Heap leaching of Cu contaminated soil with [S,S]-EDDS in a closed process loop

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Abstract

Heap leaching of Cu contaminated soil (412 ± 11 mg kg^{-1}) with 5 mmol kg^{-1} ethylenediamine disuccinate [S,S]-EDDS as a chelator was tested in a laboratory-scale soil column study. The washing solution was recycled in a closed process loop after microbial (using a microbially active permeable bed, composed of substrate and absorbent) and oxidative chemical (using combined ozonation and UV irradiation) degradation of metal–[S,S]-EDDS complexes and retention of released Cu on a commercial absorbent Slovakite. Heap leaching using the permeable bed removed $25.5 \pm 3.6\%$ of initial total Cu from the soil. Ozone/UV treatment of the [S,S]-EDDS washing solution removed much more, $47.5 \pm 7.4\%$, of Cu. Both methods yielded a clear and colorless final (waste) washing solution, with 7.0 ± 10.0 and 2.6 ± 0.7 mg L^{-1} Cu (permeable bed and ozone/UV method, respectively). The results of our study indicate that chemical treatment of chelator washing solution with ozone/UV in a closed process loop could lead to the development of a new, efficient and environmentally safe remediation method with controllable Cu emissions.
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Keywords: Cu contaminated soil; Heap leaching; [S,S]-EDDS; Advanced oxidation processes

1. Introduction

Cu enters the soil by deposition from local foundries and smelters, through manuring with contaminated sludges, and from application of fungicides. With its known antifungal and algicidal properties, elevated levels of Cu in soil adversely affect microbially mediated soil processes. In EU countries, the warning and critical limits of Cu in soil are set at 50 and 140 mg kg^{-1}, respectively [1].

Treatment methods for heavy metal contaminated sites include containment, soil excavation, solidification/stabilisation and extraction. Extractive processes, e.g. soil washing, involves mobilisation of heavy metals by soil acidification or formation of water-soluble complexes with chelators. This can be done in a reactor (extraction of soil slurry) or as soil heap leaching. Heavy metals are then removed from the soil with a washing solution. The most common chelator used in soil washing is ethylenediamine tetraacetate (EDTA), although many

other chelating agents have also been tested. Lee and Kao [2] reported that Cu removal efficiencies from two contaminated soils followed the descending order EDTA > diethylenetriamine pentaacetate (DTPA) > citric acid. The main disadvantage of EDTA is that it is persistent, due to its low biodegradability and may carry toxic metals into an environment. It is apparent that to protect the environment, procedures suitable for destruction of the chelator after soil washing are needed. Tandy et al. [3] investigated biodegradable chelators and reported that at pH 7 and for equimolar ratios of chelators to Cu, all tested chelators were more efficient than EDTA. The order of Cu extraction efficiency was [S,S]-stereoisomer of ethylenediamine tetraacetic acid ([S,S]-EDDS) > nitrilotriacetic acid (NTA) > iminodisuccinic acid (IDSA) > methylglycine diacetic acid (MGDA) > EDTA.

We recently proposed combined [S,S]-EDDS-induced phytoextraction and washing of Cu contaminated soil using a horizontal reactive permeable barrier placed below the contaminated soil to prevent emissions of Cu [4]. [S,S]-EDDS is an easily biodegradable, low toxic chelator with strong chemical affinity for heavy metals and produces benign degradation products [5]. [S,S]-EDDS was first isolated as a metabolite of

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the soil actinomycete *Amycolatopsis orientalis*, and it is therefore naturally present in soil [6]. Application of 5 mmol kg^{-1} of biodegradable [*S,S*]-EDDS removed 32% of total initial Cu from the soil, mostly due to soil washing. In this process, Cu–[*S,S*]-EDDS complexes were washed from the soil into the barrier, where they were (probably microbially) degraded. The released Cu ions chemically reacted with absorbents in the barrier to form an insoluble product and, consequently, accumulated in the barrier. Excess washing solution flowed through the barrier. Although the use of a reactive barrier effectively reduced the Cu concentration in effluents by more than 40 times compared to control treatments, it did not entirely prevent Cu emissions.

The aim of this laboratory-scale study was to evaluate the feasibility of using [*S,S*]-EDDS for heap (or column) leaching of Cu contaminated soil and a permeable reactive bed for microbial degradation of chelator complexes and absorption of released Cu in a closed process loop. Another aim was to use chemical oxidation for the degradation of Cu–[*S,S*]-EDDS. Advanced oxidation processes (AOP) have recently been proposed [7] for the destruction of EDTA (structural analogue to [*S,S*]-EDDS) and its metallic complexes. AOP involves the use of ozone, H_2O_2, ultrasonic waves, UV irradiation, Fenton's reagent (Fe^{2+} and H_2O_2), alone or in combination, to generate free hydroxyl radicals; powerful, effective, non-specific oxidizing agents. In this study, we used a combination of ozone and UV irradiation.

2. Materials and methods

2.1. Soil properties

Soil samples were collected from the 0–20 cm surface layer of a vineyard in the southwestern part of Slovenia. The following soil properties were determined: pH ($CaCl_2$) 7.4, organic matter 3.9%, total N 0.21%, sand 15.4%, coarse silt 15.3%, fine silt 35.3%, clay 34.0%, P 70.6 mg kg^{-1}, K 36.3 mg kg^{-1} and Cu 412.0 mg kg^{-1} (6.48 mmol kg^{-1}). The soil texture was silty-clay loam. After being air-dried, the soil was passed through a 5 mm sieve.

2.2. Small-scale soil washing experiments

The reaction time for soil washing with [*S,S*]-EDDS (Octel, Cheshire, UK) was determined using 50 g of soil placed in perforated flasks ($D = 45$ mm), in triplicates. The soil was saturated to 100% soil water-holding capacity with 22.5 mL of 5 mmol kg^{-1} [*S,S*]-EDDS solution (prepared from 0.855 M stock solution) and incubated at room temperature from 6 to 240 h. The soil was then rinsed with tap water (20 mL), filtrated (Whatman No. 1) and stored in cold for analysis.

2.3. Heap leaching using a microbially active permeable bed

Air-dried soil (4.6 kg) was placed in a 24 cm high 15 cm diameter column, in four replicates. Plastic meshes were placed at the bottom of the columns ($D = 0.2$ mm) to retain the soil. Permeable beds were constructed in separate 6.5 cm wide columns as
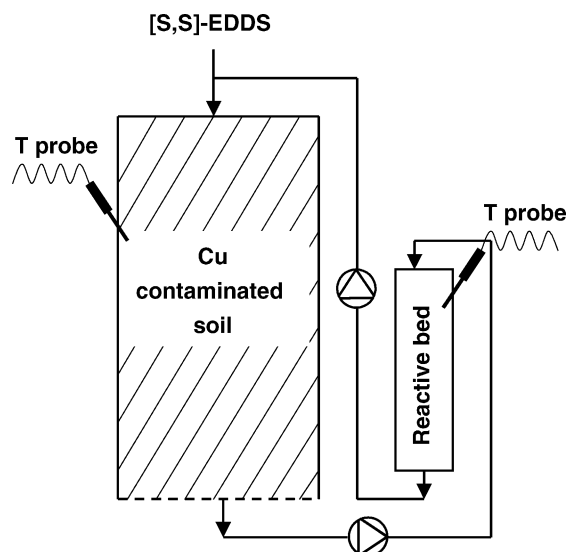

Fig. 1. Schematic representation of soil heap leaching with chelator, using a microbially active permeable bed for treatment of the washing solution in a closed loop.

shown in Fig. 1. They were composed of a mixture of sawdust (70 g), soya meal (20 g), vermiculite (40 g) and adsorbent Slovakite (IPRES, Bratislava, Slovak Republic, 50 g). The mixture of sawdust and soya meal was selected among other tested substrate mixtures (sawdust in combination with fish flour, maize gluten, sunflower meal and sugar-rape meal) since it supported high and long-lasting microbial activity. We determined the microbial activity in tested substrate mixtures by measuring CO_2 generation rate and as a *T* difference due to the microbially generated metabolic heat (data not shown). Slovakite is a mixture of natural raw materials: dolomite, diatomite, smectite basaltic tuff, bentonite, alginite and zeolite. The microbial activity in the beds was determined as the metabolic heat. Temperature probes were inserted into the permeable bed and soil column, and the difference in *T* recorded. Beds were saturated with tap water and incubated for 6 days before use. Soil was treated with 5 mmol kg^{-1} [*S,S*]-EDDS in 2.4 L of unbuffered tap water (110% of soil water retention capacity). The washing solution was collected and first circulated only through the soil columns for 72 h using a peristaltic pump. The washing solution was then circulated (flow rate 14 mL min^{-1}) through permeable beds and soil columns for heap leaching in a closed loop. The washing solution was periodically sampled and filtrated, pH was measured and samples stored in the cold for further analysis.

2.4. Heap leaching using advanced oxidation of [*S,S*]-EDDS metallic complexes

Soil columns were prepared as described above, but in triplicates. Soil was treated with 5 mmol kg^{-1} [*S,S*]-EDDS in 2.4 L of unbuffered tap water. The washing solution was collected and first circulated through the soil column for 24 h using a peristaltic pump. The washing solution was then circulated (flow rate 14 mL min^{-1}) through the ozone/UV unit, until the Cu concentration in the washing solution decreased to approximately
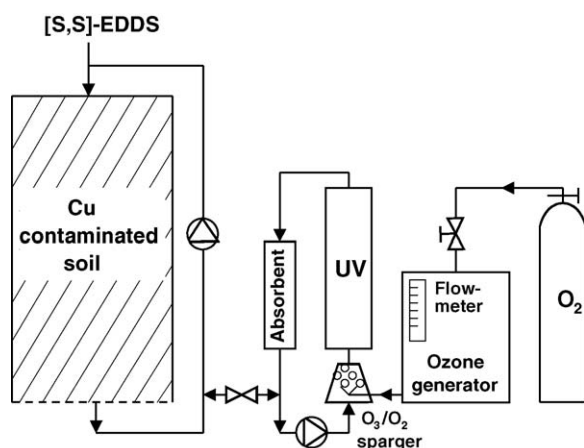
Fig. 2. Schematic of soil heap leaching with chelator, using advanced oxidation for treatment of metallic complexes in the washing solution in a closed loop.

10% of the initial level. The treated washing solution was reused for washing soil residual Cu–[S,S]-EDDS in a closed loop in several washing cycles. The washing cycle consisted of circulations of the washing solution through the soil (24 h) followed by ozone/UV treatment. The washing solution was sampled during each washing cycle, pH was measured and samples stored. A schematic diagram is presented in Fig. 2.

The ozone/UV unit consisted of an ozone generator, ozonation flask with porous gas sparger (oxygen/ozone flow rate $0.15\,L\,min^{-1}$), UV light and absorption column. Ozone was produced in an ozone generator (V-4, Crystal Air, Surrey, British Columbia) from pure commercial oxygen (flow rate $0.45\,L\,min^{-1}$). The ozone concentration was determined by the indigo colorimetric method [8]. Ozonation with a porous oxygen/ozone sparger allowed a concentration of ozone in tap water up to $14.2 \pm 1.2\,mg\,L^{-1}$. A 320 mm long UV light bulb (MK-8, Lenntech, Delft, The Netherlands) was installed in a quartz glass and stainless steel continuous flow housing. Metals, released after advanced oxidation of [S,S]-EDDS complexes, were removed from the washing solution by passing through the absorption column ($D = 6.5\,cm$), with 50 g of Slovakite mixed with 50 g of vermiculte as a carrier material.

2.5. Cu determination

For the analysis of Cu content, the soil samples were ground in an agate mill for 10 min and then passed through a 250 μm sieve. After the digestion of soils in *aqua regia*, AAS was used for the determination of Cu concentrations. The Cu concentration in washing solutions was determined directly by AAS. Controls of the analytical procedure were performed using blanks and reference materials (BCR 141R, Community Bureau of Reference) treated in the same way as experimental samples.

3. Results and discussion

The kinetics of the small-scale soil washing experiments showed that times from 24 to 168 h (7 days) are the optimum reaction times for 5 mmol kg^{-1} [S,S]-EDDS. After 7 days, the
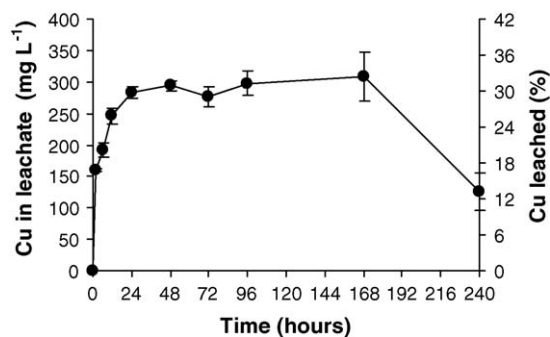

Fig. 3. Washing of Cu contaminated soil using 5 mmol kg^{-1} [S,S]-EDDS and different reaction times (small-scale experiments). The concentration of Cu in the leachate was measured and the percentage of Cu removed from the soil calculated. Error bars represent standard deviation from the mean value ($n = 3$).

extraction efficacy started to decline (Fig. 3). This could presumably be explained by a microbial degradation of the Cu–[S,S]-EDDS complex and re-sorption of released Cu from the washing solution back to the soil solid phase. It seems that a 7-day period was the necessary leg phase for the appearance of soil microbial populations, capable of Cu–[S,S]-EDDS degradation. In contrast to this indication of Cu–[S,S]-EDDS biodegradability, Vandevivere et al. [9] reported that activated sludge fed with EDDS as the sole C and N source readily biodegraded a 1 mM concentration of Ca–EDDS, Cr(III)–EDDS, Fe(III)–EDDS, Pb–EDDS, Al–EDDS, Cd–EDDS, Mg–EDDS, Na–EDDS, or Zn–EDDS, while Ni–EDDS, Co–EDDS, Hg–EDDS and also Cu–EDDS complexes remained essentially undegraded.

3.1. Heap leaching using a microbially active permeable bed

[S,S]-EDDS (5 mmol kg^{-1}) was first circulated through soil columns to react with Cu. We then started to circulate the washing solution through both permeable beds (for degradation of Cu–[S,S]-EDDS complexes and retention of released Cu) and soil columns (Fig. 1). After 13 days, the concentration of Cu in the washing solution was reduced to $7.0 \times 10.0\,mg\,L^{-1}$ (Fig. 4), with $25.5 \pm 3.6\%$ of the initial total Cu being removed from the soil.
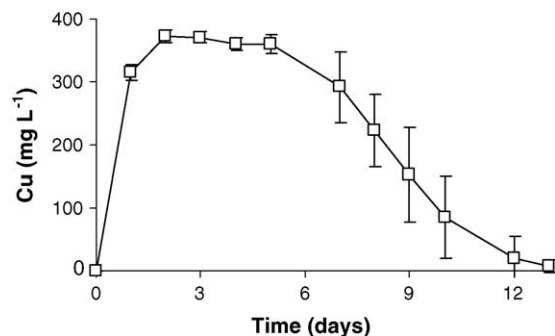

Fig. 4. The concentration of Cu in the washing solution during column simulation of soil heap leaching using 5 mmol kg^{-1} [S,S]-EDDS and a microbially active permeable bed. Error bars represent standard deviation from the mean value ($n = 4$).

The concentration of Cu in the washing solution started to decrease 5 days after we started treatment of the solution in a permeable bed (Fig. 4). The trend was quite similar that observed in the small-scale soil washing experiment (Fig. 3). It is likely that part of the [*S*,*S*]-EDDS mobilised Cu was not degraded and absorbed in the permeable bed. Some Cu–[*S*,*S*]-EDDS degradation (probably microbially mediated) is likely to have occurred in the soil, with the re-adsorption of released Cu back into the soil solid phase. This presumably explains why only $25.5 \pm 3.6\%$ of Cu was removed from the soil, compared to 32.7 ± 4.1 after 7 days extraction in the small-scale soil washing experiment (Fig. 3).

The *T* difference between soil and permeable bed fell from an average $0.9\,°C$ soon after we started to circulate the washing solution through the bed to an average $0.4\,°C$ during simulated heap leaching. This indicates lower than maximal (given the substrates used) microbial activity in the permeable bed during the process. A possible reason for the lower microbial activity is the fairly high pH of the washing solution, ranging from an initial 7.89 ± 0.15 to 7.92 ± 0.39 after 13 days. However, measurement of *T* increase, due to the generated metabolic heat, is probably not a very sensitive tool for assessing microbial activity.

In the setup used, soil heap leaching using a microbially active permeable bed did not prove to be a particularly effective method. Using pre-grown microbial populations, selected for their ability to degrade Cu–[*S*,*S*]-EDDS complex and adjusting the pH of the washing solution to allow maximal microbial activity in the permeable bed, might improve the efficiency of the method.

3.2. Heap leaching using advanced oxidation with ozone/UV

Rather than relying on apparently unreliable microbial degradation of Cu–[*S*,*S*]-EDDS, we decided to test a combination of ozone and UV for chemical degradation of the complex. This is the first report on using AOP in soil washing of Cu contaminated soil. The setup of the laboratory simulation of the proposed new heap leaching method is shown in Fig. 2. After a $5\,mmol\,kg^{-1}$ [*S*,*S*]-EDDS application, we allowed 24 h reaction time before we started to treat the washing solution in the ozone/UV unit. The treated washing solution was reused for soil rinsing to remove residual Cu–[*S*,*S*]-EDDS complexes. As expected, the initial concentration of Cu in the washing solution was lower after each washing cycle (Fig. 5), and the washing solution lost its initial very intensive blue-green color. After the fourth washing cycle, the concentration of Cu in the final (waste) washing solution was $2.6 \times 0.7\,mg\,L^{-1}$. The solution was completely clear and colorless, with pH 8.91 ± 0.03. The pH of the washing solution after the first washing cycle was 7.74 ± 0.46.

Heap leaching with treatment of the washing solution with ozone/UV removed $47.5 \pm 7.4\%$ of initial total Cu from the soil. This was even better efficiency than the $32.7 \pm 4.1\%$ of Cu removed in the small-scale soil washing experiments (Fig. 3). The difference can presumably be explained by incomplete removal of Cu complexes from the soil in the small-scale experiments (after [*S*,*S*]-EDDS application, the soil was rinsed with
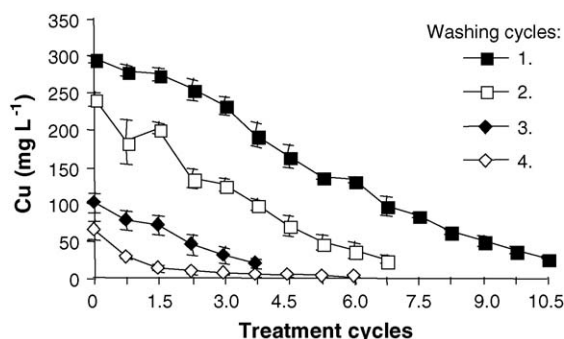

Fig. 5. The concentration of Cu in the washing solution during treatment in the ozone/UV unit. Heap leaching was simulated in soil columns using $5\,mmol\,kg^{-1}$ [*S*,*S*]-EDDS and four washing cycles. Error bars represent standard deviation from the mean value ($n = 3$).

tap water only once). Another possible explanation is oxidation of soil fractions where Cu was bound with the ozone-saturated washing solution during simulated heap leaching, and release of Cu otherwise non-attainable by [*S*,*S*]-EDDS. The concentration of ozone in the washing solution, before it was further used for soil irrigation, was quite high, up to $15\,mg\,L^{-1}$. For example, Plaue and Czerwinski [10] treated Pu and Am contaminated soil with ozone and reported that soil ozonation followed by soil extraction with EDTA increased removal of both radionuclides.

In the experimental setup used in this study, treatment of the washing solution in the ozone/UV unit within each washing cycle was excessively long (Fig. 5). The total duration of the experiment was 138 h. The bottleneck was the very low hydraulic permeability of Slovakite (used as a powder) and vermiculite mixture in the absorption column. The use of another absorbent, or Slovakite in granulate form, should allow higher flow rates of the washing solution through the ozone/UV unit and thus reduce the treatment time.

4. Conclusion

The results of our laboratory-scale study indicated that the use of ozone/UV for treatment of chelator washing solution in a closed process loop is a viable new option for remediation of Cu contaminated soils. The final (waste) washing solution was almost free of Cu and safe for discharge. Alternatively, it could be reused as a medium for subsequent soil treatment with new chelator addition, and thus reduce the requirements for process water. The biodegradability of the chelator is not an issue in the proposed method. Other chelators such is EDTA, perhaps less efficient for Cu soil removal but much cheaper than [*S*,*S*]-EDDS (price approximately $5000\,GBP\,tonnes^{-1}$), and more optimal operational conditions will be tested in our further experiments.

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