



Article

Soil Washing Optimization, Recycling of the Solution, and Ecotoxicity Assessment for the Remediation of Pb-Contaminated Sites Using EDDS

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Abstract: This paper presents the results of an experimental study aimed at investigating the applicability of ethylenediamine-*N,N'*-disuccinic acid (EDDS) as a washing solution for the remediation of Pb-contaminated soil. All aspects of the treatment are analyzed and optimized, including the reuse and the final disposal of the EDDS spent solution. Different molar concentrations of the washing solutions and the efficiencies of varying solid/liquid ratio are tested at different pH values. More than 90% of the mobile Pb fraction is removed in about 24 h at pH 6. Accordingly, soil toxicity strongly decreases as a consequence of the treatment. The regenerated solution exhibits a reduced, but not negligible, extractive capacity. The total extraction of Pb is approximately 50% of the initial value after one regeneration cycle, and almost 20% after a second regeneration cycle. Respirometric tests, conducted using an activated sludge sampled in a municipal wastewater treatment plant, indicate that the spent solutions are not biodegradable, but they do not exert any toxic effect on the biomass. On the contrary, tests on regenerated solutions displayed the same biodegradability as the fresh ones.

Keywords: EDDS; enhanced soil washing; Pb-contaminated soil; respirometric test; spent solution regeneration

1. Introduction

Soil washing is certainly one of the most widespread and studied off-site techniques for the remediation of soils and sediments that are highly contaminated by potential toxic metals (PTMs) [1–3]. The involvement of acid solutions and/or chelating agents allows for the removal of both the most and the least mobile fractions of metals in cationic form, potentially achieving very high removal efficiency if the operative conditions of the process are correctly chosen and optimized [4]. The choice of an appropriate washing solution is a critical point, not only to guarantee the required performances, but also to avoid any problems related to its final disposal [5–7]. The management of spent washing solutions (SWSs), in fact, makes up a significant cost of the whole remediation process. Moreover, major environmental concerns can be associated with the use of toxic or non-biodegradable agents, as well as negative consequences linked to the use of strong acidic solutions, which may compromise the possible reuse of the treated soil [8,9]. Due to this, in recent years, the use of biodegradable chelating agents, mainly ethylenediamine-*N,N'*-disuccinic acid (EDDS), is becoming prominent in soil washing applications [10–12]. EDDS belongs to the class of aminopolycarboxylic acids (APCs), which

also includes the more famous and less expensive ethylenediamine-tetracetic acid (EDTA). As is well known, these acids have the capacity to form stable complexes with metal ions, because of the presence in their structure of carboxylate groups linked to nitrogen atoms, and therefore, they are excellent chelating agents. Unfortunately, most of these acids are characterized by an elevated toxicity [13–15], as well as low biodegradability. As a result, APCs' applicability for soil washing treatment is somehow limited, because of the mentioned concern related to the management of SWSs. However, EDDS, or in particular, one of its stereoisomers [S,S]-EDDS, displayed complete degradation in natural environmental conditions, in less than 10 days [16,17]. EDDS has been, therefore, widely used for in-site interventions, exploiting its ability to increase the PTMs' mobility, so that the latter are successively removed by soil flushing or phytoextraction [18,19]. Less numerous, instead, are the off-site and on-site applications [20]. This is probably not ascribable to the extractive efficiencies, which have always been very high, but to the uncertainties related to the management of the SWSs. While EDDS is highly biodegradable, its metal complexes may not be to the same extent [21,22]. Moreover, the cost of EDDS solution is quite significant, and therefore, the regeneration and reuse of SWSs could play an important role in decreasing the costs of the process. Both aspects are investigated, in the present paper, referring to a Pb-contaminated site, in order to make the use of EDDS solutions for soil washing treatment in similar studies more appealing and feasible. At this aim, along with the optimization of the washing process operative parameters involving fresh EDDS solutions, the results are presented below related to (i) soil washing conducted with regenerated solution; (ii) respirometric tests simulating the disposal of the SWSs in a municipal wastewater treatment plant; (iii) ecotoxicity tests, carried out on treated and untreated soil. These aspects are rarely considered all together in a single research work, reflecting the uniqueness of this study. The choice of Pb-contaminated soil is due to the large number of sites contaminated by this metal and to the high toxicity of Pb [23–25]. Lead, in fact, is used for many industrial processes, including the production of paints, glasses, batteries, explosives, fertilizers, and pesticides. Moreover, Pb has been used, and is still used in many countries, as a fuel additive. It follows that Pb contamination is common, not only in industrial areas, but can also occur in rural areas, and sediments of urban creeks [26,27]. However, it is also reported that Pb displays limited solubility in soil, as well as low availability for plant uptake, due to the formation of insoluble precipitates [28,29]. Nonetheless, this Pb is mainly bioavailable for human beings, due to its transfer through the food chain [18], representing a serious threat, because of its documented toxicity [30].

2. Materials and Methods

2.1. Soil Characterization

The investigated soil was sampled in a pottery sludge disposal site, located in Gualdo Tadino (Italy), and was characterized by a high level of Pb concentration. Experimental tests and successive analysis were carried out on soil particle size fraction smaller than 1.00 mm to investigate the Pb extraction efficiency on the soil's finest fraction.

Total concentration of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn was determined in soil samples after the wet digestion according to the United States Environmental Protection Agency (USEPA) method 3051 [31].

Specifically, 1 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 min, and kept between 170 °C and 180 °C for at least 10 min. A nitric acid solution and a hydrogen peroxide solution were used, in 10 mL HNO₃ to 1 mL H₂O₂ ratio, as the extraction reagents.

The 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). The detection limits for each

metal are reported in Table 1. AAS standards for Ca, 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.

Table 1. Metal concentrations in the soil sample.

Metal	Concentration [mg/kg]	LD ^a —F-AAS [mg/L]	LD ^a —GF-AAS [mg/L]
Cd	1 ± 0.2	5.0 × 10 ⁻²	5.0 × 10 ⁻⁴
Zn	50 ± 3.2	5.0 × 10 ⁻²	2.0 × 10 ⁻⁴
Pb	8600 ± 300	1.0	5.0 × 10 ⁻³
Cu	25 ± 1.7	0.2	5.0 × 10 ⁻³
Cr	2 ± 0.7	0.5	5.0 × 10 ⁻³
Ni	40 ± 2.5	0.3	5.0 × 10 ⁻³
Ca	35,411 ± 634	1.0 × 10 ⁻²	-
Fe	8974 ± 289	0.25	5.0 × 10 ⁻³
Mn	300 ± 18	0.1	1.0 × 10 ⁻³

^a Limit of Detection.

The Community Bureau of Reference (BCR) sequential extraction procedure was carried out to obtain Pb concentration in the different fractions of the soil in according to the procedure [32,33].

2.2. Soil Washing and Recycle of the SWS

Washing tests were conducted in batch, at lab scale, using one-liter glass reactors, each equipped with a mechanical stirrer. Experiments were performed in triplicates, to reduce experimental errors. EDDS solutions of varying molarities (from 0.002 to 0.01 M) were used as washing agents. Liquid to solid ratio was varied from 1:10 to 1:20, in order to test both 10% and 5% suspended solid concentrations. pH values of the washing solution was varied through the addition of NaOH and HCl, in order to test both acidic (pH 5.0 and pH 6.0) and basic (pH 7.6 and pH 8.0) conditions. At established interval times, 5 mL samples were extracted from the reactor, filtered at 0.45 µm, and analyzed for Pb concentration determination. The treatment process lasted for 48 h, to reach steady state conditions.

After that time, SWSs were separated from the slurry through a paper filter, and mixed with a concentrated H₂SO₄ solution in a 1:1 volumetric ratio, to be regenerated. The mixing time of the SWS regeneration tests lasted 30 min, and was followed by a 2 h sedimentation and a final filtration at 0.45 µm. The regenerated solutions were used as washing agents in a new series of washing tests carried out according to the optimal operative conditions selected from soil washing batch tests. The regeneration and reuse procedure of SWSs were repeated two times, to test the efficiency of the washing solution after both first cycle and second regeneration cycles.

2.3. Ecotoxicity Tests

Treated and untreated soil samples were used to perform ecotoxicity tests on *Daphnia magna* and *Lepidium sativum*, following the procedure described by Alvarenga et al. [34].

Fresh, spent, and regenerated solutions, instead, were used to perform respirometric tests on an activated sludge, sampled in the oxidation tank of a municipal wastewater treatment plant located in Nola (Italy), using the inorganic medium, in accordance with Spasiano et al., 2016 [35]. At this aim, an electrochemical respirometer Martina (Spes, Fabriano, Italy), equipped with two oxygen probes (WTW, Weilheim, Germany), was used to measure the oxygen uptake rate as a function of time, in the presence and absence of substrate addition.

3. Results and Discussion

3.1. Soil Characterization

The soil pH and the organic matter content were 7.6 ± 0.3 and 4.5 ± 0.1, respectively. The measurements of the content of heavy metals in the sampled soil are shown in Table 1.

Soil analysis revealed that no PTMs other than Pb were present in the samples. Pb concentration was very high, and ranged around 8600 ± 300 mg/kg, almost equally divided between the residual fraction ($45 \pm 3\%$), and the mobile one ($55 \pm 3\%$ of the total amount) deriving from the sum of the exchangeable, the reducible, and the oxidizable fractions (Figure 1). This indicated the extreme toxicity of the soil, confirmed by the tests reported further on.

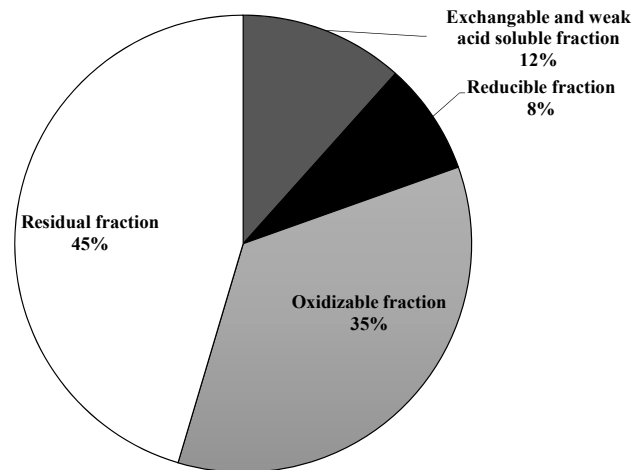


Figure 1. Pb partition in the different fractions of the soil obtained by the BCR sequential extraction (RSD_{max} < 7.52%).

3.2. Soil Washing and Recycle of the SWS

The results of the soil washing, summarized in Figure 2a–e, were very promising, and suggested the possibility of complete detoxification of the investigated site. The extraction process developed regularly, and apparently no big differences could be noted between the two-tested suspended solid concentrations.

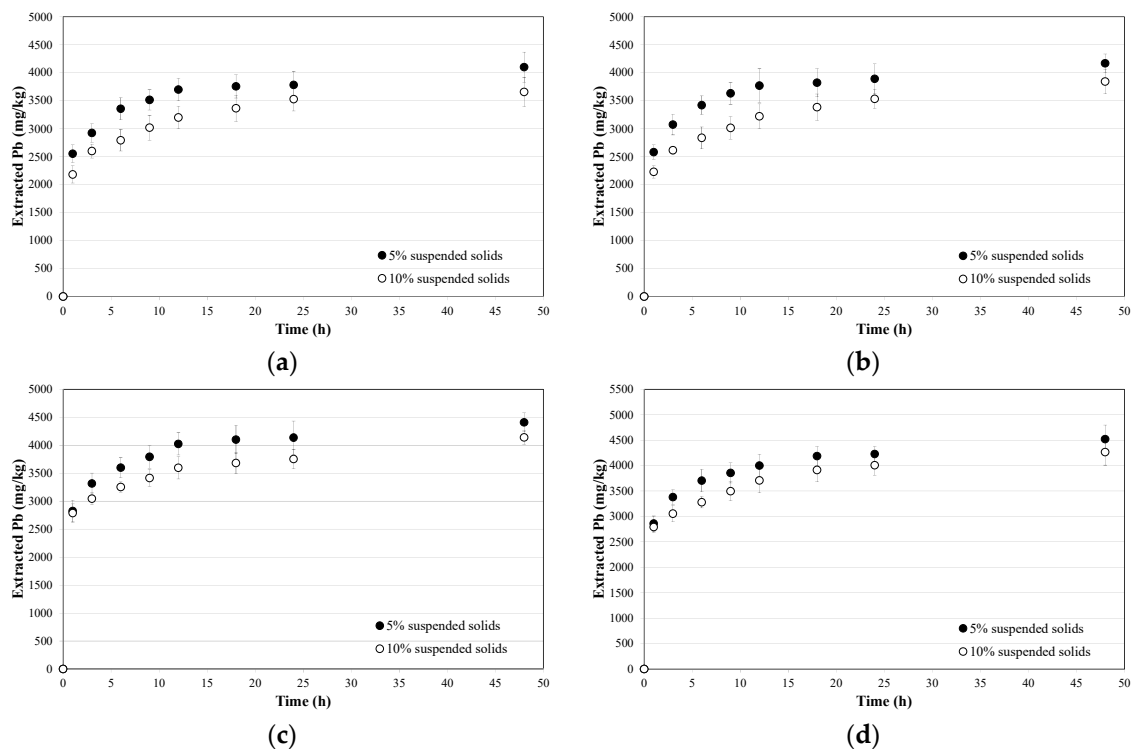


Figure 2. Cont.

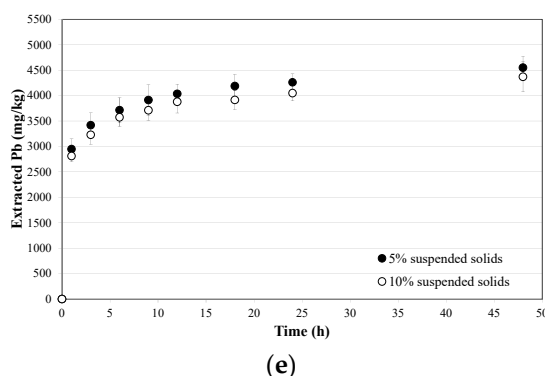


Figure 2. Pb extraction, varying suspended solids concentration and EDDS solution molarity: (a) 0.002 M; (b) 0.003 M; (c) 0.005; (d) 0.008 M; (e) 0.01 M.

In agreement with previous studies [36,37], process kinetics were characterized by an initial fast reaction rate, which lasted about 5 h, followed by a slower extraction rate. The obtained trend was therefore modeled using the following mathematical equation [38]:

$$E_{Pb} = b_1 \cdot (1 - \exp^{-k_1 t}) + b_2 \cdot (1 - \exp^{-k_2 t}) \quad (1)$$

where E_{Pb} = amount of extracted Pb; t = time; b_1, b_2 = the maximum extracted Pb percentage during the fast and slow kinetic steps, respectively; k_1, k_2 = the reaction rates of the fast and slow kinetic steps, respectively.

Table 2 reports, as an example, the values of the four kinetic parameters, obtained by data fitting minimizing the normalized root-mean-square error (NRMSE) (Equation (2)) to assess the agreement between model prediction and experimental data around the mean value of the observed data [39]:

$$NRMSE = \frac{\sqrt{\frac{\sum_i (x_i - x'_i)^2}{K}}}{x_M} \quad (2)$$

where x_i = simulated value; x'_i = measured value; x_M = average of measured values; K = number of measured values.

Data fitting was carried out for some of the tested operative conditions, referring to the washing operated at 5% suspended solids and various EDDS solution molarities. Together with the kinetic parameters, the so-called modeling efficiency (M_{eff}) value is also reported, calculated as [38]:

$$M_{eff} = 1 - \frac{\sum_i (x_i - x'_i)^2}{\sum_i (x'_i - x_M)^2} \quad (3)$$

where x_i, x'_i, x_M have the same meaning as in Equation (2).

M_{eff} gives an indication of the agreement between observed data and simulated one after the fitting procedure.

Table 2. Kinetic parameters and values of the modeling efficiency, for tests conducted at 5% suspended solid concentration.

	k_1 [1/h]	k_2 [1/h]	b_1 [mg/kg]	b_2 [mg/kg]	M_{eff}
EDDS 0.002 M	0.2	6	1500	2280	0.939
EDDS 0.003 M	0.2	6	1560	2330	0.957
EDDS 0.005 M	0.2	6	1690	2420	0.952
EDDS 0.008 M	0.2	6	1800	2520	0.964
EDDS 0.010 M	0.2	6	1890	2580	0.963

As can be easily seen, generally the fitting was very good. The obtained values of the parameters b_1 and b_2 could be expressed as a linear function of the solution molarity as

$$b_1 = 47.92 \cdot (M_{EDDS}) + 1419.6 \quad (R^2 = 0.988) \quad (4)$$

$$b_2 = 37.21 \cdot (M_{EDDS}) + 2217.6 \quad (R^2 = 0.992) \quad (5)$$

where M_{EDDS} = EDDS solution molarity; R^2 = regression coefficient.

The parameters k_1 and k_2 , instead, were found to be constant at different solution molarities. Although the suggested kinetic equation is valid whatever the soil characteristics and the operative parameters of the process, it is obvious that the kinetic parameters are dependent on some key elements affecting the removal process, such as pH, natural organic matter in soil, redox potential, and soil particle size, distribution, and mineralogy [4].

The results suggested that the process, at least during the initial hours, was mainly dominated by convective diffusion and ion exchanges on the surface of the grains. Intraparticle diffusion and internal exchanges, instead, were likely to be responsible only for the late extraction, taking place at a slower rate, during the last part of the treatment [40].

It is worth noting that the possibility of reaching quite good performances already with a 0.002 M solution (which corresponded to a 1:1 volumetric ratio between the chelant and the available Pb fraction) was extremely important for the whole optimization of the process. In such a situation, the extraction of other components of the soil could be avoided. This makes it possible to prevent negative effects on the soil, since component extraction could alter soil composition [41].

Furthermore, an increase of the extractive capacity could be obtained simply decreasing the pH from 7.8 to 6, as indicated in Figure 3. According to the displayed data, the increase was not progressive with pH decrease. pH values around 5 resulted in a reduced extractive capacity with respect to pH 6. To explain such a result, it was supposed that, in acidic conditions, two different phenomena took place at the same time, with opposite effects on process performances: (i) the protonation of the soil, which was favorable to the formation of Pb–EDDS complexes, and therefore increased the extraction of the metal; and (ii) the competition between hydrogen and Pb ions for the available sites of EDDS, which, instead, was unfavorable to the chelation process, and reduced the amount of extracted Pb [42]. At pH close to neutral values, the first effect prevailed, while at lower pH, the second effect became prominent, and the overall efficiency tended to decrease. Of course, the effect of pH variation on Pb release was also due to the solubility of different soil fractions bound to the metal (Figure 4), which is pH-dependent.

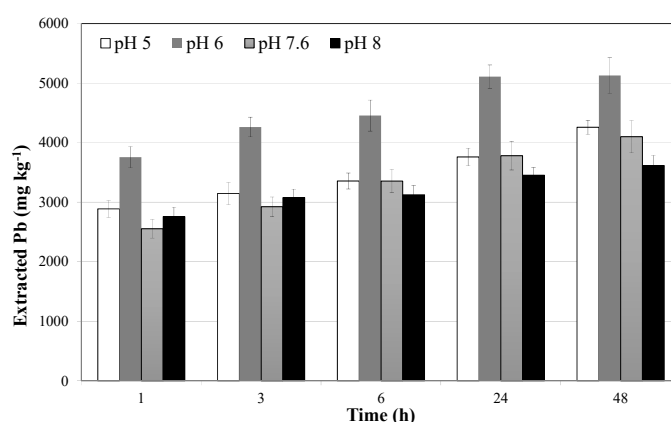


Figure 3. Pb extraction at EDDS 0.002 M and 5% suspended solid concentration with varying pH.

The possibility of SWS regeneration and reuse is indicated by the results summarized in Figure 4. The Figure shows the residual extractive capacity of a regenerated solution resulting from the soil

washing conducted at EDDS 0.002 M and 5% suspended solid concentration, but similar results could also be obtained for the other tested conditions (data not shown). The obtained trend confirmed that the recovery of the washing agent was convenient. Pb extraction, in fact, was still possible after two regeneration cycles, although the removed amount of the metal became less than 20% of the original extracted value. It can also be noted that the regeneration process affected the extraction kinetics. In the case of the fresh solution, the equilibrium was reached in about 24 h, while for the regenerated solution, the maximum removed amount was obtained almost immediately. This indicated that the contribution of the intraparticle diffusion process was more important for the regenerated solution than for the fresh one. In fact, applying the Weber and Morris equations [43]:

$$E_{Pb} = k_D \cdot t^{0.5} + c$$

the linear dependence between the square root of the contact and the extraction capacity of the Pb was observed, confirming the influence of the intraparticle diffusion process increase from the fresh solution ($R^2 = 0.89$) to the second cycle regeneration ($R^2 = 0.99$).

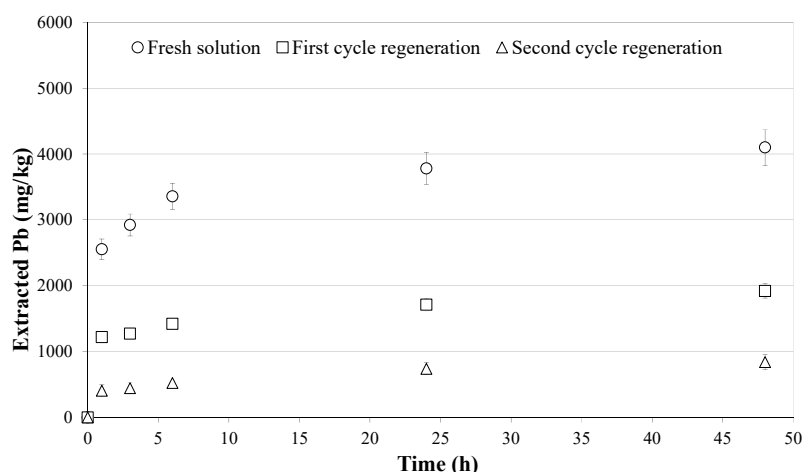


Figure 4. Pb extraction with fresh and regenerated solutions. Operative conditions: EDDS = 0.002 M; pH = 7.6; suspended solid concentration = 5%.

Other cations in the soil competed with Pb, so that Ca, Mg, Al, Fe, and Mn were also extracted together with Pb. Nonetheless, the extracted amount was not relevant compared to the original concentration of these metals. Moreover, it is also reported that marginal soil mineral dissolution occurs during soil washing at low EDDS concentration [44]. Finally, the variation of soil composition was not relevant in the specific case, as the soil had no natural vocation for agricultural use or plant growth [20].

3.3. Ecotoxicity Tests

As suggested by the obtained efficiencies in terms of Pb removal, soil toxicity greatly decreased as a consequence of the applied remediation process.

Figure 5 reports the results of ecotoxicity tests conducted on the untreated soil, and on the soil treated at natural pH (7.6) and 5% suspended solids in the slurry with various EDDS concentrations. According to the plotted data, it can be said that the untreated soil exerted a strong acute toxic effect on the living organisms and on the tested seeds, because of the large bioavailability of Pb, confirmed by its distribution among the different fractions of the soil. *Daphnia magna* immobilization percentage at 48 h, in fact, was 100%, while the germination index for *Lepidium sativum* was only 40%.

On the contrary, after the washing process, even the soil treated with the most diluted solution presented characteristics that were more favorable for living species, allowing a decrease of the

Daphnia magna immobilization percentage to 20%, and the doubling of the *Lepidium sativum* germination index. The residual toxicity became negligible, when not absent, in case of more efficient treatment, with EDDS concentration increase to 0.005 or 0.008 M, and total removal of Pb mobile amount in the soil.

The obtained results confirmed also that no toxic effect was induced by the residue of EDDS–Pb chelates, remaining adsorbed to the soil after the washing process and the successive separation of the SWS from the solid phase, obtained by filtration [11,45].

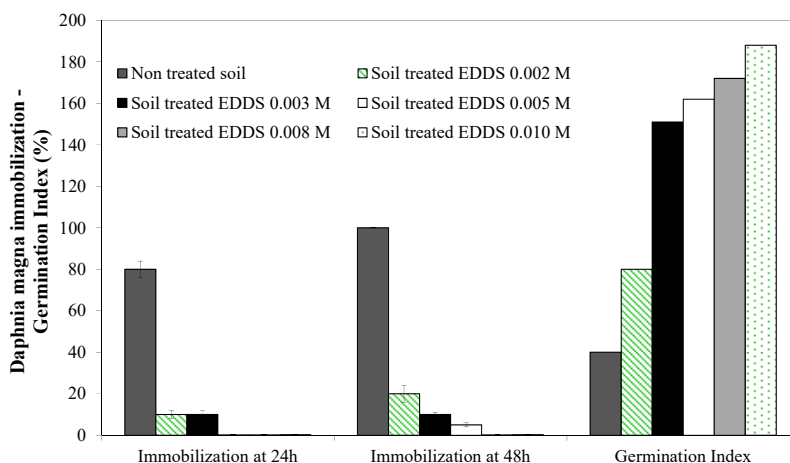


Figure 5. Results of ecotoxicity test on untreated soil and treated soil. Treatment conditions: pH = 7.6; suspended solid concentration = 5%.

Further indications concerning EDDS–Pb chelates' potential toxic effect and eventual biodegradability could be obtained from the results of respirometric tests, summarized in Figure 6a–d.

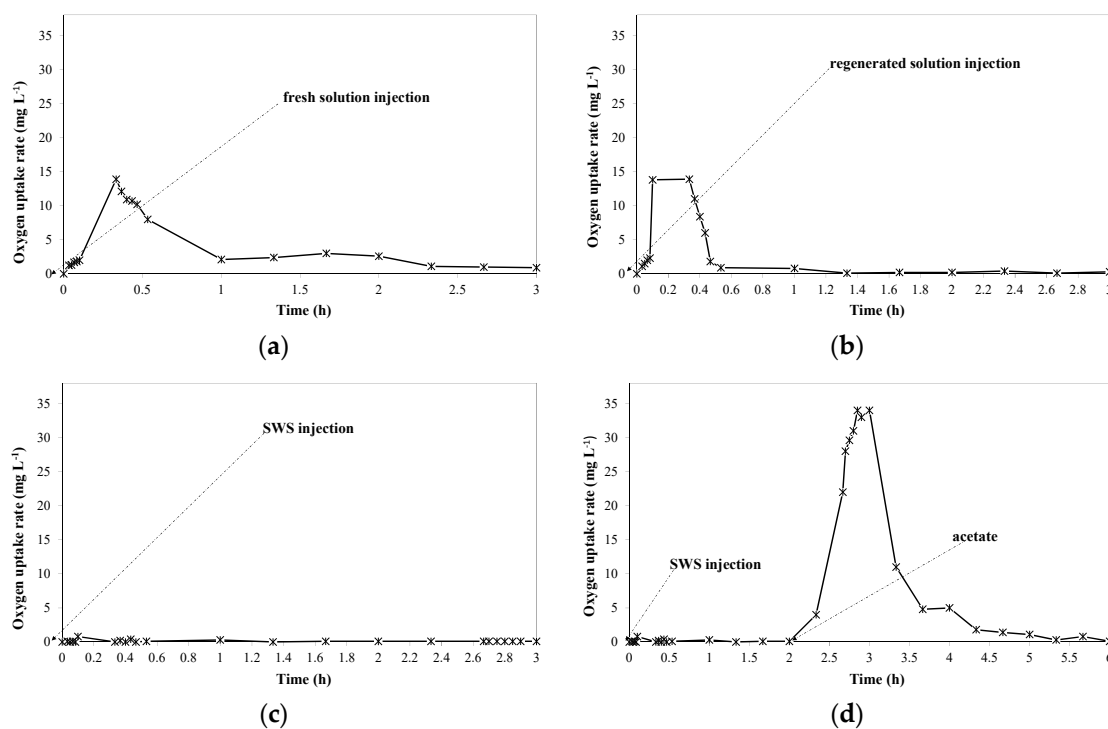


Figure 6. Results of respirometric tests: (a) effect of fresh solution injection; (b) effect of regenerated solution injection; (c) effect of spent solution injection; (d) effect of spent solution injection followed by acetate injection.

In more details, Figure 6a,b report the oxygen uptake rate variation, as a consequence of the injection of fresh and regenerated EDDS solutions, respectively, while Figure 6c,d report the oxygen uptake rate variation as consequence of the injection of the SWS only, and SWS followed by acetate, respectively.

As can be easily seen, both the fresh and the regenerated EDDS solution caused a sharp increase of the oxygen uptake rate value, which rapidly decreased in about 1 h, as a consequence of the removal operated by the sludge. On the contrary, no variation was caused by the injection of the spent solution. Therefore, while the fresh and the regenerated solutions were recognized as available substrates by the biomass, and were consumed in quite a short time, the spent solution was not. Such a result not only confirmed the well-known biodegradability of EDDS, but also the success of the regeneration process, which was able to completely remove the formed complexes, making the solution once more biodegradable [21].

It is worth noting that, although the SWS was not biodegraded, it had no toxic effect on the biomass. In fact, after the injection of the spent solution, the successive addition of acetate (Figure 6d) caused a sharp peak, followed by a fast decrease, of the oxygen uptake rate, revealing that the biomass was still very active, although not able to degrade the EDDS complexed by the metal.

4. Conclusions

From the experimental study described in the paper, the following conclusions can be drawn:

1. use of EDDS for soil washing of Pb-contaminated soil is an available option to almost completely remove the mobile fraction of the metal bound to the soil particles;
2. process kinetics are characterized by two distinctive steps, corresponding to an initial fast external exchange, followed by a slower internal exchange dominated by intraparticle diffusion, and can be modeled using a two-step exponential expression;
3. kinetics parameters corresponding to the maximum extractive capacity linearly depend on washing solution molarity, while those corresponding to the extraction rates are almost independent of it;
4. extraction efficiencies are optimal at pH close to the neutrality, because of the possible competition between hydrogen and Pb ions at lower values, and the possible formation of Pb hydroxide at higher values;
5. the spent solutions can be regenerated and reused for more than one washing cycle, decreasing the overall cost of the treatment;
6. spent solutions containing Pb–EDDS chelates do not have any toxic effect on the activated sludge of the wastewater treatment plant, but they are not biodegradable, therefore requiring the involvement of appropriate chemical processes before final disposal;
7. the soil treated with EDDS has no toxic effect on living species, and can be returned to its original location after treatment.

Author Contributions: Ludovico Pontoni and Vincenzo Luongo performed all the experiments, conducted all the analyses and contributed to writing the manuscript. Massimiliano Fabbicino designed the study, participated in performing the experiments as well as in writing the manuscript up to its final version. Alberto Ferraro supervised the whole work, edited the manuscript and revised it critically. Marco Race participated in writing the manuscript and in conducting analyses.

Conflicts of Interest: The authors declare no conflict of interest.

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