

Photocatalytic processes assisted by artificial solar light for soil washing effluent treatment

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Received: 23 November 2015 / Accepted: 7 March 2016
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Abstract Contaminated soil has become a growing issue in recent years. The most common technique used to remove contaminants (such as metals) from the soil is the soil washing process. However, this process produces a final effluent containing chelating agents (i.e., ethylenediaminedisuccinic acid, also known as EDDS) and extracted metals (i.e., Cu, Fe, and Zn) at concentrations higher than discharge limits allowed by the Italian and Brazilian environmental law. Therefore, it is necessary to develop further treatments before its proper disposal or reuse. In the present study, soil washing tests were carried out through two sequential paths. Moreover, different artificial sunlight-driven photocatalytic treatments were used to remove Cu, Zn, Fe, and EDDS from soil washing effluents.

Metal concentrations after the additional treatment were within the Brazilian and Italian regulatory limits for discharging in public sewers. The combined TiO₂-photocatalytic processes applied were enough to decontaminate the effluents, allowing their reuse in soil washing treatment. Ecotoxicological assessment using different living organisms was carried out to assess the impact of the proposed two-step photocatalytic process on the effluent ecotoxicity.

Keywords Soil washing effluent · Metal removal · Sacrificial photocatalysis · “Land of Fires” · Soil remediation

Responsible editor: Philippe Garrigues

Electronic supplementary material The online version of this article (doi:10.1007/s11356-016-6431-9) contains supplementary material, which is available to authorized users.

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Introduction

Heavy metal pollution of soils and sediments is a global concern due to the negative impact of such metals on living organisms (Järup 2003). Hence, different remediation techniques based on physical, chemical, and even biological processes have been proposed to remove metals from contaminated soils (Mulligan et al. 2001). Among the chemical techniques, the soil washing using organic chelating agents is one of the most promising “ex situ” processes (Voglar and Lestan 2012), 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 metal removal from polluted soils (Dermont et al. 2008). The main disadvantage of such processes is the subsequent need to remove heavy metals extracted from contaminated soils and residual chelating agent from soil washing effluents 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 chelating

agents which inhibit the separation of heavy metals from the liquid phase (Vohra and Davis 2000).

Literature reviews (Liu et al. 2001; Molinari et al. 2004; Englehardt et al. 2007; Liu et al. 2007; Pocięcha and Lestan 2009) show that solar-driven photocatalytic systems are of great interest due to their simplicity and low cost (Bandala et al. 2008). Previous studies carried out on synthetic (Satyro et al. 2014a) and real soil washing solutions (Satyro et al. 2014b; Satyro et al. 2016) using only UV-A lamps as radiation source showed the possibility to remove metals, such as Cu and Zn, and the chelating agent from soil washing effluents through different photocatalytic treatments or by adopting 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 TiO₂-photocatalytic treatments of the soil washing effluent. This allows the simultaneous concentration decrease of unwanted metals and chelating agent reaching the acceptable values, so that the soil washing effluent can be reused in process and/or discharged to municipal sewers.

Material and methods

Materials

(*S,S*)-Ethylenediamine-*N,N'*-disuccinic acid-trisodium salt 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.

Methods

Soil sampling

Superficial soil samples (top 20 cm) were manually collected over an area of about 1 m², stored in hermetic containers, and sieved (2.0 mm) before use. The sampling was in the province of Naples (Italy), in the “Land of Fires” region (Pi et al. 2006; Albanese et al. 2008). More information about this area can be found in Supporting Material.

Soil washing procedure

The EDDS (chelating agent) initial concentration was 0.36 mM, as suggested by Yan et al. (2010). The tests were performed in triplicates (standard deviation ~8 %) and 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 bidistilled water.

The aim was to improve Cu and Zn removal efficiency, and in addition, to test the possibility of reusing the soil washing solution after photocatalytic treatments. Two different plant configurations were adopted (Fig. 1a, b). The configuration reported in Fig. 1a was applied for long-duration washing (96 or 192 h) without any further treatment, whereas in the configuration reported in Fig. 1b, it was applied for two washing cycles (96 h each). The first washing effluent was treated and then reused for the second washing cycle when more EDDS was added.

Photocatalytic procedure

The photocatalysis was conducted using an 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 (Andreozzi et al. 2000). A description of the technical data is provided in Supporting Material.

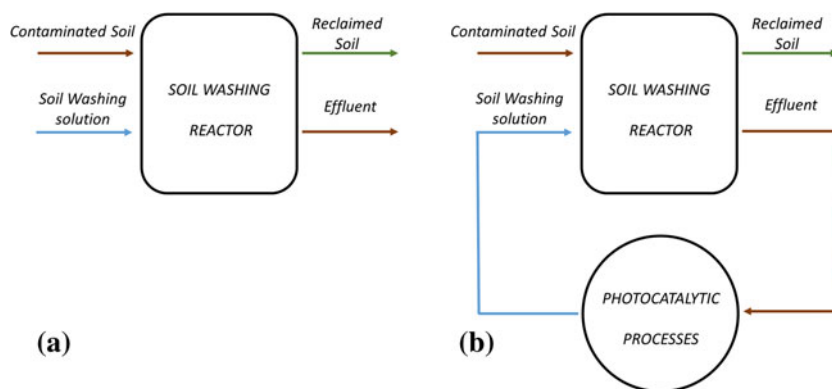
For the effluent treatment, a photocatalytic processes sequence was performed according with the used radiation type, Hg or Na lamp. In the case of Hg lamp, the process began with Cu and EDDS total removal, and Zn and Fe partial removal, through a sacrificial TiO₂ photocatalysis, followed by two different photocatalytic steps, such as TiO₂ photocatalysis and assisted photo-Fenton. These last two steps were carried out under oxygenated conditions for organic substances and residual metal (i.e., Fe) removal. Eventually, an alkalization step could be added to further increase the efficiency of metal ions. On the other hand, when the Na lamp was used, the sequence started with the TiO₂ photocatalysis under oxygenated conditions, thus lowering Fe, Zn, and EDDS concentrations. Afterward, a sacrificial TiO₂ photocatalysis under an inert atmosphere for residual metal (i.e., Cu) removal and organic substances was carried out.

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

Analytical procedures

Metal concentrations were determined by atomic absorption spectrometry (AAS), using a Varian Model 55B SpectrAA (F-AAS) or GBC Avanta AAS with a graphite furnace (GF-AAS). For the soil, the EPA method 3051 (USEPA 2001) was followed. The soil pH was measured according to EPA Method 9045C (EPA 2003). Organic matter was evaluated using the loss on ignition (LOI) index (Schulte 1995). Elemental analysis was performed using a Perkin-Elmer Series II 2400 CHNS/O Elementary Analyzer. The EDDS analysis was performed using a modified colorimetric method (Satyro et al. 2014a)

Fig. 1 Soil washing processes based on different approaches: **a** one washing cycle (no effluent reuse) and **b** two washing cycles (photocatalytically treated effluent reuse)



previously reported by Vandevivere et al. (2001). Total organic carbon analyses were performed using a TOC analyzer (Shimadzu 5000A). All the analyses were carried out in triplicate.

Ecotoxicological tests

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*) (OECD 2006) and on three different target organisms: a bacterium (*Vibrio fischeri*) (ISO 11348-3 2008), a green microalga (*Pseudokirchneriella subcapitata*) (ISO 8692 2012) and a crustacean (*Daphnia magna*) (ISO 6341 2012). More details are reported in Supporting Material.

Results and discussion

Soil characterization

The soil characteristics are reported in Table 1. The pH was close to neutrality and the LOI index is 7.19 %. The metal concentrations were lower than the Italian and Brazilian regulatory limits for natural soils, with the exception of Zn for Italian limits and Cu for both Italian and Brazilian limits (D.Lgs.152/2006 2006; CONAMA 2009).

Cu and Zn contamination in soil is highly diffuse because these elements are present in several common pesticides and fertilizers (Wuana and Okieimen 2011). The US Environmental Protection Agency classifies them as toxic and priority pollutants. Therefore, in soil washing experiments, the major aim was to remove Cu and Zn. As suggested by Yan et al. (2010), the soil washing tests were carried out with a molar ratio of EDDS/(Cu+Zn) equal to 0.6.

One soil washing cycle

The results at different extraction times are presented in Fig. 2. During the first 24 h of soil washing, Cu and Zn extraction reached 33.1 and 33.2 %, respectively, and after 96 h, approximately 39.9 and 37.7 %, respectively. Fe removal was up to 1 %, as previously reported (Satyro et al. 2014b). Final concentrations of Cu and Zn in the soil after the washing procedure were 136 and 114 ppm, respectively. These concentrations do not meet the Italian regulatory limits for completely clean soil. Thus, a second washing cycle was required. We proposed to use the

Table 1 Comparison between collected soil parameters and the Italian and Brazilian regulatory limits

	Soil	^a Italy	^b Brazil	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			
ppm	Mg $2.1 \times 10^4 \pm 1.0 \times 10^2$			
	Ca $4.4 \times 10^5 \pm 8.2 \times 10^2$			
	Cu $2.2 \times 10^2 \pm 39.2$	1.2×10^2	2.0×10^2	51
	Pb 24.37 ± 2.3	1.0×10^2	1.8×10^2	1.0×10^2
	Cr 33.17 ± 1.1	1.5×10^2	1.5×10^2	5.0×10^2
	Ni 8.27 ± 0.8	1.2×10^2	70	2.5×10^2
	Zn $1.8 \times 10^2 \pm 11.8$	1.5×10^2	3.0×10^2	1.5×10^2
	Cd 0.40 ± 0.1	2	3	0.35
	Fe $1.4 \times 10^4 \pm 3.2 \times 10^2$			2.78×10^5
	Mn $5.1 \times 10^2 \pm 72.1$			1.5×10^3

^a D.Lgs.152/2006 (2006)

^b CONAMA (2009)

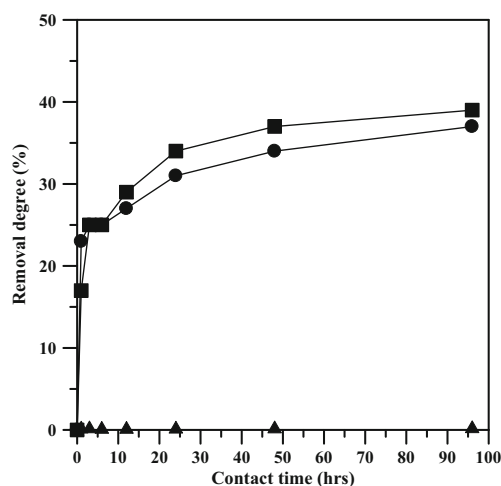


Fig. 2 Cu (black circle), Zn (black square), and Fe (black triangle) removal through EDDS soil washing at varying time. $[\text{EDDS}]_0 = 0.36\text{mM}$; L/S ratio = 10; $\text{RSD}_{\text{max}} < 8.11$

effluent produced in the first washing stage after its photocatalytic treatment.

Combined photocatalytic processes for soil washing effluent treatment

UV-A radiation source

On the basis of previously reported findings (Satyro et al. 2014b), an optimal sequence of combined photocatalytic processes that ensures the highest efficiency in Cu, Zn, Fe, and EDDS removal, was established as follows: sacrificial TiO_2 photocatalysis (Step 1), TiO_2 photocatalysis (Step 2), and assisted photo-Fenton (Step 3). The final removal percentage of Cu, Zn, Fe, and EDDS is reported in Fig. 3. During Step 1 (deaerated condition), Cu and EDDS were completely

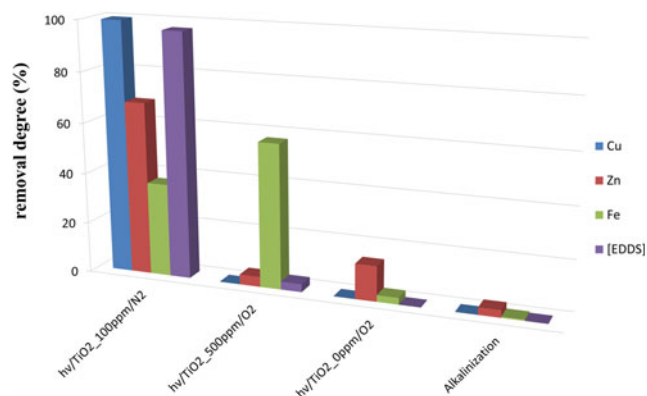


Fig. 3 Cu, Zn, Fe, and EDDS removal from soil washing effluents using three sequential photocatalytic steps with Hg lamp irradiation. $[\text{EDDS}]_0 = 0.36\text{ mM}$, $\text{pH} = 7.8$ (not regulated). TiO_2 _100ppm/ N_2 /hrv: $t_r = 16\text{ h}$. TiO_2 _500ppm/ O_2 /hrv: $t_r = 6\text{ h}$. TiO_2 _0ppm/ O_2 /hrv: $t_r = 8\text{ h}$. $[\text{Cu}]_0 = 8.9 \pm 1.7\text{ ppm}$; $[\text{Zn}]_0 = 6.7 \pm 1.3\text{ ppm}$; $[\text{Fe}]_0 = 7.8 \pm 4.6\text{ ppm}$. $\text{RSD}_{\text{max}} < 4.43$

removed, whereas a lower percentage removal was achieved for Zn (68 %) and Fe (37 %). Additional heterogeneous (Step 2) and homogeneous (Step 3) photocatalytic treatments carried out under aerated conditions and the alkalization process were able to remove residual Fe and Zn.

In Step 1, the deaerated condition allows the Cu removal due to the reduction of cupric ions to zero-valent copper by photogenerated electrons (r_1) (Satyro et al. 2014a),



and its precipitation as Cu(OH)_2 ($K_{\text{ps}} = 4.8 \cdot 10^{-20}\text{ M}^3$ — $T = 25\text{ }^\circ\text{C}$), leading to EDDS degradation by its reaction with positive holes (r_2),



The sequence applied was able to remove all the metals. The final residue had concentrations within the Brazilian and Italian legal limits as shown in Table 2.

The use of UV-A artificial radiation for soil washing effluent decontamination is not economically viable for industrial applications due to the high energy consumption (Satyro et al. 2014b). Therefore, another set of experiments was carried out using an artificial solar light irradiation source (Na lamp), more similar to natural sunlight, to evaluate the system behavior.

Artificial solar light irradiation

In this case, the sequence was changed since previous results (Satyro et al. 2014b) suggested that starting with TiO_2 photocatalysis in the presence of O_2 , followed by sacrificial TiO_2 photocatalysis has the best efficiency. As a result, Fe, Zn, and EDDS concentrations are firstly reduced, and residual metals (i.e., Cu) are secondly removed together with organic substances (Fig. 4).

Results obtained in terms of Fe and Zn removal efficiency at varying TiO_2 load (data not shown) revealed that the best values of catalyst load are 500 ppm for Step 1 and 100 ppm for Step 2 (Fig. 5).

Previous results (Satyro et al. 2014b) showed that Step 1 efficiently removes EDDS, Zn, and Fe.

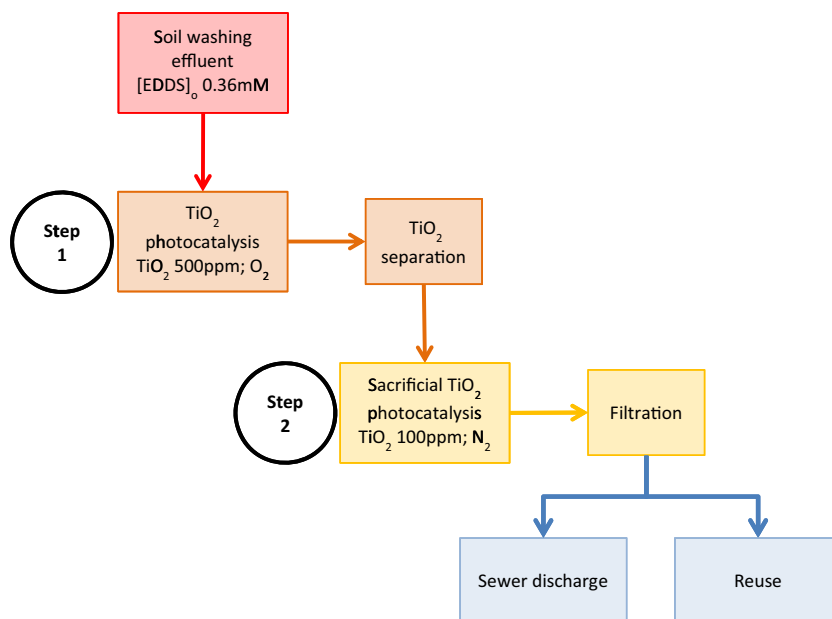
Table 2 Regulatory limits of metal ion concentrations for effluents in Brazil and Italy and concentrations achieved before and after treatment

	Cu (mg L^{-1})	Fe (mg L^{-1})	Zn (mg L^{-1})
^a Brazil	1.0	15.0	5.0
^b Italy	0.4	4.0	1.0
Before treatment	7.8	10.5	5.7
After treatment	<0.05	0.09	0.8

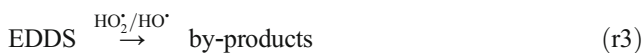
^aCONAMA (2011)

^bD.Lgs.152/2006 (2006)

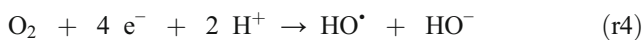
Fig. 4 Photocatalytic processes carried out using Na lamp as radiation source. Step 1: EDDS, Fe, and Zn removal; Step 2: EDDS and Cu removal



The decrease in EDDS concentration occurred mainly through EDDS reaction with hydroxyl and hydroperoxyl radicals (r₃),



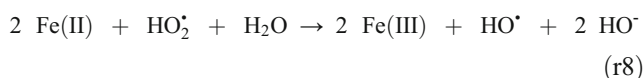
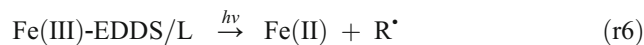
Hydroxyl and hydroperoxyl radicals are produced (i) by reaction of oxygen with photogenerated electrons (r₄),



(ii) by reaction of water molecules with TiO₂ positive holes (r₅),



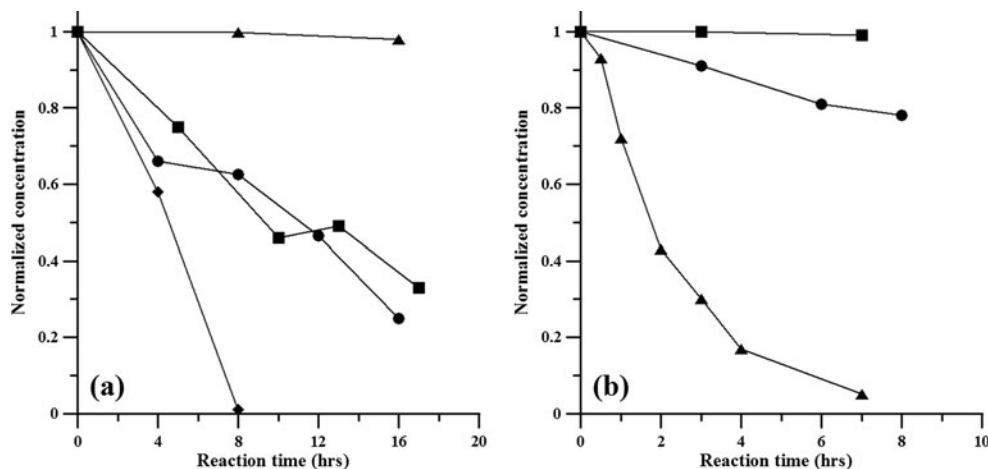
and (iii) by photolysis of Fe(III)-EDDS and Fe(III)-L complexes (r₆, r₇,r₈),



where L represents byphotoproducts.

Fe and Zn form insoluble hydroxides and are adsorbed onto TiO₂ surface being removed by precipitation. However, Step 1 was ineffective in removing Cu species probably due to

Fig. 5 Cu (black triangle), Zn (black square), Fe (black diamond), and EDDS (black circle) concentration profiles during Step 1 (a) and Step 2 (b). [EDDS]₀ = 0.36 mM; pH = 7.8 (not regulated); Na lamp. a Step 1–TiO₂ 500ppm/O₂/hrv. b Step 2–TiO₂ 100ppm/N₂/hrv. RSD_{max} < 3.61



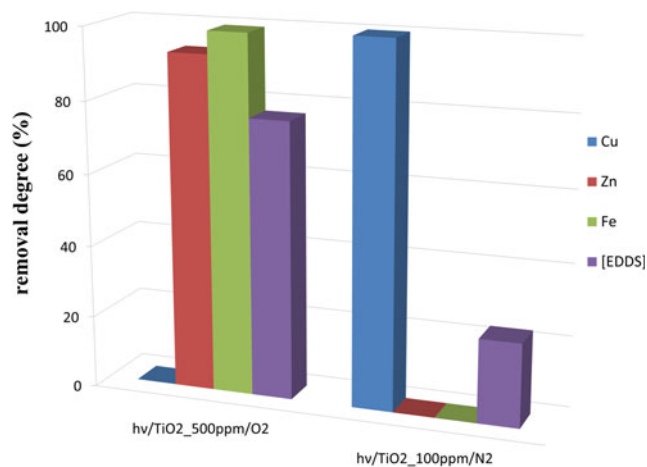


Fig. 6 Cu, Zn, Fe, and EDDS removal from soil washing effluents through two sequential photocatalytic steps with Na lamp irradiation. **a** TiO₂_500ppm/O₂/hv, $t_r = 24$ h. **b** TiO₂_100ppm/N₂/hv, $t_r = 8$ h. [EDDS]₀ = 0.36 mM, pH = 7.8 (not regulated). RSD_{max} < 4.73

the existence of soluble Cu-hydroxo-complexes, such as Cu(OH)⁺, at the adopted pH (Cuppert et al. 2006).

Cu and residual EDDS removal required a further step (Step 2—sacrificial TiO₂ photocatalysis), which was carried out using TiO₂ under deoxygenated conditions through reactions r_1 and r_2 . Reaction times of 24 h for Step 1 and 8 h for Step 2 were required to lower metal concentrations below Brazilian and Italian limits.

The final removal of Cu, Zn, Fe, and EDDS through a two-step process (with catalyst filtration between Step 1 and Step 2), without any pH regulation, is shown in Fig. 6. Fe, Cu, and EDDS were completely removed and 93 % of the Zn removal was achieved. These results indicate that soil washing effluents could be efficiently treated using artificial solar light instead of UV-A lamp irradiation.

Two soil washing cycles

The treated effluent (artificial solar light irradiation) was used to rewash the soil sample for a second time, as shown in Fig. 1b. EDDS was used at the same initial concentration of the first washing cycle. The extraction efficiency increase was marked (Fig. 7). In fact, for a fixed contact time of 192 h, rewashing the soil using the treated effluent allowed a further reduction of 7 and 12 % for Cu and Zn, respectively. The kinetics of extraction (data not shown) were similar to the first soil washing (Fig. 1b), with higher extraction in the first 24 h. The two washing cycles resulted in Cu and Zn concentrations (106 ppm for Cu and 79 ppm for Zn), much lower than the Italian and Brazilian legal limits for soils (Table 1) and allowed the effluent reuse in the washing process.

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).

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 (4.3 % 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

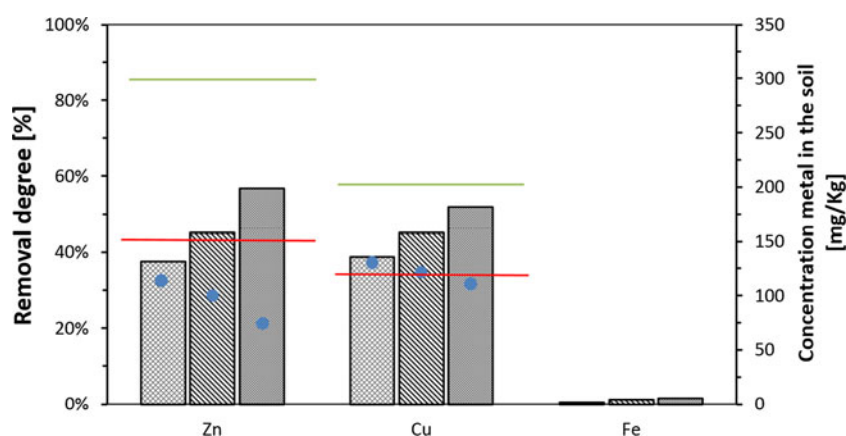


Fig. 7 Comparison of Cu, Zn, and Fe extraction by soil washing tests under different operating conditions. (▨) single soil washing after 96 h of contact time, configuration reported in Fig. 1a; (▩) single soil washing after 192 h of contact time, configuration reported in Fig. 1a; (▧) double soil washing with a contact time of 96 h for each step, configuration

reported in Fig. 1b. Red line: Italian regulatory limits; green line: Brazilian regulatory limits; (blue circle) Cu and Zn concentration in the soil after the soil washing process. [EDDS]₀ = 0.36 mM; L/S ratio = 10; RSD_{max} < 6.73

Table 3 Ecotoxicological tests on untreated and treated soil washing effluents

<i>Vibrio fischeri</i>			
Before the treatment		After the treatment	
Exposition time (min)	I _B (%)	Exposition time (min)	I _B (%)
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 _M (%)	Exposition time (h)	I _M (%)
24	33.3	24	0
48	40.4	48	0
<i>Pseudokirchneriella subcapitata</i>			
Before the treatment		After the treatment	
Exposition time (h)	I _N (%)	Exposition time (h)	I _N (%)
72	76.5	72	40.1
<i>Lepidium sativum</i>			
Before the treatment		After the treatment	
Exposition time (h)	I _G (%)	Exposition time (h)	I _G (%)
72	76.2	72	75.9

V. fischeri bioluminescence inhibition percentage (I_B, %) exposed for 5', 15', and 30'; *D. magna* immobilization index percentage (I_M, %) after exposure for 24 and 48 h; *P. subcapitata* growth inhibition (I_N, %) after exposure for 72 h; *L. sativum* index of germination percentage (I_G, %) after exposure for 72 h. The results are relative to average of effects

significant immobility) was detected for the treated samples at the same exposure times.

Results using *P. subcapitata* indicated that the untreated effluent exerts 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_G). 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 (Babay et al. 2001; Huang et al. 2012) to which some bioindicators were found to be sensitive (Pintar et al. 2004).

The results collected indicate different sensitivities and responses for the bioassays on treated soil washing effluents, which is probably due to different interactions of metal-organic complexes with the organisms. However, the proposed two-step TiO₂-photocatalytic soil washing treatment

reduced the ecotoxicity of the effluents for three organisms tested (*V. fischeri*, *D. magna*, and *P. subcapitata*).

Conclusion

Combined photocatalytic processes (TiO₂-based) can be used for the simultaneous removal of heavy metals, such as Cu and Zn, from effluent produced in washing process of polluted soil when EDDS is used as organic chelate. It was demonstrated that it is possible (i) to use artificial solar light on the photocatalytic treatment of the effluent produced by the first washing and (ii) to reuse this effluent for further rewashing. Ecotoxicity assessments on final effluents also showed the efficiency of photocatalytic treatment in reducing levels of ecotoxic effects for three living organisms tested.

Acknowledgments This work was carried out within the project LIFE11 ENV/IT/000275 (ECOREMED). Satyro S. acknowledges her scholarship supported by the Brazilian National Council of Technological and Scientific Development (CNPq) (Process n. 201106/2012-4). The support received from Antonietta Siciliano in the toxicology analysis was highly appreciated.

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