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Solar photocatalytic processes for treatment of soil washing wastewater

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HIGHLIGHTS

- Solar photocatalytic sequential treatment of soil washing effluents.
- Efficient removal of copper, zinc, EDDS and TOC from effluents.
- A plate solar collector with a multitubular reactor is used.
- Procedure for the estimation of illuminated area of the solar photoreactor.
- The ecotoxicity of the soil washing effluents is noticeably reduced.

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ABSTRACT

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

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

The ecotoxicological assessment, using different living organisms (*Daphnia magna*, *Vibrio fischeri*, *Pseudokirchneriella subcapitata*, *Lepidium sativum* and *Caenorhabditis elegans*), showed a noticeable decrease of the ecotoxicity of the soil washing effluents after the two-step photocatalytic process.

1. Introduction

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

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

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

For this purpose, different physical [2,3], chemical [4–6], or integrated physico-chemical [7] processes have been recently proposed to enhance the removal of heavy metals and chelating agents from wastewater effluents before their release into the environment. Among the processes proposed for treating soil washing solutions, solar driven photocatalytic systems can be

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preferred due to their simplicity and cheapness [8–10]. However, previous studies on the possibility of decontaminating EDDS containing soil washing effluents are so far restricted to synthetic solutions [11] or real soil washing solutions [12] only under artificial solar radiation. To the best of the Authors' knowledge, no reports are found in the literature dealing with outdoor solar photocatalytic treatments of real soil washing effluents containing at the same time copper, iron, zinc, and ethylenediaminedisuccinic acid, used as chelating agent.

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

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

2. Materials and methods

2.1. Materials

(S,S)-ethylenediamine-N,N′-disuccinic acid-trisodium salt solution (35% in H_2O) [CAS 178949-82-1], perchloric acid (ACS reagent 70%) [CAS 7601-90-3], nitric acid (ACS reagent >67% v/v) [CAS 7697-37-2], oxalic acid (ACS reagent 99.8% w/w) [CAS 6153-56-6] and titanium(IV) oxide pure cristalline anatase powder (99.8% w/w) [CAS 1317-70-0] were purchased from Sigma–Aldrich and used as received.

2.2. Soil sampling and soil washing procedure

Polluted soil samples were collected from the area of Giugliano (Fig. S1), in the province of Naples (Campania, Italy). A description of the soil sampling procedure has been previously reported [12].

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

2.3. Photocatalytic procedures

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

2.3.1. Artificial solar radiation

Solar simulated photocatalytic runs were carried out in an annular batch glass reactor having an irradiated volume (V_{ir}) and an illuminated surface area (A_{ir}) equal to 0.28 L and 3.39 dm^2 respectively. The reactor was equipped with a polychromatic sodium lamp (Helios Italquartz, model Na 15F) with a nominal power of 150 W and a wavelength range between 350 and 800 nm. The device has been described elsewhere [14]. The photon fluxes of the Na-lamp, measured by UVA radiometer (DELTA OHM, model HD2102.1, detection limit: 1.00×10^{-3}–2.00×10^{3} $W \cdot m^{-2}$), were 2.84 $W \cdot m^{-2}$ (280–400 nm) and 2.02×10^{3} $W \cdot m^{-2}$ (400–800 nm). The emission spectrum of the Na-lamp is reported in Fig. S2.

Some photocatalytic runs were carried out using a high pressure Hg lamp with a nominal power of 125 W mainly emitting in the wavelength range of 300–400 nm (Helios Italquartz). The photon flux of the Hg-lamp in the wavelength range 280–400 nm was 30.03 $W \cdot m^{-2}$.

2.3.2. Natural solar radiation

The photocatalytic runs under sunlight were carried during the period June–July 2015 at University of Naples (Italy, local latitude 40° 50′ 00″ N, longitude 14°12′ 00″ E) by using a flat plate collector supported by an aluminum structure (Fig. 1) with a multitubular reactor (PTC). The flat plate collector (9 dm^2) was made up of 8 parallel borosilicate glass tubes (internal diameter 4 mm, external diameter 7 mm, length 34.6 cm) connected by plastic junctions. The soil washing effluent to be treated was kept re-circulating at a rate of 80 $L \cdot h^{-1}$. Some runs were carried out varying the re-circulating rate (60 $L \cdot h^{-1}$). The solution recirculation between the refrigerated tank (1.5 L, 25 °C) and the collectors was carried out using a peristaltic pump (Watson Marlow 505S). The total volume of the reactor (V_t) is constituted by the irradiated PTC volume (V_{ir}) and the dead volume (recirculation tank and connecting tubes). The irradiated volume of PTC was 3.42×10^{-2} L. The total volume of the device ranged between 0.30 L and 0.85 L. The flat plate collector surface was covered with aluminum foils. The average incident solar radiation was typically about 15 ± 10 $W \cdot m^{-2}$ in the wavelength range 315–400 nm and 950 ± 150 $W \cdot m^{-2}$ in the range 400–1100 nm.

The amount of UVA solar energy received by the nth sample ($Q_{j,n}$, $kJ \cdot L^{-1}$), per unit volume of solution, in the time interval Δt_n was calculated from the following equation:

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

where t_n is the experimental time corresponding to the nth sample, V_t the total volume of the reactor, A_{ir} the illuminated surface area, and $UV_{G,n}$ the average solar ultraviolet radiation (300–400 nm) measured during the period Δt_n.

2.4. Analytical procedures

The soil washing samples were centrifuged at 4800 rpm for 15 min using an IEC Centra GP8R centrifuge. The initial pH of the soil washing effluent was close to 7.7 ± 0.2. Solution samples were

Fig. 1. Solar photoreactor adopted.