



# Simultaneous removal of heavy metals from field-polluted soils and treatment of soil washing effluents through combined adsorption and artificial sunlight-driven photocatalytic processes



Suéllen Satyro<sup>a</sup>, Marco Race<sup>b</sup>, Francesco Di Natale<sup>c</sup>, Alessandro Erto<sup>c</sup>, Marco Guida<sup>d</sup>, Raffaele Marotta<sup>c,\*</sup>

<sup>a</sup> Federal University of Rio de Janeiro, COPPE – Chemical Engineering Program, Centro de Tecnologia, Bloco G, sala 115, Cidade Universitária, Rio de Janeiro, Brazil

<sup>b</sup> Dipartimento di Ingegneria Civile, Edile ed Ambientale, Università di Napoli “Federico II”, via Claudio, 21, 80125 Napoli, Italy

<sup>c</sup> Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli “Federico II”, P.le V. Tecchio 80, 80125 Napoli, Italy

<sup>d</sup> Dipartimento di Biologia, Università di Napoli “Federico II”, via Cinthia ed. 7, 80126 Napoli, Italy

## HIGHLIGHTS

- Removing heavy metals from a real contaminated soil using EDDS.
- Sequence of photochemical and adsorption processes for soil washing effluents.
- Kinetic and equilibrium models for soil washing and adsorption processes.
- Ecotoxicological assessment of the soil washing effluents.

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## ABSTRACT

This paper proposes a process for reducing the content of copper and zinc in polluted soils and a combined photocatalytic-physical process for the treatment of the soil washing effluents. For this purpose, real soil samples were taken from the “Land of Fires”, a region in Southern Italy which is known for its high incidence of cancer mortality. Ethylenediamine-*N,N'*-disuccinic acid (EDDS) was used to extract the heavy metals from the contaminated soil. The soil washing effluents were treated through a sequence of photocatalytic and adsorption processes to lower the concentration values of metals (Cu, Zn, Fe and Mn) below the limits of national legislation for discharge in municipal sewers and to remove the EDDS from the soil washing solutions. Ecotoxicological tests, using different living organisms (*Daphnia magna*, *Vibrio fischeri*, *Pseudokirchneriella subcapitata* and *Lepidium sativum*), were performed on the soil washing effluents before and after the treatments to assess the effects of the proposed combined process on the ecotoxicity of the soil washing solutions.

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## 1. Introduction

Soil washing is one of the most promising “ex-situ” techniques for cleaning of soils contaminated by toxic metals [1]. Different organic agents can be used to extract the metals from the polluted soils. Ethylenediaminetetraacetic acid (EDTA) is the most commonly used chelating agent, due to its ability to form stable complex species with several metals [2]. Unfortunately, EDTA is quite persistent in the environment due to its poor biodegradability. Therefore, ethylenediaminedisuccinic acid (EDDS) has recently been proposed as a safe and environmentally-friendly substitute for EDTA in soil washing processes [3]. However, a proper

treatment of the exhausted soil washing solutions containing the chelating agent and the extracted metals is necessary before these effluents can be discharged into the environment. The treatment of metal-chelating agent leachate using traditional techniques, such as precipitation or adsorption, is generally unsuitable due to the thermodynamic stability of the metal–organic complexes [4]. The possibility of destroying the organometallic complexes by simultaneously removing the chelating agent (i.e. EDDS, EDTA) and the metals through heterogeneous and homogeneous photocatalytic chemical processes has been recently proposed [5–7]. However, these studies are restricted to synthetic solutions or real soil washing solutions at a low trisodium EDDS salt-to-metal molar ratio (i.e. MR = 0.6), whereas chelating agent-to-metal molar ratios greater than 1 have been often suggested in the literature in order to achieve higher metal extraction from field-polluted soils [8].

\* Corresponding author. Tel.: +39 817682968; fax: +39 815936936.

E-mail address: [raffaele.marotta@unina.it](mailto:raffaele.marotta@unina.it) (R. Marotta).

In addition, these techniques require the use of reagents such as oxalic acid and hydrogen peroxide, and a pH adjustment is needed to destroy the chelating agent [7].

For higher EDDS-to-metal molar ratios, adsorption processes using activated carbon could be used to remove the toxic metals from the soil washing effluents, even if the formation of stable metal–EDDS complexes, which enhance the dissolution of the metals in water, could be expected to limit their effective removal. To avoid this, EDDS can be removed, before the adsorption process, through a proper solar photocatalytic advanced oxidation process [6]. Among the solar driven photocatalytic advanced oxidation processes previously proposed for the decontamination of soil washing solutions [6], the Fe(III)-EDDS/hv/air system can be preferred due to its simplicity and low cost (absence of solid catalyst and additional reagents, such as hydrogen peroxide). This system works like a “homogeneous photo-Fenton process” (Fig. 1) in which Fe(III)-EDDS complexes, present in the soil washing solution, undergo photochemical reactions through a ligand-to-metal-charge-transfer (LMCT) process. In the presence of oxygen, which also regenerates ferric species by photo-oxidation of Fe(II) ions, this leads to the production of hydroxyl and hydroperoxyl radicals capable of destroying the chelating agent and organic molecules present in the soil washing effluents [9]. In turn, the removal of the metals, no longer chelated, can be enhanced by physical processes (e.g. adsorption, precipitation). These processes can also potentially be integrated into realistic multi-component systems in order to treat soil washing solutions polluted by different metals. This paper aims to focus on the possibility of:

- (1) removing heavy metals from a real contaminated soil using EDDS as the chelating agent (trisodium EDDS salt-to-metal molar ratio higher than 1, i.e. MR = 6);
- (2) decontaminating the soil washing solutions through an integrated combination of sunlight-driven homogeneous photocatalysis (photo-Fenton-like) and an activated carbon adsorption process, without using additional reagents and pH adjustment, to achieve EDDS and metal concentrations within the sewer discharge limits established by Italian legislation;
- (3) investigating the ecotoxicity of the untreated and treated soil washing effluents through specific ecotoxicological tests on target organisms.

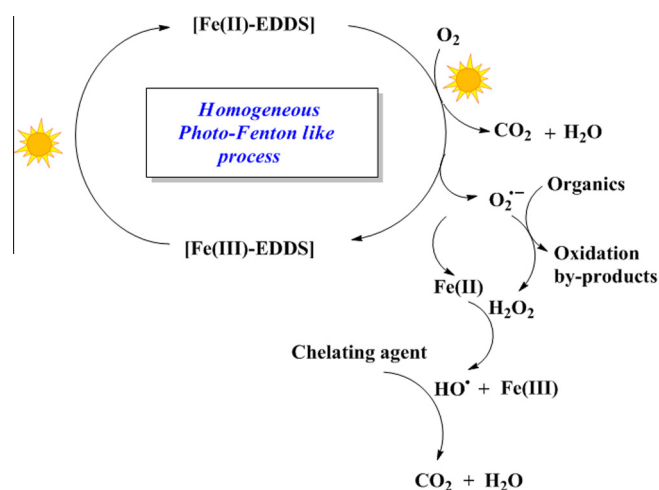


Fig. 1. Homogeneous photocatalytic cycle for the Fe(III)-EDDS/hv/air process.

## 2. Materials and methods

### 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] and nitric acid (ACS reagent > 67% v/v) [CAS 7697-37-2], were purchased from Sigma–Aldrich and used as received. The reagents for algal growth medium (ISO 8692:2012) were of analytical grade (Sigma–Aldrich). The freeze-dried bioluminescent bacterium *V. fischeri* and the test solutions for bioluminescence inhibition testing were purchased from Ecotox LDS S.r.l. (Milan, Italy).

Organosorb-10<sup>®</sup>, produced by Desotec from a bituminous coal, was used as non-impregnated granular activated carbon. This material has a narrow particle size distribution with an average diameter of 1.2 mm. The textural properties of the sorbent were studied by means of BET (Carlo Erba SORPTOMATIC 1900) and SEM (Environmental Scanning Electron Microscope Philips XL30) analyses. The BET surface area is 884 ± 10 m<sup>2</sup> g<sup>-1</sup> and the micropore volume is about 0.234 cm<sup>3</sup> g<sup>-1</sup>. The chemical composition of the sorbent was evaluated by elemental analysis (Perkin Elmer 2400 series – CHNS Analyser) which revealed a high ash content (10.49%). The sorbent has a slightly basic surface, with a pH<sub>PZC</sub> = 8.0 estimated by the Noh and Schwarz method [10]. A complete list of chemical and physical characteristics can be found in the literature [11].

### 2.2. Soil sampling

The sampled soil was taken from a site located in the countryside of Giugliano, a city in the province of Naples (Italy), characterized by some of the highest levels of solar irradiation in Europe. This area, so-called “Land of Fires”, has been used for decades by criminal organizations as a dumping ground for toxic wastes [12]. It is known for its high incidence of cancer mortality, which exceeds both the Italian and European average values [13]. This excess mortality is also related to the presence of heavy metals [14], mainly arising from the illegal disposal of industrial wastes.

Soil samples were manually collected from the top 20 cm over an area of about one square meter and then stored in hermetic containers. The samples were sieved and only the particles smaller than 2.0 mm were used in the tests and analytical determinations.

### 2.3. Analytical procedures

A description of the analytical procedures is provided in the [Supporting Material](#).

### 2.4. Soil washing procedure

Soil washing experiments were carried out in 50 mL polyethylene bottles at room temperature. The tests were performed at a natural pH (7.8), with a trisodium EDDS salt aqueous solution at a proper initial concentration and a liquid-to-solid ratio (L:S) varying from 5:1 to 20:1. The chelating agent concentration was chosen so that the molar ratio of trisodium-EDDS salt in 1 L of aqueous solution to Cd, Cr, Cu, Ni, Pb and Zn present in 1 kg of sampled soil was close to 6 (MR ≈ 6). For example, if a liquid-to-solid ratio equal to 10:1 was used, the initial concentration of EDDS containing solution was 3.6 mM.

Blank tests (soil washing solutions without EDDS) were carried out using bidistilled water. The samples were stirred in a mechanical shaker (Edmund Bühler, Kombischüttler KL2) at 190 rpm up to 96 h at room temperature. After washing, the samples were

centrifuged at 4800 rpm for 15 min using an IEC Centra GP8R centrifuge and filtered with 0.45  $\mu\text{m}$  regenerated cellulose filters (from Scharlau). The concentration of metals in the washing solution was determined by Atomic Absorption Spectrometry (AAS). All the experimental tests were conducted in triplicate (standard deviation  $\sim 6\%$ ).

### 2.5. Treatment of the soil washing effluents

The soil washing solutions were treated with experimental tests: the photocatalytic process was tested to check its efficiency in destroying the chelating agent, while the adsorption process was applied to remove the dissolved metals.

#### 2.5.1. Photocatalytic procedure

UV-solar simulated photocatalytic runs adopting the Fe(III)-EDDS/hv/air system were carried out in an annular batch glass reactor equipped with a Helios Italquartz lamp with a nominal power of 125 W and a wavelength of  $\lambda = 300\text{--}400$  nm. The device has been described elsewhere [6]. The photon fluxes of the lamp at 305, 313 and 366 nm were  $1.07 \times 10^{-6} \text{ E s}^{-1}$ ,  $1.62 \times 10^{-6} \text{ E s}^{-1}$  and  $5.13 \times 10^{-6} \text{ E s}^{-1}$  respectively. For all the photocatalytic experimental runs, the initial pH of the soil washing effluent was around 7.8. The initial concentration of EDDS was 2.85 mM.

Before the lamp was turned on, the soil washing solution was purged with air for 30 min in the dark. Solution samples were collected at different reaction times, filtered through regenerated cellulose filters (pore diameter 0.20  $\mu\text{m}$ ) and analyzed to determine the EDDS and metal concentrations.

#### 2.5.2. Adsorption procedures

Adsorption tests were carried out on soil washing solutions both before and after the photocatalytic treatment. All the experiments were performed in batch stirred glass reactors kept in a PID controlled thermostatic oven ( $T = 20^\circ\text{C}$ ). All the lab-ware used in the study was previously washed with nitric acid (1 M), then rinsed three times with distilled water and oven-dried. To determine the adsorption isotherms, a variable mass of sorbent was added to a fixed volume of the EDDS-containing solution (20 mL) and kept in contact under gentle stirring for 240 h. Kinetic tests were carried out on a sample solution containing  $5 \text{ g L}^{-1}$  of activated carbon. Several identical samples were taken and analyzed at fixed time intervals until equilibrium was achieved. This usually occurred within 6 h for the soil washing solutions and within 2 h for the photocatalytically treated effluents. Each sample was analyzed to determine EDDS, metals and pH levels.

To assure the accuracy, reliability and reproducibility of the collected data, all batch isotherm tests were recorded in triplicate and only the average values were reported. In the repeated tests, the standard deviations of the metal concentration and adsorption capacity were below 7% and 6%, respectively.

### 2.6. Ecotoxicity tests

Ecotoxicological tests were carried out to evaluate the ecotoxicity of the soil washing effluents before and after the combined photocatalytic-adsorption process. The ecotoxicological assessment was performed on four different target organisms: a bacterium (*Vibrio fischeri*), a green microalga (*Pseudokirchneriella subcapitata*), a crustacean (*Daphnia magna*) and a seed (*Lepidium sativum*). A description of the procedures is provided in the [Supporting Material](#).

## 3. Results and discussion

### 3.1. Soil characterization

The average radius of the soil particles was  $0.023 \pm 0.001$  mm. The soil pH and the organic matter content were 7.27 and 7.55% respectively. The Measurements of the content of heavy metals in the sampled soil are shown in [Table 1](#) (column 2). The procedures used have been previously reported [6]. The data indicate that copper, iron, manganese and zinc were detected in the soil at high concentration levels. However, the concentrations of iron and manganese were lower than the average values for unpolluted soils [15], whereas the Cu and Zn levels were higher than the permissible regulatory limits for natural soils ([Table 1](#), column 4) [16]. Consequently, during the soil washing process, the attention was exclusively focused on the extraction of copper and zinc.

Copper and zinc are frequently found in contaminated sites. They are in the US Environmental Protection Agency's (EPA) list of priority pollutants and considered highly toxic metals [17]. These metals enter the soil compartment mainly from fertilizers, pesticides and undisposed wastes (televisions, tires, batteries, building materials, paints, galvanized products, etc) [23]. An attempt was made to remove the copper and zinc from the sampled soil through a soil washing process, and subsequently to treat the resulting aqueous effluents.

### 3.2. Soil washing process

Under the adopted experimental conditions (L:S 5:1  $\div$  20:1, MR 6, pH 7.8), the soil washing process using EDDS as chelating agent was particularly effective in removing copper and zinc, reaching extraction efficiencies ranging from 41.6% to 65.5% after 96 h of treatment.

The kinetics of the extraction of Cu and Zn from the contaminated soil at a high EDDS-to-metal molar ratio (MR 6) and variable liquid-to-solid ratio (L:S) are shown in [Fig. 2a](#) and [2b](#).

The recovery percentage of copper did not show any substantial L:S ratio-dependent variations. On the other hand, it can be observed that the extraction percentage of zinc rose by increasing the L:S ratio from 5 to 10, whereas higher values did not have any appreciable incremental effect. Therefore, from the perspective of process efficiency, it was assumed that a L:S ratio of 10 allows a satisfactory degree of removal of metals from soil. In particular, the adoption of a molar ratio much higher than 1 (i.e. MR 6) and a L:S ratio equal to 10 resulted in satisfactory extractions in terms of Cu and Zn removal efficiency, reaching values close to 65% and 55% after 96 h of treatment, respectively. During the first 24 h of soil washing, 45% and 38% of the total soil content of Cu and Zn, respectively, were removed. After 48 h of soil washing, Cu and Zn species were extracted more slowly and gradually tended to reach an apparent equilibrium, as previously reported [18].

Moreover, measurement of concentration of heavy metals remaining in the solid sample after the soil washing processes indicated that the treatment was sufficient to reduce metal levels to values within the national regulatory limits for soils (column 3, [Table 1](#)).

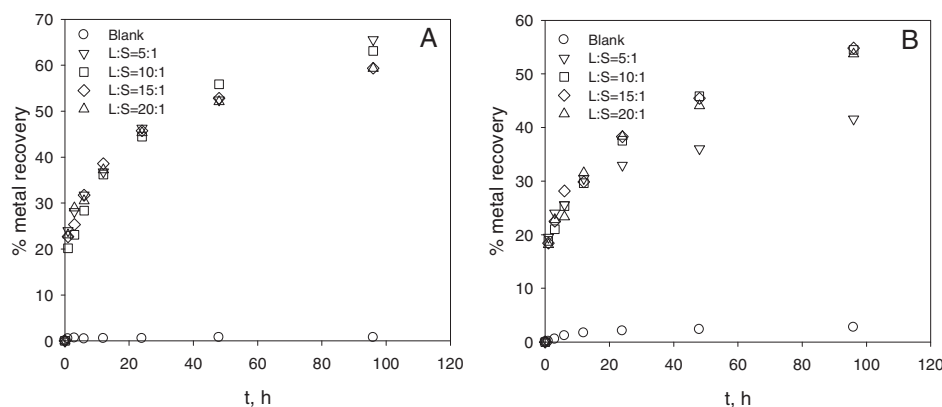
Despite the high extraction efficiencies reached with an L:S ratio of 10:1, the resulting washing effluent cannot be directly discharged into the municipal sewer as further treatments are required to reduce the metal (Cu, Zn, Fe and Mn) concentrations below the Italian regulatory limits for discharge in public sewers ([Table 1](#), column 9) [16].

With the aim of predicting the EDDS extraction efficiency of Cu and Zn species as a function of time and examining the rate controlling mechanism, different mathematical models were tested ([Table 2](#)).

**Table 1**

Resume of the process performances: Average metal content in soil and in the effluents of soil washing, photocatalytic, adsorption and integrated processes, coupled with the corresponding Italian regulatory limits for soils and for water discharge in public sewer [16].

Species	Soil (ppm)	Reclaimed soil (ppm)	Regulatory limit for soil (ppm) [16]	Soil washing effluent, $t = 96$ h, $pH = 7.8$ ( $mg L^{-1}$ )	Photocatalytic process effluent, $t_{ph} = 8$ h, $pH = 8.2$ , ( $mg L^{-1}$ )	Adsorption effluent, $m/V = 40 g L^{-1}$ ( $mg L^{-1}$ )	Combined treatment effluent, $m/V = 40 g L^{-1}$ ( $mg L^{-1}$ )	Regulatory limit for public sewer ( $mg L^{-1}$ ) [16]
EDDS	–	–	–	$832 \pm 10$	<0.5	$309 \pm 8$	0	n.a.
Cd	$0.33 \pm 0.011$	$0.32 \pm 0.03$	2	<0.01	<0.01	<0.01	<0.01	0.02
Cr	$15 \pm 2.7$	$15.3 \pm 3.1$	150	<0.5	<0.5	<0.5	<0.5	4
Cu	$181.6 \pm 10$	$69 \pm 6.6$	120	$11.41 \pm 0.55$	$10.76 \pm 0.4$	$2.24 \pm 0.05$	$0.4 \pm 0.01$	0.4
Fe	$11530 \pm 1400$	$11288 \pm 1360$	–	$24.23 \pm 5.23$	$4.39 \pm 1.05$	$2.96 \pm 0.65$	$0.24 \pm 0.01$	4
Mn	$529 \pm 24.9$	$472 \pm 14.5$	–	$6.61 \pm 0.31$	$3.99 \pm 0.2$	$1.73 \pm 0.1$	$1.13 \pm 0.03$	4
Ni	$8.9 \pm 1$	$8.5 \pm 1.4$	120	<0.5	<0.5	<0.5	<0.5	4
Pb	$19.9 \pm 0.3$	$20 \pm 0.4$	100	<0.01	<0.01	<0.01	<0.01	0.3
Zn	$166 \pm 3$	$76.1 \pm 5.43$	150	$9.5 \pm 0.87$	$9.25 \pm 0.52$	$1.64 \pm 0.09$	$0.95 \pm 0.05$	1



**Fig. 2.** Metal recovery percentage with EDDS washing solution at different time and L:S ratio.  $T = 20$  °C,  $pH = 7.8$ ,  $MR = 6$ . Cu (A), Zn (B).

**Table 2**

Mean values for  $k_1$ ,  $k_2$ ,  $a$ ,  $b$ , and  $\frac{D_p}{r^2}$  constants obtained by modelling analysis of experimental data of soil washing.

Pseudo-first order Model (A)	Pseudo-second order Model (B)	Elovich Model (C)	Diffusion Model (D) (Parabolic Model)
$\ln(q_e - q_t) = \ln(q_e) + k_1 t$	$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} t$	$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t)$	$\frac{q_t}{q_e} = \frac{4}{\sqrt{\pi}} \sqrt{\frac{D_p t}{r^2}} - \frac{D_p t}{r^2}$
$q_t$ and $q_e$ are the amounts of desorbed metal at time $t$ and at equilibrium respectively ( $mg g^{-1}$ ).	$q_t$ and $q_e$ are the amounts of desorbed metal at time $t$ and at equilibrium respectively ( $mg g^{-1}$ ).	$a$ and $b$ are empirical constants	$q_t$ and $q_e$ are the amounts of metal leaving a sphere of radius $r$ at time $t$ and after infinite time respectively ( $mg g^{-1}$ ) $D_p$ and $r$ are the intraparticle diffusion coefficient for metal–EDDS complexes and the radius of the particles
$k_1$ ( $s^{-1}$ )	$k_2$ ( $g mg^{-1} s^{-1}$ )	$a$ ( $mg g^{-1} s^{-1}$ ), $b$ ( $g mg^{-1}$ )	$\frac{D_p}{r^2}$ ( $s^{-1}$ )
Cu: $7.09 \times 10^{-6}$ Zn: $6.06 \times 10^{-4}$	Cu: $3.01 \times 10^{-4}$ Zn: $5.17 \times 10^{-4}$	Cu: $1.92 \times 10^{-5}$ (a), 52.7 (b) Zn: $4.42 \times 10^{-5}$ (a), 91.3 (b)	Cu: $6.35 \times 10^{-6}$ Zn: $6.85 \times 10^{-6}$
$R^2$ range: 0.977–0.998	$R^2$ range: 0.986–0.997	$R^2$ range: 0.962–0.999	$R^2$ range: 0.969–0.995

The very high coefficients of determination ( $R^2$ ) calculated for models A–D showed that all the tested models were realistic in describing Cu and Zn releases from the soils sampled. However, models A–C are essentially empirical and their usefulness is questionable, whereas model D has a physical meaning and indicates that the process of intraparticle diffusion of EDDS–Cu and EDDS–Zn complexes is the rate-limiting step for the soil extraction of these metals by the chelating agent.

The relative diffusion rate coefficient ( $\frac{D_p}{r^2}$ ) for EDDS–Cu and EDDS–Zn complexes was found to be in the order of magnitude of  $10^{-6} s^{-1}$ . Considering an average value for  $r$  equal to 0.023 mm, the mean value  $D_p$  proves to be close to

$4.5 \cdot 10^{-15} m^2 s^{-1}$  for Cu and Zn chelates. This value is comparable with the intraparticle diffusion coefficients of organic substances in soils and sediments reported in the literature [19]. Obviously, further research is needed to assess whether the mechanism is micropore and/or macropore diffusion.

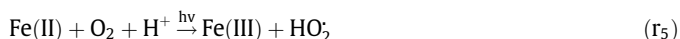
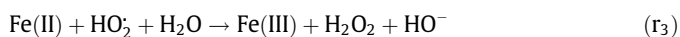
### 3.3. Treatments of soil washing effluents

#### 3.3.1. Artificial sunlight-driven photocatalytic process

The aqueous effluents collected after 96 h of soil washing, using an L:S ratio equal to 10, were submitted to the Fe(III)-mediated photo-Fenton treatment in the presence of air. The experimental

results indicated a complete EDDS abatement after 8 h of treatment (Fig. 3). However, under the experimental conditions adopted, after the photocatalytic process the soil washing effluent failed to meet the Italian regulatory limits (Table 1), particularly in the case of the copper and zinc species, hence it can not be discharged into the municipal sewers. Thus, a further treatment step was needed to increase the efficiency of metal ion removal and an adsorption process with activated carbon was therefore applied.

Removal of EDDS was ascribed both to the photolysis of Fe(III)–EDDS complexes ( $r_1$ ) and to the radical attack by the hydroxyl and hydroperoxyl species ( $r_6$ ) generated by  $r_2$ ,  $r_4$  and  $r_5$  reactions:



Among the possible chemical intermediates and by-products formed by reaction of HO radicals with EDDS or its isomers (i.e. EDTA), short chain carboxylic acids (i.e. oxalic, formic, glyoxalic, glycolic, oxalacetic and oxamic acids), formaldehyde and ammonia were previously detected [9,20]. Moreover, ferric ions are regenerated by photo-oxidation of ferrous ions ( $r_5$ ).

The percentages of removal of zinc, manganese and iron species were 15%, 22% and 79% respectively due to the formation of insoluble hydroxides which, as EDDS was removed, partially precipitate at the adopted pH ( $7.8 \pm 0.15$  at  $t_{\text{ph}} = 0$  and  $8.2 \pm 0.15$  at  $t_{\text{ph}} = 8$  h). The removal degrees reflected the different solubilities of Fe ( $\text{OH}$ )<sub>3</sub> ( $K_{\text{ps}} 1.6 \times 10^{-39} \text{ M}^4$ ), Zn ( $\text{OH}$ )<sub>2</sub> ( $K_{\text{ps}} 3.0 \times 10^{-16} \text{ M}^3$ ) and Mn ( $\text{OH}$ )<sub>2</sub> ( $K_{\text{ps}} 9.0 \times 10^{-14} \text{ M}^3$ ) species formed at the time of EDDS oxidation. However, the photocatalytic process was ineffective in removing copper species probably due to the existence of soluble Cu-hydroxo-complexes such as  $\text{Cu}(\text{OH})^+$  at the adopted pH [21].

Since the proposed photocatalytic system is an electric-energy-intensive process, a proper figure-of-merit, named electrical energy-per-order ( $EE/O$ ), was calculated with the aim of estimating, under the adopted experimental conditions, the electrical

energy (kWh) required to reduce the EDDS concentration by one order of magnitude in  $1 \text{ m}^3$  of soil washing effluent [22]:

$$EE/O \text{ (kWh} \cdot \text{m}^{-3} \cdot \text{order}^{-1}) = 38.4 \frac{P}{V_a \cdot k} \quad (1)$$

where  $P$  is the nominal lamp power (0.125 kW),  $V_a$  the volume of the soil washing solution in the reactor (0.250 L) and  $k$  is the pseudo-first-order kinetic constant for EDDS removal ( $1.19 \times 10^{-2} \text{ min}^{-1}$ ) estimated by plotting  $\ln \frac{[\text{EDDS}]_t}{[\text{EDDS}]_0}$  vs the treatment time (data not shown). The estimated  $EE/O$  value for this study was  $1.613 \times 10^3 \text{ kWh m}^{-3} \text{ order}^{-1}$  and, as generally  $EE/O$  values no greater than 2.5 are considered suitable for field-applications with artificial sunlight, the elevated  $EE/O$  values demonstrates a poor economic feasibility of the proposed photocatalytic process using UV-A lamps, thus providing an incentive to use natural sunlight and solar collectors for the removal of EDDS from soil washing effluents.

The final concentration of the investigated metals in the soil washing effluent after 8 h of photocatalytic treatment is reported in Table 1 (column 6).

HPLC analysis carried out on some samples, withdrawn from the reactor after the photocatalytic process, indicated the presence of glyoxylic and oxalacetic acids as main reaction by-products.

Even though the adopted photocatalytic process was able to reduce the concentration of EDDS, iron, manganese and zinc, it is clear that the effluent, do not still meet the requirements of the national legislation for metals (column 9, Table 1) and an additional treatment step with activated carbon was necessary to further lower the concentrations of metals.

### 3.4. Adsorption process

#### 3.4.1. Adsorption equilibrium

Fig. 4 depicts the adsorption isotherm of EDDS for the untreated soil washing effluent and for metal-free synthetic (home-made) solutions. The term  $\omega$  was calculated from the following mass balance equation:

$$\omega = \frac{(c_0 - c_{eq}) \cdot V}{M} \quad (2)$$

where  $c_0$  ( $\text{mg L}^{-1}$ ) and  $c_{eq}$  ( $\text{mg L}^{-1}$ ) are the initial and equilibrium concentrations of the analysed species in solution respectively,

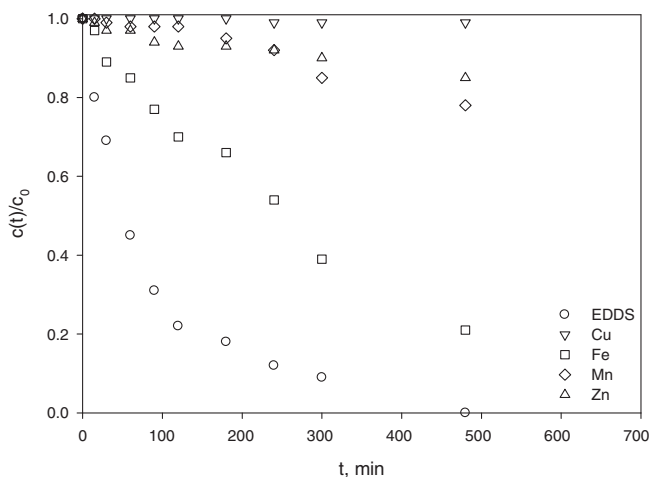


Fig. 3. Normalized EDDS, Cu, Fe, Mn and Zn concentrations vs reaction time using Fe(III)–EDDS/hv/air process.  $[\text{EDDS}]_0 = 2.85 \text{ mM}$ ,  $T = 25 \text{ }^\circ\text{C}$ ,  $\text{pH} = 7.8$ .

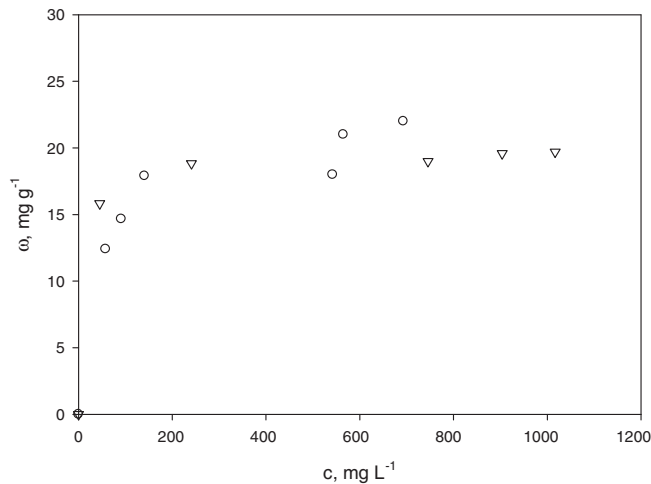


Fig. 4. EDDS adsorption isotherms for untreated soil washing solution (circles,  $\text{pH} 7.9$ ;  $[\text{EDDS}]_0 = 2.85 \text{ mM}$ ) and synthetic EDDS solution (triangles,  $\text{pH} 7.8$ ;  $[\text{EDDS}]_0 = 3.1 \text{ mM}$ ).  $T = 20 \text{ }^\circ\text{C}$ .

$V(L)$  is the volume of the solution treated and  $M(g)$  is the amount of activated carbon used.

The EDDS adsorption isotherm reached a saturation level (at about  $18 \text{ mg g}^{-1}$ ) when the EDDS concentration reached  $30 \text{ mg L}^{-1}$ . To further investigate the effect of the composition of the soil washing effluents on the EDDS adsorption process, equilibrium tests were also performed with synthetic EDDS solutions, prepared in bidistilled water and without metal species at pH 7.8 (Fig. 4, circles). The EDDS adsorption profiles almost coincided revealing that the adsorption of EDDS was negligibly affected by the nature of the soil washing solution and independent of the presence of chelated heavy metal ions. However, it was not possible to determine whether the different EDDS–metal complexes – which constitute a minor fraction of the total EDDS dissolved in the solution – were actually adsorbed onto the activated carbon.

Data regarding the adsorption ability of activated carbon with respect to the four metal ions in the soil washing solutions, as experimentally determined both before and after the photocatalytic treatment, are shown in Fig. 5a–d. The experiments revealed that the photocatalytic and adsorption treatment sequence is particularly effective in removing Cu and Fe species. In fact, these species are strongly chelated to EDDS at the adopted pH value (LogK 18.6 and 20.6 for cupric and ferric ions respectively) [23] and their adsorption onto activated carbon increases when the EDDS concentration is reduced. However, data on ferric ions are difficult to compare, since the adsorption data lie in different concentration ranges due to the different initial iron concentrations in the untreated and photocatalytically (Fe(III)-EDDS/hv/air) treated soil washing solutions.

In contrast, the manganese and zinc species were adsorbed to the same extent, regardless of the photocatalytic pre-treatment. This result may likely be due to a strong affinity of zinc and manganese ions towards the active sites of the activated carbon, which seems to overcome the chelating action of EDDS.

Neither the photocatalytic nor the adsorption process, applied as singly, were able to achieve a compliance with Italian regulatory requirements for metal concentration discharges into municipal sewers (Legislative Decree 152/2006) (column 9, Table 1). However, the combined physical-photocatalytic process, using  $40 \text{ g L}^{-1}$  of activated carbon, successfully reduced metal concentrations to acceptable regulatory levels.

Due to the complexity of the soil washing solutions, a detailed analysis of multi-component adsorption mechanisms for the investigated system is beyond the capacity of current modelling approaches. However, in order to provide reference models to describe the adsorption isotherms, the single-component equations of Freundlich (3) and Langmuir (4) were used to fit the curves in Fig. 5a–d.

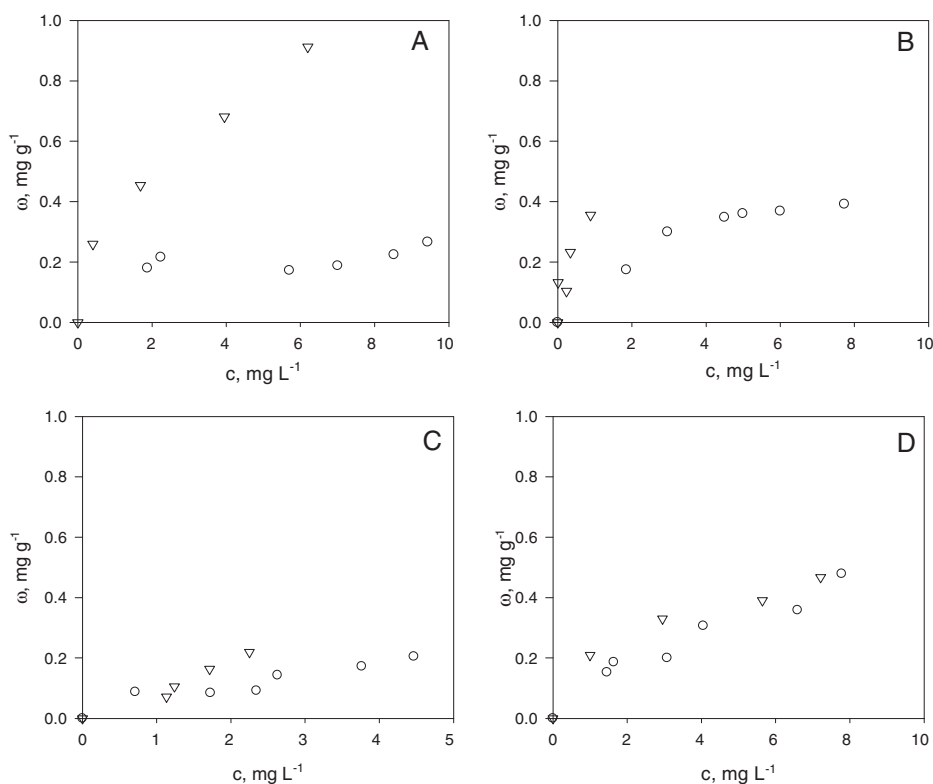
$$\omega = k \cdot c^n \quad (3)$$

$$\omega = \omega_{\max} \cdot \frac{K \cdot c}{1 + K \cdot c} \quad (4)$$

The Freundlich parameters  $k$  and  $n$  are empirical. The Langmuir parameters,  $\omega_{\max}$  and  $K$  are the maximum carbon adsorption capacity and the equilibrium constant for the specific ion in the liquid matrix. The Freundlich and Langmuir parameters were calculated by best fitting of experimental data: the results are summarised in Table 3. The parameters of Freundlich and Langmuir and the values of  $R^2$  showed that, in most of the cases, the Freundlich model provided a better interpretation of the experimental results.

### 3.4.2. Adsorption kinetics

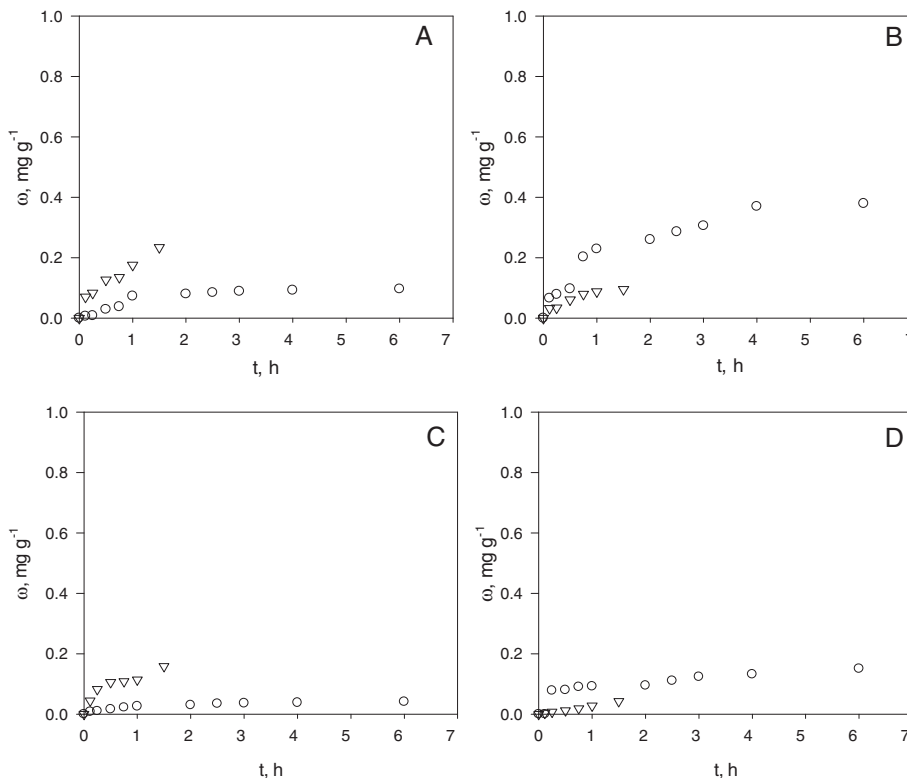
Fig. 6a–d show the results of adsorption rates collected during the batch adsorption test series on the soil washing solutions before and after the Fe(III)-EDDS/hv/air process, respectively. Several adsorption rate models were considered for data analysis and



**Fig. 5.** Metal ions adsorption isotherms in soil EDDS-washing solutions (circles, pH 7.9) and after (triangles, pH 8.2) the Fe(III)-EDDS/hv/air photocatalytic treatment. Cu (A), Fe (B), Mn (C) and Zn (D).  $T = 20 \text{ }^\circ\text{C}$ .

**Table 3**  
Parameters of Langmuir and Freundlich single-component adsorption equation for the untreated soil washing solution and for the effluents treated with Fe(III)-EDDS/hv/air system.

Species	Test	Freundlich isotherm			Langmuir isotherm		
		$k, 10^{-3} (\text{g L}^{-1})^{-n}$	$n, -$	$R^2$	$\omega_{\text{max}}, \text{mg g}^{-1}$	$K, \text{L g}^{-1}$	$R^2$
Copper	Untreated	$0.171 \pm 0.0345$	$0.120 \pm 0.113$	0.217	$0.228 \pm 0.031$	$2.437 \pm 3.329$	0.876
	Treated	$0.360 \pm 0.021$	$0.495 \pm 0.371$	0.995	$1.224 \pm 0.230$	$0.386 \pm 0.178$	0.969
Iron	Untreated	$0.189 \pm 0.022$	$0.373 \pm 0.070$	0.980	$0.543 \pm 0.053$	$0.361 \pm 0.095$	0.986
	Treated	$0.425 \pm 0.052$	$0.864 \pm 0.116$	0.841	$0.711 \pm 0.643$	$1.131 \pm 1.728$	0.746
Manganese	Untreated	$0.068 \pm 0.014$	$0.692 \pm 0.172$	0.905	$0.605 \pm 0.547$	$0.107 \pm 0.132$	0.884
	Treated	$0.084 \pm 0.0076$	$0.475 \pm 0.036$	0.907	$3.767 \pm 2515$	$2423 \pm 0.163$	0.952
Zinc	Untreated	$0.114 \pm 0.018$	$0.661 \pm 0.092$	0.962	$0.916 \pm 0.289$	$0.118 \pm 0.061$	0.950
	Treated	$0.157 \pm 0.013$	$0.496 \pm 0.038$	0.970	$0.550 \pm 0.047$	$0.555 \pm 0.152$	0.987



**Fig. 6.** Metal ions adsorption kinetics on activated carbon for soil EDDS-washing solutions before (circles) and after (triangles) the Fe(III)-EDDS/hv/air photocatalytic treatment. Cu (A), Fe (B), Mn (C) and Zn (D).  $T = 20^\circ\text{C}$ ,  $\text{pH} = 8.05 \pm 0.15$ .

the simplest and most reliable description of the results was achieved using a first order model.

In a first order model, using the liquid concentration of single ions as the driving force, the adsorption rate can be written as:

$$\frac{dc}{dt} = k_c a \cdot [c(t) - c^*(t)] \quad (5)$$

where  $c(t)$  and  $c^*(t)$  are the metal ion concentrations in the liquid and in the corresponding value in equilibrium with the ion uptake on the solid  $\omega(t)$ , respectively,  $k_c$  is the adsorption rate coefficient ( $\text{m s}^{-1}$ ), and  $a$  is the specific surface area of the sorbent particles ( $\text{m}^{-1}$ ), calculated as:

$$a = \frac{m}{V \cdot \rho_a} \cdot \frac{6}{d_p} \quad (6)$$

where  $m$  is the sorbent mass (g),  $V$  is the solution volume ( $\text{m}^3$ ) and  $\rho_a$  is the solid density ( $1100 \text{ kg} \cdot \text{m}^{-3}$ ) and  $d_p$  is the average Sauter particle diameter (1 mm).

Assuming that adsorption isotherms follow the Freundlich model with an exponent  $1/n$  expressed as the ratio of two natural numbers  $n_1/n_2$  [26], Eq. (3) can be rearranged as (see Supporting Materials):

$$n_2 \cdot \sum_{\forall W: -(\frac{V}{mK})W^{n_1+1} + W^{n_2} - 1 = 0} \left[ \frac{\log(-W + \sqrt[n_2]{X})}{-n_1(\frac{V}{mK})W + n_2} \right] = k_c a \cdot t \quad (7)$$

A simpler solution occurs for  $1/n = 1/2$ . The left-hand side of Eqs. (S6 and 7) can be determined from experiments for each value of  $c(t)$  and the value of the adsorption rate coefficient  $k_c$  can be determined from the slope of the curve  $f(t)$  vs  $t$ ,  $f(t)$  being the function representing the left-hand side of Eq. (7). With reference to the series of adsorption experiments carried out on untreated and treated soil washing solutions, the curves  $f(t)$  vs  $t$  for the four metal ions derived by using the Freundlich isotherm model reported in Table 4 are shown in Fig. 7a–d. The values of the adsorption rate coefficient obtained for each ion and for both series of adsorption tests are shown in Table 4.

**Table 4**

Adsorption rate coefficients in batch adsorption test series for the for soil washing effluents before and after the Fe(III)-EDDS/hv/air process.

	Copper	Iron	Manganese	Zinc
<i>Untreated solution</i>				
$k_c, \text{m s}^{-1}$	$1.96 \times 10^{-7}$	$2.45 \times 10^{-7}$	$1.93 \times 10^{-7}$	$3.31 \times 10^{-7}$
$R^2$	94.51	92.60	99.36	75.00
<i>Treated solution</i>				
$k_c, \text{m s}^{-1}$	$4.18 \times 10^{-7}$	$4.39 \times 10^{-7}$	$5.49 \times 10^{-7}$	$1.24 \times 10^{-7}$
$R^2$	98.61	88.70	85.30	99.11
<i>Intraparticle diffusion mass transfer estimation</i>				
$D, \text{m}^2 \text{s}^{-1}$	$7.33 \times 10^{-10}$	$6.07 \times 10^{-10}$	$6.88 \times 10^{-10}$	$7.15 \times 10^{-10}$
$k_t, \text{m s}^{-1}$	$6.35 \times 10^{-7}$	$5.26 \times 10^{-7}$	$5.96 \times 10^{-7}$	$6.2 \times 10^{-7}$

The values of the parameter  $k_c$  are always of the order of  $10^{-7} \text{ m s}^{-1}$  and are usually slightly lower for the tests carried out on untreated soil washing effluents as compared to the values calculated after the photocatalytic treatment. Moreover, these values are always lower than those that might be expected from a solid–fluid external mass transfer as predicted by the equations of Bas-madjian and Treybal [24] for an agitated vessel, or by the Ranz and Marshall equation for pure diffusion of a single sphere (i.e.  $Sh = 2$ ). This result suggests that the adsorption rate is controlled by an intraparticle diffusion in the carbon pores: in fact, the values of the parameter  $k_c$  appear consistent with the estimation of an internal mass transfer coefficient for macro-mesopore diffusion,  $k_t$ , expressed as:

$$k_t = \frac{D \cdot \varepsilon_p}{\delta \cdot \tau} \quad (8)$$

where  $D$  is the ion diffusivity,  $\varepsilon_p$  is the particle porosity, equal to 0.26 from carbon used in the present study, and  $\tau$  is the tortuosity, assumed equal to 3 [24]. The mass transfer boundary layer

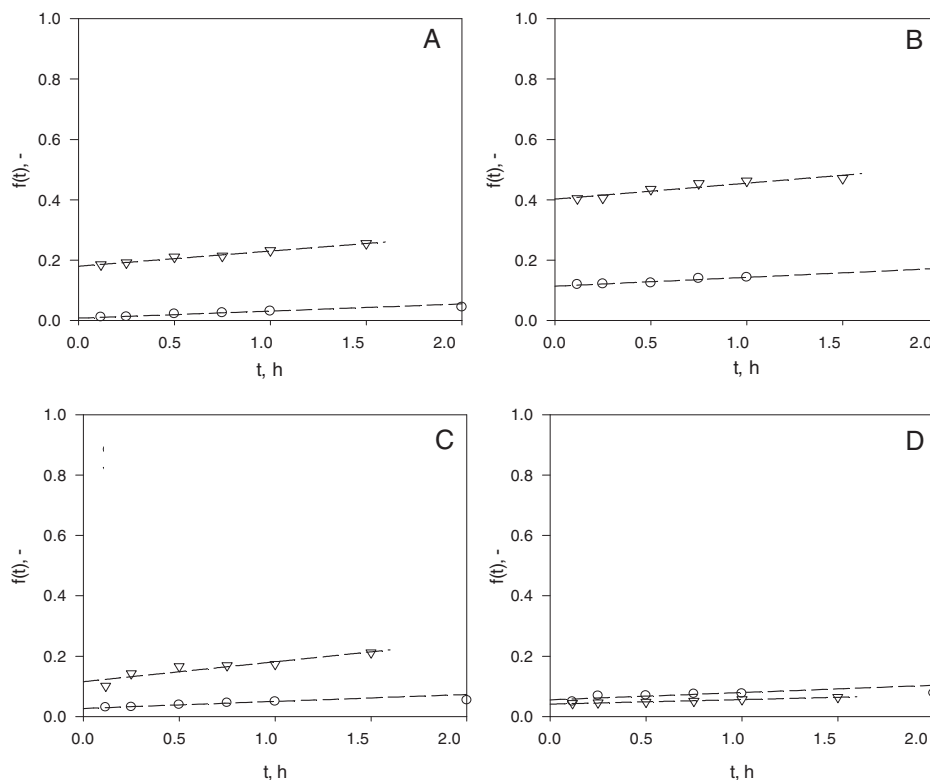
thickness of the particle is assumed equal to  $d_p/10$ . The values of  $k_t$  are reported in Table 4 for comparison.

### 3.5. Cost estimation

An analysis of the process cost is beyond the scope of this work. It is complicated by the high variability of EDDS market prices and by the lack of test results with direct solar irradiation rather than artificial light with its associated cost. However, a preliminary comparison of the relative cost of soil washing solution can be based on the relative consumption of activated carbon needed to comply with regulation, assuming that the cost of the photocatalytic process is negligible if properly applied with direct solar irradiation. In this case, the mass of carbon required to treat the soil washing effluent by direct adsorption is  $100 \text{ g L}^{-1}$ , against the  $40 \text{ g L}^{-1}$  required for the combined system. This means that the cost per cubic meter of treated soil washing effluent is about 60% lower for the combined system compared with the conventional one. This result emphasizes the potentialities of the combined process also in terms of economical reliability.

### 3.6. Ecotoxicity assessment

The ecotoxicity assessment was carried out on both the untreated and treated soil washing solutions using different target organisms. The treated samples used for the ecotoxicological tests were obtained through the combined photocatalytic–physical treatment consisting of 6 h of the Fe(III)-EDDS/hv/air process, followed by an activated carbon adsorption process. The concentrations of iron, copper, manganese and zinc before and after the treatments were previously reported in Table 1. The results of ecotoxicological investigation are summarized in Table 5. It is noteworthy observing that the data indicate different sensitivities



**Fig. 7.** Plot of  $f(t)$  vs  $t$  for soil EDDS-washing solutions before (circles) and after (triangles) the photochemical treatment. Cu (A), Fe (B), Mn (C) and Zn (D).  $T = 20^\circ\text{C}$ ,  $\text{pH} = 8.05 \pm 0.15$ .



**Table 5**  
Inhibition index (%  $I_N$ ) of *V. fischeri* through bioluminescence, Inhibition index (%  $I_N$ ) of *P. subcapitata* through cell growth, Immobilization index (%  $I_M$ ) of *D. magna*. Index of growth (%  $I_C$ ) of *L. sativum*. Values less than 20 indicate no effect and higher than 50 indicate a toxicity. Negative values denote biostimulation. SW: soil washing.

Taxonomic group	Species	Endpoint measured	Response ( $I_N$ , $I_M$ , $I_C$ %)	
			Untreated SW	Treated SW
Bacteria	<i>Vibrio fischeri</i>	30 min bioluminescence inhibition	-70 ± 2	13.1 ± 1.1
Algae	<i>Pseudokirchneriella subcapitata</i>	72 h cell growth inhibition	56.1 ± 6.3	40.2 ± 7.7
Terrestrial plantae	<i>Lepidium sativum</i>	72 h growth	90.6 ± 0.5	55 ± 0.5
Crustacean	<i>Daphnia magna</i>	24 h immobilization	93.0 ± 0.6	100

and responses for the bioassays on untreated and treated soil washing effluents.

In particular, the screening of the ecotoxicity carried out on untreated samples showed that *D. magna* was the most sensitive organism showing high toxicity due to crustacean immobilization for both untreated and treated samples. The untreated sample was very toxic, causing 93.0% immobility after 24 h. However, toxicity did not decrease in the sample after the process (100% of immobilization after 24 h).

It is more likely that the residual toxicity of the soil washing effluent after the physico-photocatalytic treatment could be ascribed to different factors such as:

- the presence of short chain carboxylic acids, such as glyoxilic and oxalacetic acids identified in the final mixture, or/and other substances (i.e. formaldehyde and ammonia) produced by photocatalytic oxidation of EDDS and its structural isomers [9,20] which the bioindicator was found to be sensitive [25];
- the presence of metal species whose final concentrations approached the  $EC_{50}$  values reported in the literature (Table 1S, Supporting Material);
- probable synergistic effects of the residual metal species mix.

The results collected on *L. sativum* showed that the phytotoxicity increased after the physical-photocatalytic processes. In fact, there was no effect on the germination index for the untreated sample (90.6%  $I_C$ ), whereas a slight inhibition was detected in the treated samples (55.3%  $I_C$ ). This effect was not associated with seed germination (95% of seed germinated, data not shown), but with a root elongation, probably due to a higher bioavailability of heavy metals and/or synergistic effects, since the  $EC_{50}$  value for each single metal was higher than the respective residual concentration at the end of the combined treatment (Table 1). The growth of *P. subcapitata*, as shown in Table 5, was strongly inhibited (56.1%) in the untreated sample, in agreement with previously reported results [9], due to the high sensitivity of the alga to EDDS containing solutions. The inhibition markedly decreased after the combined physico-photocatalytic process (40.2%), probably due to a significant reduction in the concentration of cupric species to values close to  $EC_{50}$  and consistent with those reported in the literature.

The bioluminescence inhibition test resulted in a different trend for the samples before and after the treatment. Bioluminescence was highly stimulated when the bacterium was placed in contact with the untreated sample. The increasing in luminescence, reported as negative values (-70%), might be an effect due to the contamination level, and the high values could be a sign of toxicity. On the other hand, after the treatment, only a slight toxicity was detected. Moreover, the bioluminescence inhibition decreased slightly with longer contact times (19.7 ± 1.7%, 13.8 ± 0.9%, 13.1 ± 1.1% at 5, 15 and 30 min respectively).

Although the concentration values of copper in the sample after the combined treatment were close to the  $EC_{50}$  values, the low toxicity could only be explained by a possible antagonistic effect of

metals and amino carboxylic compounds formed during the photocatalytic step.

The different toxicity exerted by the metals depends on their speciation and concentration and it is correlated with the different interactions and transformations of the metal-chelated species with the organisms tested during the bio-absorption stage [27].

Overall, the ecotoxicological results indicate that the proposed physical-photocatalytic soil washing treatment process reduces the ecotoxicity of the solutions for *V. fischeri* and *P. subcapitata*, but not for *D. magna* and *L. sativum*.

#### 4. Conclusions

The removal of heavy metals from field-contaminated soils, sampled from the "Land of Fires" located in the province of Naples in Italy, was achieved through soil washing with aqueous solutions at EDDS-to-metal molar ratios larger than 1. The soil washing process succeeded in reducing the heavy metal concentration in the sampled soils to levels that comply with Italian regulations. However, the process generated effluents containing the chelating agent and metals at concentrations exceeding the sewer discharge limits established by Italian legislation. An increase in the solution-to-soil ratio slightly improved Zn extraction percentage from 40% to 55% after 96 h of soil washing, whereas its influence on Cu extraction was negligible. In order to comply with the Italian regulatory requirements, a combination of artificial sunlight-driven photocatalytic (photo-Fenton-like) and adsorption (on activated carbon) techniques was adopted. The processes proved to be very effective in completely removing EDDS and reducing the concentrations of copper, zinc, iron and manganese to values (0.4, 0.95, 0.24 and 1.13 mg L<sup>-1</sup> respectively) within the Italian regulatory limits, without adding additional reagents and adjustment of the pH value of the soil washing effluent. However, the ecotoxicological tests carried out on the untreated and treated soil washing effluents using living organisms belonging to highly diverse taxonomic groups (bacteria, alga, crustacean and seed), gave conflicting outcomes. The different sensitivities, as measured in the treated soil washing effluents, may be ascribed to the complexity of the chemical matrix and to the by-products, such as some carboxylic acids, formed during the photocatalytic treatment. The metal-organic species could have different bioavailability among the organisms tested, also giving rise to synergistic and/or cumulative effects, which may explain the different responses obtained across the species tested.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2015.08.039>.

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