ppm load was more optimal for Step 2 (Fig. 3.5).



**Figure 3.5** Cu (▲), Zn (■), Fe (◆) and EDDS (●) concentration profiles during the first step (a) and the second step (b). [EDDS]<sub>0</sub>=0.36mM; pH=7.8 (not regulated); Na-lamp. (a): Step 1 - TiO<sub>2</sub>\_500ppm/O<sub>2</sub>/hv. (b): Step 2 - TiO<sub>2</sub>\_100ppm/N<sub>2</sub>/hv. RSD<sub>max</sub> < 3.61.

Previously published results [12], showed that the first step removes very efficiently EDDS, Zn and Fe.

The EDDS concentration reduction occurred mainly through its reaction with hydroxyl and hydroperoxyl radicals:



which are produced by reaction of oxygen with photogenerated TiO<sub>2</sub>-electrons:



by reaction of water molecules with TiO<sub>2</sub> positive holes:



and by photolysis of Fe(III)-EDDS and Fe(III)-L complexes:

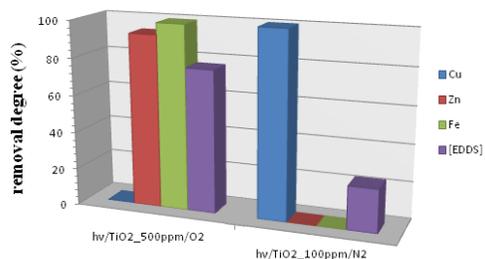


where L represents by-photoproducts.

Fe and Zn form insoluble hydroxides and are adsorbed onto TiO<sub>2</sub> catalyst being removed by precipitation. However, the 1<sup>st</sup> photocatalytic step was ineffective in removing Cu species probably due to the existence of soluble Cu-hydroxo-complexes, such as Cu(OH)<sup>+</sup>, at the adopted pH [33].

Cu and residual EDDS removal required a 2<sup>nd</sup> step (sacrificial TiO<sub>2</sub> photocatalysis), which is carried out using TiO<sub>2</sub> catalyst under deoxygenated conditions through reactions r<sub>1</sub> and r<sub>2</sub>. It was required 24 h for the 1<sup>st</sup> step and 8 h for the 2<sup>nd</sup> step to lower the final metals concentrations below the limits defined by Italian laws.

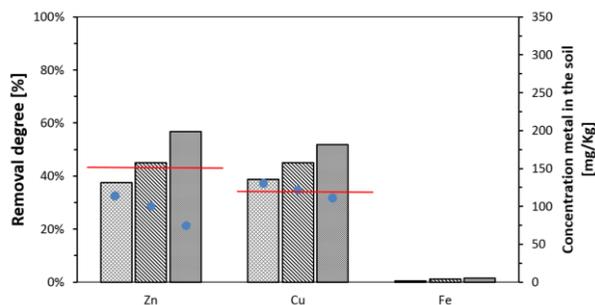
The final removal of Cu, Zn, Fe and EDDS through a two-step process with catalyst filtration between the 1<sup>st</sup> and the 2<sup>nd</sup> step without any pH regulation is shown in Fig. 3.6. Fe, Cu and EDDS were completely removed and 93% of the Zn was achieved. These results indicate that the soil washing effluents could be efficiently treated using artificial solar light instead of UV-A lamps.



**Figure 3.6** Cu, Zn, Fe and EDDS removal from soil washing effluents through two sequential photocatalytic steps by Na-lamp irradiation. (a): TiO<sub>2</sub>\_500ppm/O<sub>2</sub>/hv, t<sub>r</sub>=24 h. (b): TiO<sub>2</sub>\_100ppm/N<sub>2</sub>/hv, t<sub>r</sub>=8 h. [EDDS]<sub>0</sub>=0.36 mM, pH=7.8 (not regulated). RSD<sub>max</sub> < 4.73.

### 3.3.4 Soil washing in two cycles: effluent treated by combined photocatalytic processes using artificial solar light

Soil washing effluent decontaminated using the photocatalytic process was used to rewash the initial soil sample for a second time, as shown in Fig. 3.1b. EDDS was used at the same initial concentration of the first washing step. The extraction efficiency increase was marked (Fig. 3.7). In fact, for a fixed contact time of 192 h, rewashing the soil reusing the initial effluent after decontamination by photolysis allowed a further reduction of Cu and Zn respectively of 7% and 12%. The kinetics of extraction (data not shown) were similar to the first soil washing (Fig. 3.1b), with higher extraction in the first 24 h. The new process resulted in Cu and Zn concentrations (106 ppm for Cu and 79 ppm for Zn) much lower than the Italian legal limits for soils (Table 3.1) and allowed the effluents reuse in the washing process.



**Figure. 3.7** Comparison of Cu, Zn and Fe extraction by soil washing tests under different operating conditions. (▨) single soil washing after 96 h of contact time, configuration reported in Fig. 3.1a; (▩) single soil washing after 192 h of contact time, configuration reported in Fig. 3.1a; (▧) double soil washing with a contact time of 96 h for each step, configuration reported in Fig. 3.1b. Red line: Italian regulatory limits; (●) Cu and Zn concentration in the soil after the soil washing process. [EDDS]<sub>0</sub>=0.36 mM; L/S ratio=10; RSD<sub>max</sub> < 6.73.

### 3.3.5 Ecotoxicological assessment

An ecotoxicological investigation using different target organisms was carried out on untreated and treated soil washing effluents at the end of the process performed with Na-lamp as radiation source (Table 3.3).

<i>Vibrio fischeri</i>			
Before the treatment		After the treatment	
Exposition time (min)	I <sub>B</sub> (%)	Exposition time (min)	I <sub>B</sub> (%)
5	5.6	5	4.3
15	5.6	15	4.2
30	12.5	30	0.87
<i>Daphnia magna</i>			
Before the treatment		After the treatment	
Exposition time (h)	I <sub>M</sub> (%)	Exposition time (h)	I <sub>M</sub> (%)
24	33.3	24	0
48	40.4	48	0
<i>Pseudokirchneriella subcapitata</i>			
Before the treatment		After the treatment	
Exposition time (h)	I <sub>N</sub> (%)	Exposition time (h)	I <sub>N</sub> (%)
72	76.5	72	40.1
<i>Lepidium sativum</i>			
Before the treatment		After the treatment	
Exposition time (h)	I <sub>G</sub> (%)	Exposition time (h)	I <sub>G</sub> (%)
72	76.2	72	75.9

**Table 3.3** Ecotoxicological tests on untreated and treated soil washing effluents. *V. fischeri* bioluminescence inhibition percentage (I<sub>B</sub>, %) exposed for 5', 15' and 30'; *D. magna* immobilization index percentage (I<sub>M</sub>, %) after exposure for 24 h and 48 h; *P. subcapitata* growth inhibition (I<sub>N</sub>, %) after exposure for 72 h; *L. sativum* index of germination percentage (I<sub>G</sub>, %) after exposure for 72 h. The results are relative to average of effects.

Using the bioluminescence test with *V. fischeri* exposure, a very slight inhibition was recorded for the untreated sample (5.6 – 12.5%), whereas no ecotoxic effects were measured on the treated sample (4.2% max). The exposure time of the organisms to the solutions did not appreciably affect the results.

Ecotoxicity using the *D. magna* test varied markedly between untreated and treated soil washing effluents. In particular, the number of immobile organisms was higher in the untreated sample resulting in slight toxicity after 24 h (33.3%) and 48 h (40.4%), whereas no ecotoxicity (no significant immobility) was detected for the treated samples at the same contact times.

Results using *P. subcapitata* indicated that the untreated effluent exert a negative effect on microalga inducing marked growth inhibition of free-living *P. subcapitata* cells of 76.5% after 72 h of exposure. The toxic effect was reduced in the treated sample (40.1%).

Results using *L. sativum* showed that phytotoxicity remained unchanged before and after the photocatalytic processes, with no difference observed on the germination index for the untreated and treated samples (76% I<sub>G</sub>). This effect can probably be ascribed to carboxylic acids and other substances (i.e. formaldehyde and ammonia) formed by photocatalytic oxidation of EDDS and its structural isomers [34,35] to which some bio-indicators were found to be sensitive [36].

The results collected indicate different sensitivities and responses for the bioassays on treated soil washing effluents probably due to the different interactions of metal-organic complexes with the organisms. However, the proposed two-step TiO<sub>2</sub>-photocatalytic soil washing treatment reduced the ecotoxicity of the effluents for three organisms tested (*V. fischeri*, *D. magna* and *P. subcapitata*).

### 3.4 Conclusions

Combined TiO<sub>2</sub>-based photocatalytic processes can be used for the simultaneous removal of heavy metals, such as copper and zinc, from aqueous effluents produced during washing processes of polluted soil using EDDS as chelating organic agent. Not only by demonstrating that it is possible to use solar light on the photocatalytic treatment of the effluent produced at the end of the washing, but also by making it possible to reuse this effluent for a next washing step. Ecotoxicity assessments on final effluents also showed the efficiency of photocatalytic treatment in reducing levels of residue ecotoxic effects for three living organisms tested.

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# Chapter 4      Solar photocatalytic processes for treatment of soil washing wastewater

In the present chapter the use of a sequence of two solar photocatalytic processes was investigated for the removal of copper, iron, zinc and ethylenediaminedisuccinic acid (EDDS), used as chelating agent, from real soil washing effluents. Removal efficiencies of 93.5% (copper), 99.6% (iron), 99.4% (zinc), 97.2% (EDDS) and 80.7% (TOC) were achieved through outdoor solar photocatalytic treatments using parabolic trough collectors and carried out in Naples (Italy, N 40°50', E 14°12') in the period June-July 2015. These removal efficiencies were achieved for an incident UVA solar energy per unit volume ( $Q_{j,n}$ ) of 580 kJ L<sup>-1</sup>, calculated by taking into account the irradiated surface area of the photoreactor estimated in the present chapter ( $9.79 \cdot 10^{-2} \text{ m}^2$ ) and the solar irradiance measurements collected during the experiments.

The results suggest that the two-step solar process adopted can be proposed as a useful solution to the problem of heavy metals and chelating organic agents removals from soil washing.

An ecotoxicological assessment, using different living organisms (*Daphnia magna*, *Vibrio fischeri*, *Pseudokirchneriella subcapitata*, *Lepidium sativum* and *Caenorhabditis elegans*), was carried out in order to evaluate the ecotoxicity of the soil washing effluents before and after the two-step photocatalytic process.

## 4.1 Introduction

Ex-situ soil washing processes based on the use of biodegradable chelating agents for heavy metals removal are very promising for the treatment of contaminated soils [1].

A major disadvantage of using these processes is that wastewater effluents containing extracted heavy metals and residual chelating agents must be decontaminated by appropriate methods. Consequently, spent soil washing effluents cannot be directly discharged neither into civil sewer nor in surface waters.

Conventional technologies, such as adsorption on activated carbon or precipitation, have been demonstrated to be ineffective in treating these effluents since the presence of chelating agents inhibits the separation of heavy metals from aqueous solutions due to a high thermodynamic stability of metal-chelant complexes.

For this purpose, different physical [2,3], chemical [4–6], or integrated physico-chemical [7] processes have been recently proposed to enhance the removal of heavy metals and chelating agents from wastewater effluents before their release into the environment. Among the processes proposed for treating soil washing solutions, solar driven photocatalytic systems can be preferred due to their simplicity and cheapness [8–10]. However, previous studies on the possibility of decontaminating EDDS containing soil washing effluents are so

far restricted to synthetic solutions [11] or real soil washing solutions [12] only under artificial solar radiation. No reports are found in the literature dealing with outdoor solar photocatalytic treatments of real soil washing effluents containing at the same time copper, iron, zinc, and ethylenediaminedisuccinic acid, used as chelating agent.

Therefore, the present investigation proposes, for the first time, an integrated outdoor photocatalytic process for lowering the high concentration of copper, iron, zinc, and chelating agent present in soil washing wastewater. The effluents were produced through the use of a soil washing process adopting EDDS as chelating organic agent. The polluted soils were taken from a SIR, in Southern Italy, near Naples, which is known for its high incidence of cancer mortality also due to a marked presence of heavy metals in the environment. [13]. Ecotoxicological tests were also carried out to evaluate the ecotoxicity of the soil washing wastewater before and after the two-step photocatalytic process. The main aims of this investigation are:

- 1) to check the suitability of a solar photocatalytic approach for the decontamination of soil washing effluents contaminated with copper, iron and zinc, and containing organic chelating agents;
- 2) to evaluate the ecotoxicity of the soil washing wastewater before and after the sequential photocatalytic process.
- 3) to propose a suitable procedure for the estimation of illuminated area of a solar photoreactor.

## 4.2 Experimental

### 4.2.1 Materials

(S,S)-ethylenediamine-N,N'-disuccinic acid–trisodium salt solution (35% in H<sub>2</sub>O) [CAS 178949-82-1], perchloric acid (ACS reagent 70%) [CAS 7601-90-3], nitric acid (ACS reagent > 67% v/v) [CAS 7697-37-2], oxalic acid (ACS reagent 99.8% w/w) [CAS 6153-56-6] and titanium(IV) oxide pure crystalline anatase powder (99.8% w/w) [CAS 1317-70-0] were purchased from Sigma–Aldrich and used as received.

### 4.2.2 Soil sampling and soil washing procedure

Polluted soil samples were collected from the area of Giugliano (Fig. 4.1), in the province of Naples (Campania, Italy). A description of the soil sampling procedure has been previously reported [12].



**Figure 4.1** – Geographic location of the soil sampling sites (geographic coordinates N 40°96'05", E 14°11'84").

Soil washing solution was produced in 2 L glass bottles. EDDS was used as the chelating agent. The tests were carried out at a natural pH value of 7.5-7.9, fixing the liquid-to-solid ratio (L/S) to 10:1 and the EDDS washing solution initial concentration to 0.50 mM. The samples were stirred in a mechanical shaker (Edmund Bühler, Kombischüttler KL2) at 190 rpm for 96 hrs at ambient temperature. Further details are reported therein [12].

#### 4.2.3 Photocatalytic procedures

The photocatalytic tests were carried out using two different types of photoreactor under artificial or natural solar radiation.

##### Artificial solar radiation

Solar simulated photocatalytic runs were carried out in an annular batch glass reactor having an irradiated volume ( $V_{ir}$ ) and an illuminated surface area ( $A_{ir}$ ) equal to 0.28 L and 3.39 dm<sup>2</sup> respectively. The reactor was equipped with a polychromatic sodium lamp (Helios Italquartz, model Na 15F) with a nominal power of 150 W and a wavelength range between 350–800 nm. The device has been described elsewhere [14]. The photon fluxes of the Na-lamp, measured by UVA radiometer (DELTA OHM, model HD2102.1), were 2.84 W·m<sup>-2</sup> (280–400 nm) and 2.02·10<sup>3</sup> W·m<sup>-2</sup> (400–800 nm). The emission spectrum of the Na-lamp is reported in Figure 4.2.

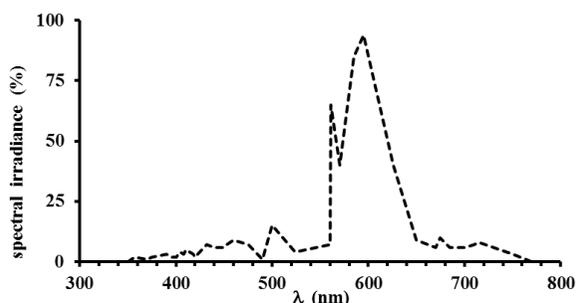


Figure 4.2 – Emission spectrum of the sodium lamp Helios Italquartz 150 W, model Na 15F.

Some photocatalytic runs were carried out using a high pressure Hg lamp with a nominal power of 125 W mainly emitting in the wavelength range of 300–400 nm (Helios Italquartz). The photon fluxes of the lamp at 305, 313 and 366 nm were 1.07·10<sup>-6</sup> E·s<sup>-1</sup>, 1.62·10<sup>-6</sup> E·s<sup>-1</sup> and 5.13·10<sup>-6</sup> E·s<sup>-1</sup> respectively.

##### Natural solar radiation

The photocatalytic runs under sunlight were carried during the period June-July 2015 at University of Naples (Italy, local latitude 40° 50' 00'' N, longitude 14°12' 00'' E) by using a flat plate collector supported by an aluminum structure (Fig. 4.3) with a multitubular reactor (PTC).



Figure 4.3 – Solar photoreactor adopted.

The flat plate collector (9 dm<sup>2</sup>) was made up of 8 parallel borosilicate glass tubes (internal diameter 4 mm, external diameter 7 mm, length 34.6 cm) connected by plastic junctions. The soil washing effluent to be treated was kept re-circulating at a rate of 80 L·h<sup>-1</sup>. Some runs were carried out varying the re-circulating rate (60 L·h<sup>-1</sup>). The solution recirculation between the refrigerated tank (1.5 L, 25 °C) and the collectors was carried out using a peristaltic pump (Watson Marlow 505S). The total volume of the reactor (V<sub>t</sub>) is constituted by the irradiated PTC volume (V<sub>ir</sub>) and the dead volume (recirculation tank and connecting tubes). The irradiated volume of PTC was 3.42·10<sup>-2</sup> L. The total volume of the device ranged between 0.30 L and 0.85 L. The flat plate collector surface was covered with aluminum foils. The average incident solar radiation was typically about 15±10 W·m<sup>-2</sup> in the wavelength range 315–400 nm and 950±150 W·m<sup>-2</sup> in the range 400–1100 nm.

The amount of UVA solar energy received by the *n*th sample (Q<sub>*j,n*</sub>, kJ·L<sup>-1</sup>), per unit volume of solution, in the time interval Δ*t<sub>n</sub>* was calculated from the following equation:

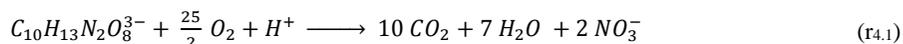
$$Q_{j,n} = Q_{j,n-1} + \Delta t_n \cdot UV_{G,n} \cdot \left[ \frac{A_{ir}}{V_t} \right] \quad 4.1$$

where *t<sub>n</sub>* is the experimental time corresponding to the *n*th sample, V<sub>t</sub> the total volume of the reactor, A<sub>ir</sub> the illuminated surface area, and UV<sub>G,*n*</sub> the average solar ultraviolet radiation (300–400 nm) measured during the period Δ*t<sub>n</sub>*.

#### 4.2.4 Analytical procedures

The soil washing samples were centrifuged at 4800 rpm for 15 min using an IEC Centra GP8R centrifuge. The initial pH of the soil washing effluent was close to 7.7±0.2. Solution samples were collected at different photocatalytic treatment times, filtered through regenerated cellulose filters (pore diameter 0.45 μm) and analyzed to determine the EDDS and metals concentrations.

The filtered washing solution samples were transferred to polyethylene containers for metals determination by atomic absorption spectrometry (AAS) in standard working conditions, using a Varian Model 55B SpectrAA (F-AAS) or a GBC Avanta AAS with a graphite furnace system (GF-AAS). All the measurements were carried out using analytical grade chemicals and ultrapure water. The determination of the EDDS concentration was performed using a colorimetric method previously reported [11]. The oxalic acid concentration was measured by HPLC chromatography (Agilent 1100) equipped with Alltech OA-1000 Organic Acids column using a sulfuric acid aqueous solution (2 N) as mobile phase. The total organic carbon was monitored by means of a TOC analyzer (Shimadzu 5000 A). COD analyses were carried out by using HACH kit (0–1500 ppm). The theoretical oxygen demand (ThOD) was calculated from the following equation:



The pH of the aqueous solutions was determined using an Orion 960 pH meter with a glass pH electrode. All measurements were carried out in triplicate and the average values were considered (standard deviation < 5%).

The identification of ethylenediaminedisuccinic acid (EDDS) photodegradation products was performed by Electrospray Mass Spectrometry (ESI-MS). ESI-MS was performed on an Agilent 1100 Series MSDTrap SL ion trap (Agilent Technologies, Palo Alto, CA, USA) operated in negative full scan ion mode. Nitrogen (supplied by a nitrogen generator N2 LCMS, Claind) was employed as both drying and nebulizer gas. The gas temperature was set at 285°C, the drying gas flow was 11 L/min with a nebulizer gas pressure of 60 psi. The capillary voltage was 3000 V. The ion trap scanned from *m/z* 50–2000. Each mass spectrum consists of 100–150 co-

added spectra. 50 µL aliquots of the samples, collected at different photocatalytic treatment times, were injected onto a Alltech OA-1000 Organic Acids (300 mm× 6.5 mm) column. The compounds were eluted at room temperature with an isocratic flow rate of 0.3 mL/min in water. A 10% (v/v) formic acid in water was also tested without any significant improvement of the peaks detection (data not shown).

#### 4.2.5 Ecotoxicity assessment

Ecotoxicological tests were carried out to evaluate the ecotoxicity of the soil washing wastewater before and after the solar photocatalytic process. The ecotoxicological assessment was performed on a seed (*Lepidium sativum*) and four different target organisms: a bacterium was performed on four different target organisms: a bacterium (*Vibrio fischeri*), a green microalga (*Pseudokirchneriella subcapitata*), a crustacean (*Daphnia magna*) and a worm (*Caenorhabditis elegans*).

##### *Vibrio fischeri*

The bioluminescence inhibition assay was performed using marine bacteria of the species *Vibrio fischeri* NRRL-B-11177 (formerly known as *Photobacterium phosphoreum*). The test evaluates the acute toxicity of a sample using as endpoint the inhibition of the luminescence naturally emitted by the bacterium. The luminescence was measured with a Microtox luminometer (Model 500, AZUR Environmental).

The drop in light emission is measured after a contact time of 5, 15 and 30 minutes with the test sample and the temperature during the exposure was 15°C [15]. Tests were carried out at least in duplicate with a control solution. The data were statistically processed by the instrument software and the result was expressed as percentage of luminescence inhibition (% I).

##### *Pseudokirchneriella subcapitata*

The algal growth inhibition test of *Pseudokirchneriella subcapitata* was carried out according to the protocol [16]. The growth of the algae exposed to the sample is compared with the growth of the algae in a negative control. The cell density in the cultures was measured after 72 hrs in a Bürker cell counting chamber. The specific growth rate of *P. subcapitata* in each replicate culture was calculated from the logarithmic increase in cell density in the intervals from 0 to 72 hrs using the following equation:

$$\psi = \frac{\ln N_n - \ln N_0}{t_n - t_0}$$

where  $N_0$  is the cell concentration at  $t = 0$ ,  $N_n$  the final cell concentration after 72 hrs of exposure,  $t_0$  the time of start measurement, and  $t_n$  the time of last measurement (hours from the start). The percentage inhibition of the cell growth at sample (% I) was calculated as the difference between the rate growth of the control and the rate growth of the sample and expressed as the mean ( $\pm$  standard deviation) of the replicates for  $p \leq 0.05$ .

##### *Daphnia magna*

The test with *Daphnia magna* allowed to evaluate the toxicity of the sample using the immobilization of the crustacean as response [17]. Tests were conducted in quadruplicate in the darkness, using 5 daphnids in a final volume of 50 mL. The test parameter considered was the number of immobile individuals in each replica, after 24 and 48 hours of exposure, compared to the number of individuals initially exposed. Each assay was considered valid only if the immobilization in the control solution was less than or equal to 10%.

##### *Lepidium sativum*

The phytoassay evaluated the possible toxicity of a sample by comparing the values of germination and root elongation of seeds placed in contact with the sample with those obtained for seeds placed in controlled conditions [18]. Germination and growth experiments were carried out in aqueous solutions at controlled pH, in three replicate experiments. Bioassays took 72 hrs and after this period, the number of seeds germinated was counted and the radical length was measured. The Index of growth (IG %) was calculated by multiplying the germinated seed number exposed to sample (G1) and length of roots exposed to sample (L1) to be divided by the factor obtained from the multiplication of germinated seed number exposed to negative control medium (Gc) and length of root exposed to negative control medium (Lc).

#### *Caenorhabditis elegans*

*C. elegans*, wild-type strain N2 Bristol, was used. Toxicity test was performed according to the Donkin and Williams procedure [19] by using age-synchronous 1 day old organisms. Ten worms each were placed into 24-well tissue culture plates containing 0.5 mL of the samples and 0.5 mL of K-medium as negative control. All treatments were done in triplicate. No feed was given during the test. The worms were exposed for 24 hr at 20°C and the number of dead worms was determined by absence of movement under stereomicroscope (Leica EZ4 HD).

### 4.3 Results and discussion

#### 4.3.1 Soil washing effluents

The average analytical concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn contained in the soil-washing effluents from the polluted soil sample after 96 h of contact time are reported in Figure 4.4. The results indicate the presence in the effluents, containing EDDS as chelating agent, of copper, iron, and zinc at concentration levels too high for their discharge in public sewers or in surface waters. Thus, one or more post-treatment processes must be performed before releasing them into the environment.

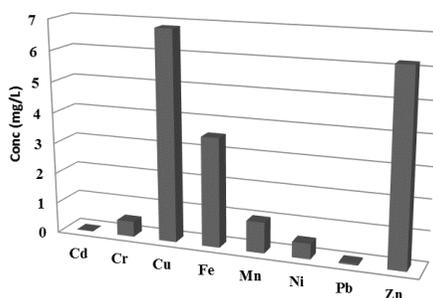


Figure 4.4 – Metals concentrations ( $\text{mg}\cdot\text{L}^{-1}$ ) in the effluent after the soil washing process, pH 7.8

#### 4.3.2 Photocatalytic combined processes with Na-lamp as radiation source

On the basis of the findings previously reported [12], a large campaign of experimental tests were carried out aiming at the establishment of an optimal sequence of photocatalytic processes capable to ensure the highest efficiency removal of copper, zinc, iron, and EDDS using a sodium lamp as radiation source. On the basis of the results collected during this campaign, the best choice has been demonstrated to be an initial removal of iron, zinc, and EDDS through  $\text{TiO}_2$ -photocatalysis in presence of oxygen, followed by a photocatalytic step under inert atmosphere (sacrificial  $\text{TiO}_2$ -photocatalysis) for the abatement of residual metals, particularly copper, and organics. A picture of the entire sequence is reported in Figure 4.5:

Chemical washing of contaminated soils and photocatalytic treatments of spent soil washing effluent

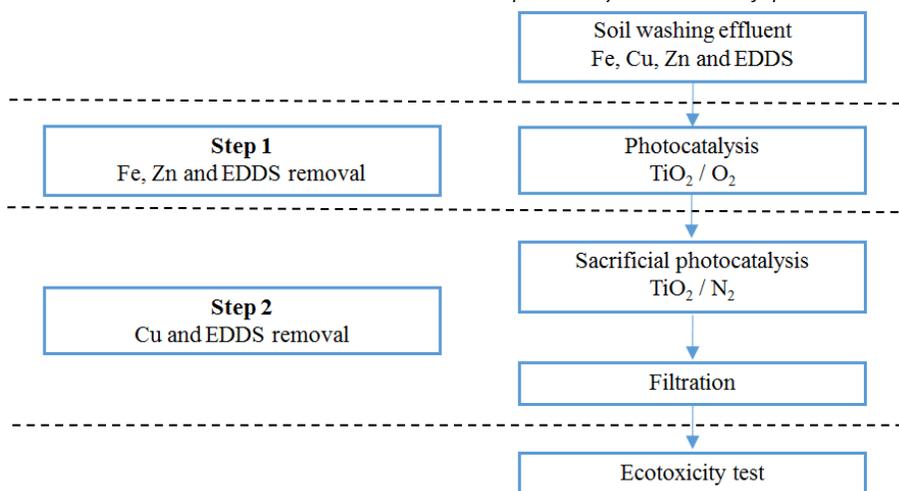


Figure 4.5 – Two-step photocatalytic process carried out.

The results of the experimental investigation (data not shown) on the effect of TiO<sub>2</sub> amount on the removal efficiencies of iron and zinc during the first stage (TiO<sub>2</sub>/O<sub>2</sub> photocatalysis) demonstrated that the optimal load of TiO<sub>2</sub> is 500 mg/L which, for sake of simplicity, was also adopted during the second step (sacrificial TiO<sub>2</sub> photocatalysis) without any catalyst replacement (no filtration).

The removal degrees of iron, copper, zinc, and EDDS by irradiating the effluent with the sodium vapor lamp without adjusting the pH are reported in Figure 4.6.

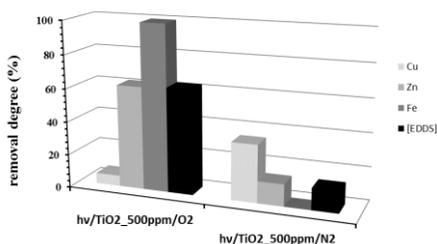


Figure 4.6 – Removal of metals and EDDS from soil washing effluents through two sequential TiO<sub>2</sub> photocatalytic steps by irradiation with a sodium vapor lamp without TiO<sub>2</sub> replacement. [EDDS]<sub>0</sub> = 0.46 mM. (■) Cu, (▒) Zn, (▓) Fe, (■) EDDS. TiO<sub>2</sub>\_500 ppm/O<sub>2</sub>/hν: tr = 16 hrs, pH = 7.9 (not regulated). TiO<sub>2</sub>\_500 ppm/N<sub>2</sub>/hν: tr = 6 hrs, pH = 8.5 (not regulated).

According to a previous investigation [12], zinc and iron were almost efficiently removed (51% for Zn and 99% for Fe) with TiO<sub>2</sub>-photocatalysis in presence of oxygen. On the other hand, copper resulted to be only partially removed (35% with respect to the initial concentration) by TiO<sub>2</sub>-sacrificial photocatalysis (second step), although an EDDS removal degree of 76% was globally achieved as a result of the two steps.

The first step allowed to reach high removals of the chelating agent due to the occurrence of reactions between EDDS and hydroxyl and/or hydroperoxyl radicals ( $r_{4.5}$ ), formed by the photolysis of Fe(III)-EDDS and Fe(III)-L complexes ( $r_{4.2}$ - $r_{4.4}$ ), where L represents by-photoproducts [20]:





by reaction of oxygen with photogenerated  $TiO_2$ -electrons:



and by reaction of water molecules with  $TiO_2$  positive holes:



Acceptable values of iron and zinc removal were also gained due to the precipitation of these metals as insoluble hydroxides and their adsorption onto  $TiO_2$  catalyst after EDDS degradation. On the other hand, the first photocatalytic step was (almost completely) ineffective in removing copper species probably due to the existence of soluble Cu-hydroxo-complexes, such as  $Cu(OH)^+$ , at the adopted pH [21].

The removal of copper and residual EDDS during the second stage is essentially ascribable to the reduction of cupric ions to zero-copper by photogenerated electrons ( $r_{4.9}$ ):



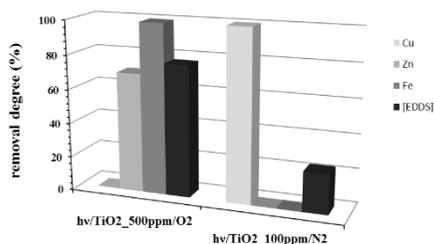
and to the oxidation of EDDS by holes ( $r_{4.10}$ )



In spite of satisfactory removal degrees of zinc and iron, the operating conditions adopted were not able to ensure an equally high removal degree of copper.

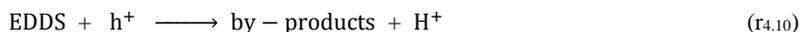
The low ability of the sacrificial photocatalytic system to remove copper from the soil washing effluents may be ascribed to the competitive role of Fe(III) species in capturing photogenerated electrons [22] and the partial catalyst deactivation due to its surface coating with insoluble hydroxides of Fe and Zn formed during the first step.

For this reason a number of tests (data not shown) were carried out aimed at determining the best load of  $TiO_2$  to be used during the second step. A load of 100 ppm resulted to be a good compromise between catalyst amount and treatment time. The results, collected through a two-step process with a catalyst removal (filtration) between the first and the second step, are shown in Figure 4.7. It is noteworthy to observe that the catalyst replacement allowed to increase of 65% the yield of copper removal (from 35% to 100%).



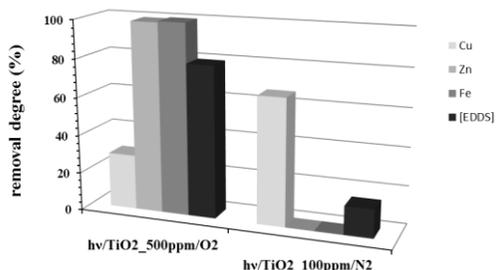
**Figure 4.7** – Removal of metals and EDDS from soil washing effluents through two sequential TiO<sub>2</sub> photocatalytic steps by irradiation with sodium vapor lamp. [EDDS]<sub>0</sub> = 0.43 mM. (■) Cu, (▒) Zn, (▓) Fe, (■) EDDS. TiO<sub>2</sub>\_500 ppm/O<sub>2</sub>/hv: t<sub>r</sub> = 16 hrs, pH = 7.6 (not regulated). TiO<sub>2</sub>\_100 ppm/N<sub>2</sub>/hv: t<sub>r</sub> = 6 hrs, pH = 9.6 (not regulated).

Unlike iron and zinc removal, copper was not removed through its precipitation as Cu(OH)<sub>2</sub>, in spite of its low K<sub>p</sub> value (4.8·10<sup>-20</sup> M<sup>3</sup>) following EDDS degradation through the reaction with positive holes (r<sub>4.10</sub>):



#### 4.3.3 Photocatalytic combined processes under natural sunlight source

The removal degrees of the chelating agent, copper, iron, and zinc in soil washing effluents under natural sunlight using the same photocatalytic treatment sequence adopted with artificial solar irradiation are shown in Figure 4.8. The results indicate that wastewaters can be successfully treated under “outdoor” conditions although longer irradiation times than those adopted for “indoor” experiments are required to reach significant pollutants removal efficiencies.

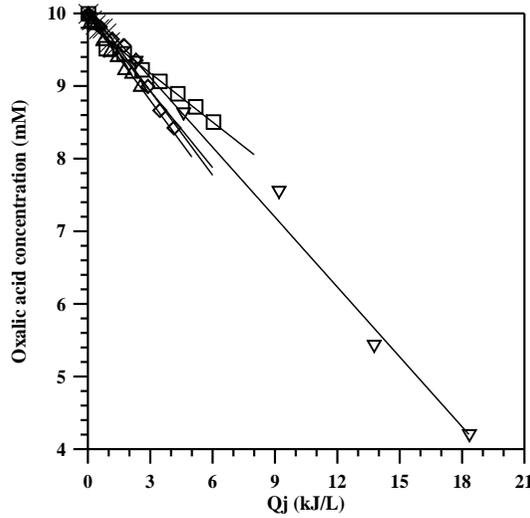


**Figure 4.8** – Removal of metals and EDDS from soil washing effluents through two sequential TiO<sub>2</sub> photocatalytic steps by irradiation with natural sunlight source. [EDDS]<sub>0</sub> = 0.45 mM. (■) Cu, (▒) Zn, (▓) Fe, (■) EDDS. TiO<sub>2</sub>\_500 ppm/O<sub>2</sub>/hv: t<sub>r</sub> = 23 hrs, pH = 7.7 (not regulated). TiO<sub>2</sub>\_100 ppm/N<sub>2</sub>/hv: t<sub>r</sub> = 20 hrs, pH = 8.7 (not regulated).

To collect valuable information for scaling-up the solar treatment plant, concentration data for the species removed should be plotted against the incident solar energy per unit of volume ( $Q_{j,n}$ , kJ·L<sup>-1</sup>), instead of the irradiation time [23]. However, to move forward in this direction it is necessary to know exactly the value of the illuminated surface area of the photoreactor ( $A_{ir}$ ). Due to the possibility of using many types of reflecting surfaces whose area may be quite different, generally, it is necessary to directly measure this value. To this purpose, a method is proposed in the following paragraph based on the concentration data collected during the oxidation of a standard species during some “indoor” and “outdoor” photocatalytic runs.

These runs were carried out using the oxalic acid containing aqueous solution on which anatase titanium dioxide (at the same load) was suspended. “Indoor” experiments were performed in a batch recirculating lab-system, using two different radiating sources (Hg-lamp or Na-lamp). For “indoor” runs, the  $Q_{j,n}$  term can be readily estimated using equation 1, since both the emitting powers of the lamps in the wavelengths range 280-400 nm and the illuminated surface area of the “indoor” reactor are known (see photocatalytic procedures). Therefore, the values for the apparent reaction rate constant ( $k_{app}$ ) can be derived by the slope of straight lines reported in the plot of oxalic acid concentration against  $Q_{j,n}$  for different total volumes of the reactor (Figure 4.9).

which were carried out using the same oxalic acid aqueous solution on which anatase titanium dioxide (at the



**Figure 4.9** – Oxalic acid concentration vs accumulated energy for different UV-Vis artificial lamps at varying total volume of the reactor ( $V_t$ ). [Oxalic acid] $_0$  = 10 mM, TiO $_2$  initial load = 500 mg·L $^{-1}$ ; pH = 2.0, T = 25 °C,  $V_{ir}$  = 0.28 L, recycle flow rate 80 L·h $^{-1}$ . Hg-lamp:  $V_t$  = 0.4 L ( $\nabla$ ); Na-lamp:  $V_t$  = 0.4 L ( $\square$ ),  $V_t$  = 0.6 L ( $\diamond$ ),  $V_t$  = 1.0 L ( $\triangle$ ),  $V_t$  = 2.0 L ( $\times$ ).

The  $k_{app}$  constant is the product of some variables which can be identified in the following way. According to literature indications [24], the following material balance can be written for a batch photocatalytic reactor:

$$V_t \cdot \frac{dc}{dt} = -V_{ir} \cdot r \quad 4.2$$

in which [23]:

$$r = k \cdot \Phi \cdot [1 - e^{(-2.3 \cdot \mu \cdot l \cdot q)}] \cdot \frac{A_{ir}}{V_t} \cdot UV_{G,n} \cdot f(c) \quad 4.3$$

where  $k$ ,  $\Phi$ ,  $\mu$ ,  $l$ ,  $q$ , and  $f(c)$  are the kinetic constant, the photocatalyst quantum yield, the suspension extinction coefficient (sum of the absorption and scattering coefficients), the light pathway length of the reactor, the photocatalyst load, and a function of the organic species concentration, respectively.

According to literature indications [25], a zero-order dependence is reported for the photocatalytic degradation of oxalic acid for which  $f(c) = k'$ .

Therefore, rearranging Equation 4.2:

$$dc = -k \cdot k' \cdot \Phi \cdot [1 - e^{(-2.3 \cdot \mu \cdot l \cdot q)}] \cdot \frac{A_{ir}}{V_{ir}} \cdot UV_{G,n} \cdot \frac{V_{ir}}{V_t} dt \quad 4.4$$

In finite terms, taking into account Eq.1:

$$\Delta c = -k'' \cdot \Phi \cdot [1 - e^{(-2.3 \cdot \mu \cdot l \cdot q)}] \cdot Q_{j,n}$$

with  $k \cdot k' = k''$ .

The oxalic acid concentration at different reaction times can be thus calculated as:

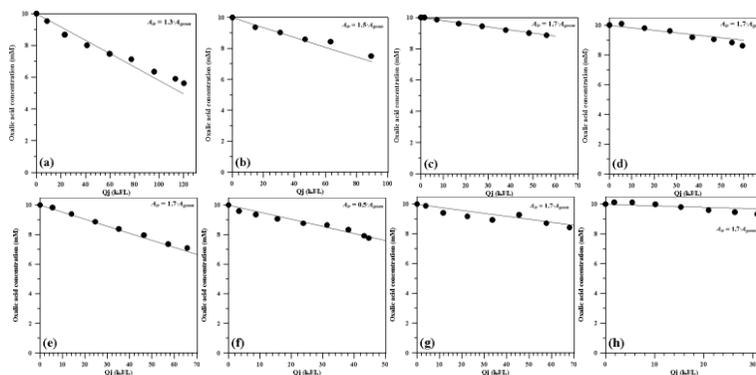
$$[\text{Oxalic acid}]_t = [\text{Oxalic acid}]_0 - k_{app} \cdot Q_{j,n} \quad 4.6$$

where:

$$k_{app} = k'' \cdot \Phi [1 - e^{(-2.3 \cdot \mu \cdot l \cdot q)}] \quad 4.7$$

Following this approach, it is possible to calculate an average value of  $0.42 \text{ mmol} \cdot \text{kJ}^{-1}$  for the term  $k'' \cdot \Phi$  reported in the equation 4.7, dividing each  $k_{app}$  constant, as those estimated, for example, through the data reported in Figure 4.9, by the  $[1 - e^{(-2.3 \cdot \mu \cdot l \cdot q)}] V_{ir}/V_t$  factor. The mean value of this product ( $k'' \cdot \Phi$ ) depends upon the type of titanium dioxide used, its load, and the organic species oxidized (oxalic acid), but it is independent on the  $V_{ir}/V_t$ . The value thus calculated for  $k'' \cdot \Phi$  term can be used to predict the decrease in concentration of oxalic acid against  $Q_{j,n}$  when one of the suspensions, previously used in “indoor” experiments, is sent to an “outdoor” solar photoreactor. When a set of data for oxalic acid concentration against time are available from solar photocatalytic oxidation runs in a selected photoreactor, for which the illuminated and total volumes are known, and the illuminated area ( $A_{ir}$ ) unknown, the latter can be estimated in the following way. First of all, a plot “oxalic acid concentration versus time” is converted in one showing “oxalic acid concentration vs  $Q_{j,n}$ ”, by fixing a value of this area. The best estimate of the latter will be thus identified as that allowing to minimize the differences between the plot “oxalic acid concentration vs  $Q_{j,n}$ ” and the straight line resulting from Eq 4.6.

According to the procedure described above and using experimental data of oxalic acid consumption vs  $Q_{j,n}$  collected varying the  $V_{ir}/V_t$  ratio, an average value of  $9.79 \cdot 10^{-2} \text{ m}^2$  was thus estimated for the illuminated area of the solar photoreactor.

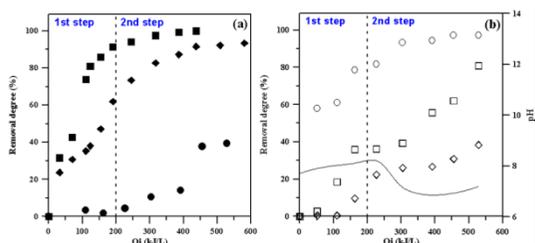


**Figure 4.10** – Oxalic acid concentration vs accumulated energy under sunlight radiation at varying irradiated ( $V_{ir}$ ) and total volumes of the reactor ( $V_t$ ), and recycle flow rates ( $Q_v$ ).  $[\text{Oxalic acid}]_0 = 10 \text{ mM}$ ,  $\text{TiO}_2$  initial load =  $500 \text{ mg} \cdot \text{L}^{-1}$ ;  $\text{pH} = 2.0$ ,  $T = 25 \text{ }^\circ\text{C}$ . (\*) with covering the flat plate collector surface area.

- (a):  $V_{ir} = 3.42 \cdot 10^{-2} \text{ L}$ ,  $V_t = 0.35 \text{ L}$ ,  $Q_v = 80 \text{ L} \cdot \text{h}^{-1}$ ; (b):  $V_{ir} = 3.42 \cdot 10^{-2} \text{ L}$ ,  $V_t = 0.45 \text{ L}$ ,  $Q_v = 80 \text{ L} \cdot \text{h}^{-1}$ .  
(c):  $V_{ir} = 3.42 \cdot 10^{-2} \text{ L}$ ,  $V_t = 0.70 \text{ L}$ ,  $Q_v = 80 \text{ L} \cdot \text{h}^{-1}$ ; (d):  $V_{ir} = 3.42 \cdot 10^{-2} \text{ L}$ ,  $V_t = 0.85 \text{ L}$ ,  $Q_v = 80 \text{ L} \cdot \text{h}^{-1}$ ;  
(e):  $V_{ir} = 3.42 \cdot 10^{-2} \text{ L}$ ,  $V_t = 0.30 \text{ L}$ ,  $Q_v = 60 \text{ L} \cdot \text{h}^{-1}$ ; (f)\*:  $V_{ir} = 3.42 \cdot 10^{-2} \text{ L}$ ,  $V_t = 0.30 \text{ L}$ ,  $Q_v = 80 \text{ L} \cdot \text{h}^{-1}$ ;  
(g):  $V_{ir} = 1.71 \cdot 10^{-2} \text{ L}$ ,  $V_t = 0.35 \text{ L}$ ,  $Q_v = 80 \text{ L} \cdot \text{h}^{-1}$ ; (h):  $V_{ir} = 8.54 \cdot 10^{-3} \text{ L}$ ,  $V_t = 0.35 \text{ L}$ ,  $Q_v = 80 \text{ L} \cdot \text{h}^{-1}$ .

This value was used to calculate the  $Q_{j,n}$  values (Eq. 4.1) required to achieve the desired removal percentage degrees of EDDS, copper, zinc, nitrate, COD, and TOC for the soil washing effluents treated through the photocatalytic sequence  $\text{TiO}_2/\text{O}_2$  and  $\text{TiO}_2/\text{N}_2$  (Figs. 4.11a,b). It is noteworthy to observe that the TOC and COD removal degree functions show a double S-shape profile, reaching maximum values close to 80% and 40%, respectively. This “anomalous” result may be explained considering that EDDS oxidation occurs in several sequential reactions pathways, which differ from each other depending on whether the degradation step involves decarboxylation and oxygenation reactions or not.

However, the value of COD/ThOD ratio (0.76) calculated for a reference solution containing the sole EDDS at a known concentration, indicates that COD data are not strictly representative for the content of oxidizable organic carbon for different treated samples. This result, which is the consequence of an incomplete EDDS oxidation during COD determination runs, leading to uncorrect COD measurements, has been reported previously for EDTA, a structural isomer of EDDS [26]. It is remarkable to observe that during the second step it was also reached a 40% value of removal degree of nitrate, initially present in the soil washing effluent at 48 ppm. This result is of significant importance because it would suggest the use of combined sunlight driven photocatalytic reduction processes also for removing nitrates from aqueous effluents.



**Figure 4.11** – Removal degrees of Zn (■), Cu (◆), NO<sub>3</sub><sup>-</sup> (●), EDDS (○), TOC (□) and COD (◇) and pH (—) profiles during the two solar sequential photocatalytic treatments

The decrease in pH from 7.70 to 6.85 (Fig. 4.11b) indicates the formation of carboxylic acids during the photodegradation of chemical intermediates, which are further mineralized thus resulting in a moderate pH increase (7.20) for more prolonged reaction times ( $Q_j > 500 \text{ kJ}\cdot\text{L}^{-1}$ ). Moreover, an iron removal of 99.6% was reached at the end of the first step (data not shown).

#### 4.3.4 Capital cost estimation

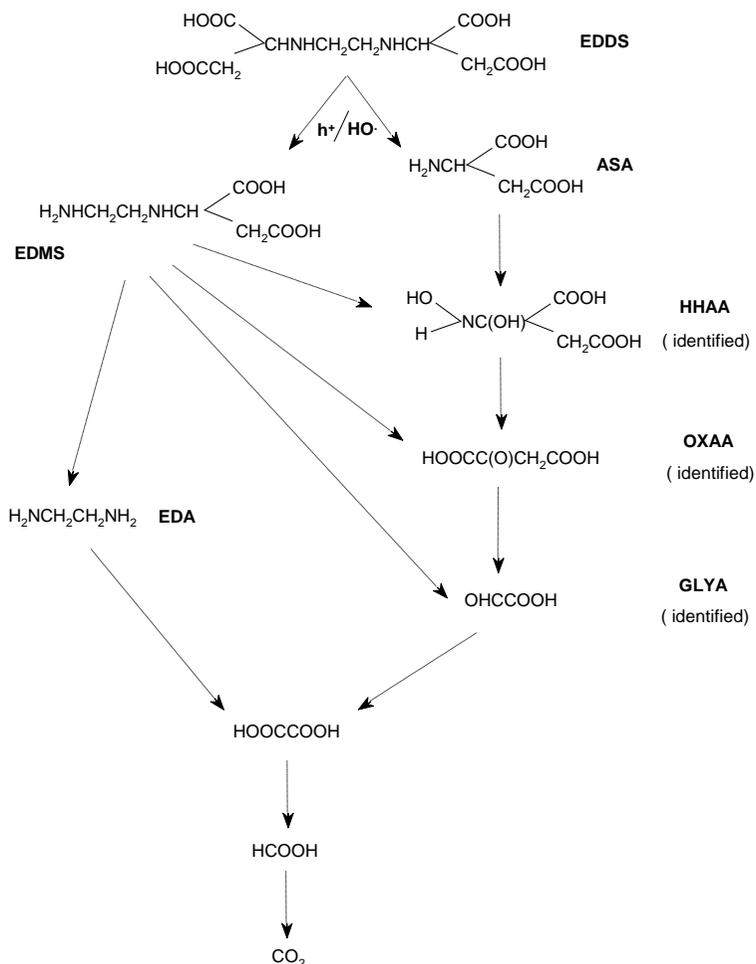
From the data reported in Figure 4.11a, it can be deduced that an incident solar energy per unit volume of  $425 \text{ kJ}\cdot\text{L}^{-1}$  is required to achieve a removal degree of 100% and 90% of zinc and copper, respectively. This result, under the adopted experimental conditions ( $UV_{G,n} = 15 \text{ W}\cdot\text{m}^{-2}$ ), was reached within 30 hrs of treatment time. Assuming that it is necessary to treat a volume of soil washing effluent equal to  $10 \text{ m}^3$ , a geometrical surface area of about  $1630 \text{ m}^2$  can be deduced from Eq. 4.1, by taking into account an average scaling factor of 1.61 (Figs. 4.10a–h). If an investment cost of  $210 \text{ \$}\cdot\text{m}^{-2}$  for a flat plate collector is considered [27], a capital cost of about  $345.000 \text{ \$}$  for the solar photoreactor is thus estimated. It is noteworthy to stress that the estimated cost is mainly affected by the photoreactor design, the solar irradiation conditions and the chemical composition of the aqueous effluents.

##### 4.3.4.1 Oxidation pathway

The main chemical intermediates determined by HPLC and ESI-MS-ion trap analyses on filtered samples after the first and the second sunlight photocatalytic processes were glyoxylic (GLYA) and oxaloacetic (OXAA) acids, copper-oxaloacetate complex (Cu-OXA) and N-hydroxy-(3-hydroxy)-aspartic acid (HHAA). Additional information are supplied in SI. Some of these species were also previously detected during the oxidation of EDDS through sacrificial TiO<sub>2</sub> photocatalysis under artificial radiation [11], and they could cause an increase in ecotoxicity of the treated effluent towards particular target organisms [11,28,29].

On the basis of the above identified chemical intermediates and by-products, TOC and COD profiles, and literature findings on the photocatalytic degradation of EDTA [30,31], it can be suggested that the oxidation of EDDS and/or Metal-EDDS complexes during the two solar photocatalytic combined processes is initiated by HO radical species and photogenerated positive holes, giving rise to low molecular weight nitrogen-containing

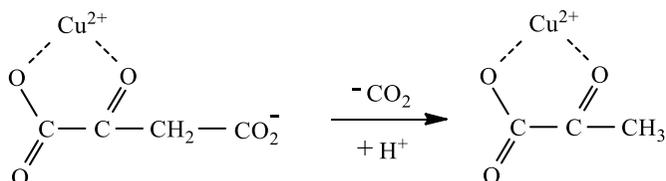
intermediates, such as aspartic acid (**ASA**), ethylene-diamine-monosuccinic acid (**EDMS**), N-hydroxy-(3-hydroxy)-aspartic acid and ethylenediamine (**EDA**) (Figure 4.12).



**Figure 4.12** – Simplified possible main pathway for the photocatalytic degradation of EDDS.

Further oxidations of **HHA** and structurally similar intermediates can lead to the formation of **OXAA**, which is successively converted through a photocatalytic oxidative decarboxylation step into **GLYA** and other short chain carboxylic acids (formic, oxalic, etc.) and finally into carbon dioxide.

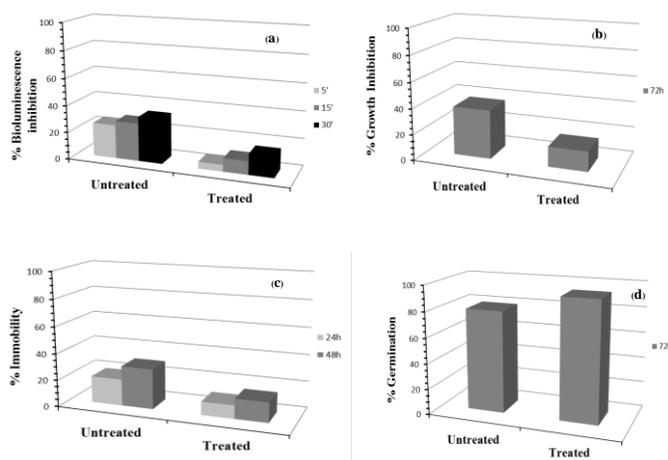
A minor route of carbon loss may be represented by the metal catalyzed decarboxylation of copper- and zinc-oxalacetate complexes and their derivatives (not reported in figure). For example, it is known that copper-oxalacetate complexes (**Cu-OXA**, **Cu<sub>2</sub>-OXA**), lose carbon dioxide to form pyruvate complexes [32,33]:



#### 4.3.5 Ecotoxicological assessment

The ecotoxicity assessment was carried out on untreated and treated soil washing effluents at the end of the process performed under natural solar radiation using different target organisms.

The results, summarized in Figures 4.13a–e, indicate different sensitivities and responses for the bioassays on treated soil washing effluents and demonstrate, for all the organisms, that the treatment of the effluent implied a marked decrease in ecotoxicity compared to non-treated soil washing solution.



**Figure 4.13** – Ecotoxicological tests on untreated and treated effluents. **a)** *V.fischeri* bioluminescence inhibition exposed for 5' (□), 15' (■) and 30' (■) (quadruplicate experiments); **b)** *P.subcapitata* growth inhibition after exposure for 72 h (triplicate experiments); **c)** *D. magna* immobilization after exposure for 24h (□) and 48h (■) (quadruplicate experiments); **d)** *L. sativum* index of germination after exposure for 72 h (triplicate experiments); **e)** survival of *C. elegans* after exposure for 24h (quadruplicate experiments). The results are relative to average of effects.

According to the bioluminescence test (Fig. 4.13a), ecotoxicity varied considerably between untreated and treated effluents. For example, after 30 min of *V. fischeri* exposure, a slight inhibition was recorded for the untreated sample ( $33.3 \pm 1.06\%$ ) whereas no ecotoxic effects were measured on the treated treatment ( $15.5 \pm 0.7\%$ ).

Furthermore, the exposition time of the organisms to the solutions did not affect on the results because the bioluminescence inhibition at 5, 15 and 30 minutes are of the same order of magnitude. The response obtained for tested specimen with *P. subcapitata* are shown in Figure 4.13b. The untreated sample exerted a negative effect on microalga inducing growth inhibition of free-living *P.subcapitata* cells of ( $37.8 \pm 1.45\%$ ) after 72 hrs of exposure. The negative effect was significantly reduced in the treated sample ( $15.5 \pm 0.7\%$ ). There was no detectable toxicity (no significant immobility) to the crustacean *D. magna*, at 24 and 48 hrs exposure to treated samples (Fig. 4.13c), whereas the number of immobile organisms was higher in the untreated sample resulting in slight toxicity after 48 hrs (30%). Little or any appreciable response was observed with *L. sativum* to the either samples (Fig. 4.13d).

As regard the untreated sample, *C. elegans* was the most sensitive organism showing low percentage survival of worms (40%) after 24 hrs of exposure (Fig. 4.13e). On the contrary a noticeable decrease of ecotoxicity was recorded for the treated sample reaching a survival percentage of 86.7%. The obtained results collected during the ecotoxicological assessment could be justified by the very low content of heavy metals (zinc and

copper), below the EC50 reported in literature [34,35], reached for the soil washing effluents after the solar photocatalytic processes.

## 4.4 Conclusions

A sequence of two solar TiO<sub>2</sub>-photocatalytic processes was tested to remove copper, iron, zinc, and EDDS from real soil washing wastewater at neutral pH conditions.

The results collected from experimental runs demonstrate that iron and zinc are mainly removed by precipitation as insoluble hydroxides during the first step (TiO<sub>2</sub>-photocatalysis with oxygen) whereas the second step (TiO<sub>2</sub>-sacrificial photocatalysis) is necessary to reduce cupric ions to zero-valent copper which precipitates from the solution.

The ecotoxicological results indicate that natural solar photocatalytic processes are able to reduce noticeably the ecotoxicity of the soil washing effluents with respect to the untreated solutions.

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## Conclusion

In this thesis the soil reclamation by chemical washing of contaminated soils and the oxidative photocatalytic treatment of aqueous stream produced during soil washing have been investigated. In particular the feasibility of soil washing procedure for treating a contaminated soil by Cu and Zn using biodegradable chelant agent has been evaluated.. For this purpose several soil washing tests were conducted at bench scale, in batch reactors by varying the operative conditions and the influence of Metal/EDDS complexes' diffusion into the soil matrix during the soil washing process was examined. Afterwards, the efficiency of photocatalytic processes for treating the spent soil washing solution (SSWS) containing heavy metals (HMs) and EDDS was evaluated. The study was initially carried out on both synthetic and real SSWS with an artificial solar-driven homogeneous as well as heterogeneous photocatalytic processes. Once the correct sequence of photocatalytic processes was found tests with a solar reactor were carried out and the ecotoxicity of SSWS was assessed before and after treatment.

The obtained results showed that the use of a biodegradable chelating agent such as EDDS can be an effective way, in soil washing processes, to remove HMs from contaminated soils.

In addition, it was possible to show that intra-particle diffusion may be one of the main mechanisms controlling the extraction of HMs from soil. In agreement with the Weber and Morris equation, the diffusion process develops at different rates according to the size of pores. The heavy metals removal takes place firstly in the macro pores and then in the micro pores.

The extraction process can be divided into two steps as a function of contact time between soil and solution. At exposure time <1 hour, HMs are removed mainly from macro pores, and the Crank equation can be applied. At longer times, the removal occurs mostly in micro pores and the appropriate equation is derived from Vermeulen. The "apparent" diffusion coefficients of Cu-EDDS and Zn-EDDS increase with the increasing concentration of chelating agent as well as soil particle size.

The best results obtained by the initial washing steps unfortunately produce effluents containing the chelating agent and metals at concentrations exceeding published sewer discharge limits. For this reason, photocatalytic processes can be used to further decontaminate the SSWS. Photocatalytic studies show that different treatments are needed to remove EDDS, Cu, Zn and Fe (each exceeding regulatory limits) from SSWS. The treatment consists of TiO<sub>2</sub>-photocatalysis with oxygen to remove Fe and Zn by precipitation as insoluble hydroxides, followed by TiO<sub>2</sub>-sacrificial photocatalysis to reduce Cu(II) ions to zero-valent Cu which precipitates from the solution. It is not possible to remove Zn through sacrificial photocatalysis because the direct reduction of Zn(II) to the corresponding zero-valent state is thermodynamically unfavorable. However, sacrificial photocatalysis is needed because, at the adopted pH, soluble Cu-hydroxo-complexes are not present. Furthermore it is possible to achieve adequate decontamination of the SSWS with a contact time equal to 30 hours and an incident solar energy per unit volume of 425 kJ·L<sup>-1</sup>. The cost of the solar photoreactor for 10m<sup>3</sup> is estimated at 300,000 euros.

This study also proved the effective possibility to reuse the treated effluent for another soil washing process with an appreciable percentage of removal of contaminants from the soil. Ecotoxicity studies underline the

real effectiveness of solar photocatalytic processes in decontaminating SSWS. Marked reductions in the levels of residual ecotoxicity can be observed for all organisms in the tests applied.