



## Soil remediation using soil washing followed by Fenton oxidation



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### HIGHLIGHTS

- ▶ Soil washing with a nonionic surfactant Tween 80 was analyzed.
- ▶ A model considering surfactant adsorption and *p*-Cresol extraction was proposed.
- ▶ Soil washing was used in combination with Fenton oxidation.
- ▶ Reaction is selective to the contaminant degradation.
- ▶ Reaction allows the recovery and reuse of the surfactant.

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### ABSTRACT

Soil washing was applied to a contaminated soil with *p*-Cresol by using a nonionic surfactant (Tween 80). A mathematical model has also been proposed to describe both the pollutant desorption and the surfactant adsorption, taking place simultaneously. The effect of temperature (20–40 °C) and surfactant concentration (0.1–10 g L<sup>-1</sup>) have been analyzed on both kinetic rates. The kinetic desorption rate of *p*-Cresol increases as the initial solubilizer concentration. Desorption of *p*-Cresol was slightly greater with increasing temperature. The obtained kinetic model represents quite well the experimental results.

Soil washing wastewater (20 mg L<sup>-1</sup> of *p*-Cresol and 0.86 g L<sup>-1</sup> of Tween 80) has been treated with Fenton Reagent to remove the pollutant extracted (*p*-Cresol) and to recover the surfactant solution. The pH of the soil washing wastewater was about 6.5 and did not change significantly during the Fenton Reagent treatment. Total conversions of *p*-Cresol were observed, at very short times, at the conditions tested for the Fenton reaction (100 mg L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub> and 10 mg L<sup>-1</sup> of Fe<sup>2+</sup>). The hydrogen peroxide was not totally exhausted, showing conversions near 60% at 120 min. Besides, the removal of Tween 80 during the Fenton's reaction was lower than 10%, which suggests that the reaction is mainly selective to *p*-Cresol degradation. The toxicity of the liquids, measured by Microtox bioassay, was significantly reduced after the oxidation reaction, suggesting the negligible formation of degradation intermediates with higher toxicity than *p*-Cresol.

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### 1. Introduction

Contamination of soils by toxic and/or hazardous organic pollutants is a widespread environmental problem and the removal of hydrophobic organic compounds (HOCs) from them has become a major concern. A potential technology for rapid removal of HOCs sorbed to soils is soil washing with a solubilizer solution.

Soil washing is a process that uses physical and/or chemical techniques to separate contaminants from soils and sediments. Contaminants are concentrated into a much smaller volume of contaminated residue, which is either recycled or disposed. This technique can be used to treat a wide range of inorganic and organ-

ic contaminants, being used independently or in combination with other treatment technologies.

Among the different HOCs, cresol has been selected as target pollutant. Cresols are isomeric substituted phenols with a methyl substituent at either ortho, meta or para position relative to the hydroxyl group. These compounds are contained in crude oil, coal tar, and fly-ash from coal and wood combustion and are used as solvents, disinfectants, and in the production of fragrances, antioxidants, dyes, pesticides, resins, and as wood preservatives. Among cresols, *p*-Cresol is mainly used in the formulation of antioxidants for lubricating oil and motor fuel, rubber, and polymers. *p*-Cresol is considered to be toxic and has been classified as hazardous pollutants. *p*-Cresol has been selected as a representative of HOCs, since it is difficult to desorb from subsurface media because of slow desorption kinetics from soils and sediments [1,2].

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In a previous work [3], the use of different extracting agents on the *p*-Cresol extraction from a loamy sand soil was compared. The best results were obtained by the nonionic surfactant Tween 80 (TW80), with extraction efficiencies higher than 70%. This extracting agent was very selective to *p*-Cresol extraction, minimizing the mobilization of soil organic matter and maintaining the natural pH of the soil. This solubilizer has been used, in this work, to evaluate both the kinetic desorption of *p*-Cresol and the adsorption of this nonionic surfactant into the soil at different experimental conditions.

In literature, various studies reported the use of soil washing in combination with other remediation techniques such as photocatalysis [4–6], photo-Fenton oxidation [7,8], electrochemical degradation [9], and bioremediation [10]. These works are mainly focused on the removal of the corresponding pollutant and, the extracting agent in the liquid waste is majority or totally degraded in most of them.

Soil washing has also been used as an initial step to decrease the pollutant concentration in soils. The remaining pollutant in soil was subsequently oxidized by using a Fenton Like process. [11–13]. Another recent work [14] proposes the simultaneous use of surfactants and chemical oxidants to improve the abatement of NonAqueous Liquids Phases in soils.

To our best knowledge, only few works analyze the contaminant removal, by coupling soil washing with the oxidation technique based on Fenton's reagent (FR), to treat the washing solution [15,16]. In one of them, the authors analyzed the remediation of a contaminated soil with TNT by soil washing, and the subsequent treatment with FR to treat the liquid residue. The authors use water as extracting agent and, as they reported, they consumed large volumes of water to meet remediation goals, increasing significantly the washwater volume to be treated with Fenton's reagent [15]. The other work monitored the removal of PAH, by using Triton X-100 and Igepal CA-720 as extracting agents, followed by the use of FR to treat the soil washing washwater. These authors used a wash solution containing 1% surfactant, and they obtained a high degradation of the surfactant during the Fenton reaction [16], avoiding the recovery and reuse of the surfactant solution. In this sense, the surfactant cost supposes the major implementation cost of the techniques.

In this work, a nonionic surfactant (TW80) previously selected was used to extract *p*-Cresol from a loamy sand at neutral pH with a soil organic matter content of 5%. The liquid contaminant residue obtained by soil washing was followed by Fenton oxidation process. A kinetic model is proposed to describe the kinetic desorption of *p*-Cresol in the presence of TW80, as well as the surfactant adsorption kinetic. The effect of temperature and surfactant concentration is taken into account in both kinetic expressions. Furthermore, the viability of using Fenton oxidation to treat the soil washing washwater, containing *p*-Cresol and TW80, is also evaluated, in order to remove the pollutant and to get the recovery of the most surfactant solution, and, therefore, to improve the economy of the soil washing treatment.

## 2. Materials and methods

### 2.1. Reagents

*p*-Cresol was supplied by Aldrich with a reported purity of 99%. The extracting agent, TW80, was purchased from Sigma–Aldrich. The soil used in this study is a loamy sand from Madrid. Prior to use, the soil was air-dried and sieved (<2 mm), and then characterized by the following: soil pH (H<sub>2</sub>O), 7.8; organic matter content, 4.9%; cation exchange capacity, 12.8 cmol kg<sup>-1</sup>, external surface area, 2 m<sup>2</sup> g<sup>-1</sup>; pore volume, 0.004 cm<sup>3</sup> g<sup>-1</sup>; total Fe, 8600 mg kg<sup>-1</sup> and Mn, 1250 mg kg<sup>-1</sup> [3].

### 2.2. Contaminated soil

The contaminated soil was artificially prepared by using uncontaminated control soil. The soil was spiked with a solution of *p*-Cresol (400 mg L<sup>-1</sup>) dissolved in water (aqueous solubility of *p*-Cresol is ~19,000 mg L<sup>-1</sup> at 25 °C). The sorption experiments were performed by using the standard batch equilibrium method, performed in vials, on a shaking water bath (50 rpm), at 20 °C. The liquid to solid ratio ( $V_L/W$ ) was 2.5 mL g<sup>-1</sup>, with contact time of 48 h. After equilibrium conditions, the samples were collected and centrifuged. The supernatant fraction was used to determine the concentration remaining in the water phase.

### 2.3. Desorption kinetics study

A kinetic study to predict, simultaneously, the *p*-Cresol desorption and the solubilizer (TW80) adsorption at different experimental conditions was carried out by using a series of batch experiments, varying the batch temperature between 20 and 40 °C. The solubilizer concentration was also varied between 0.1 and 10 g L<sup>-1</sup> at liquid to solid ratio ( $V_L/W$ ) = 2.5 mL g<sup>-1</sup>. These experimental conditions were selected based on a previous work [3]. Duplicate tests were performed for each experiment and the average value was used for figures with an experimental error lower than 5%. Desorption kinetic of the pollutant and adsorption of the surfactant has been evaluated by fitting experimental data. Differential equations have been solved by using an Euler integration method coupled to a non-linear regression (Marquardt algorithm) to optimize the corresponding kinetic parameters.

### 2.4. Fenton oxidation

The liquid contaminant residue derived from the soil washing with 1 g L<sup>-1</sup> of TW80 after 48 h was treated by Fenton's reagent. The soil washing wastewater contains approximately 20 mg L<sup>-1</sup> of *p*-Cresol, 0.86 g L<sup>-1</sup> of Tween 80 and 130 mg L<sup>-1</sup> of dissolver organic matter. Fenton oxidation experiments were carried out in 600 mL glass batch reactors shaken at an equivalent stirring velocity around 200 rpm for 1 h at room temperature. The reaction volume was 500 mL, and the reactants were added simultaneously to the liquid waste residue at the beginning of each run. The starting H<sub>2</sub>O<sub>2</sub> concentration was approximately 100 mg L<sup>-1</sup>, which nearly corresponds to the stoichiometric amount of H<sub>2</sub>O<sub>2</sub> necessary to oxidize *p*-Cresol to CO<sub>2</sub> and H<sub>2</sub>O. The Fe<sup>2+</sup> dose was 10 mg L<sup>-1</sup>. The initial pH value of the solution after the soil washing was 6.5, when TW80 was used as extracting agent. This pH was not necessary adjusted in these experimental conditions. Duplicate tests were performed for each experiment and the average value was used for figures with an experimental error lower than 5%.

### 2.5. Analytical methods

*p*-Cresol concentration was determined by HPLC. The surfactant concentrations were measured by a potentiometer titration method (by using an Ag/AgCl electrode) supplied by Metrohm (Metrohm, Switzerland, Application Bulletin No. 230/1e) [17]. Hydrogen peroxide concentration in the supernatant was also measured by using a potentiometer titration method (with a Pt electrode) supplied by Metrohm. Organic acids were analyzed by ion chromatography. The Total Carbon (TOC) was measured by a Shimadzu TOC-V CSH solid analyzer, as described in the standard procedure EN 13137. Fe and Mn extracted from the soil were analyzed by acid extraction/atomic absorption spectroscopy (EPA 3050B Method). The toxicity of the liquid samples after treatment was determined by means of a bioassay following the standard Microtox test procedure (ISO 11348-3, 1998), by using a Microtox

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