Anodic oxidation for the remediation of soils polluted with perchloroethylene

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Abstract

BACKGROUND: This work focuses on the removal of perchloroethylene from soils spiked with this hazardous chlorinated hydrocarbon and oil by a combination of two technologies: soil washing and anodic oxidation with diamond electrodes. The first attains the transfer of the pollutant from the soil to a soil washing fluid, from which the organics are then efficiently removed.

RESULTS: Results show that high concentrations of Sodium Dodecyl Sulphate (SDS) are required in the soil washing fluid for an efficient extraction of the chlorinated hydrocarbon and this forces to apply electrolysis not only to the clarified liquid but to also to the interphase. Surfactant used interacts strongly with soil not only during the washing step but also during the electrolysis. This interaction seems to play a protective role against the oxidation of SDS. First moments of the electrolysis are rather complex and there are several processes which modifies importantly the results obtained.

CONCLUSIONS: Removal of perchloroethylene (PCE) is less efficient than that obtained during the electrolysis of synthetic solutions of this chlorinated pollutant and there are two first order kinetic zones, which indicate an important competition for the oxidation of the different organics contained in the soil washing fluid during the electrolysis.

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26 **Keywords**

27 Perchloroethylene; soil washing; electrolysis; diamond anodes

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29 **Highlights**

- 30 – Combined soil washing and anodic oxidation can treat successfully polluted soils
- 31 – Perchloroethylene can be extracted from soils spiked with oils by soil washing
- 32 with SDS.
- 33 – Strong interactions of the SDS with soil and pollutants.
- 34 – Anodic oxidation with diamond can remove perchloroethylene from soil-washing
- 35 fluids
- 36 – Degradation kinetic is slower when treating soil-washing fluid than synthetic
- 37 solutions of perchloroethylene.

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1. Introduction

In recent years, remediation of soil and groundwater polluted with chlorinated hydrocarbons has gained a lot of interest, as emphasized by EU and national regulations concerning clean-up of pollutants sites. Numerous studies were carried out to face this great challenge evaluating, among other technologies, bioremediation¹, soil-vapor extraction, ozone oxidation², surfactant soil washing³, dehalogenation⁴, electrokinetics⁵⁻⁸, etc. Unfortunately, each of these processes exhibit different technical or cost limitations and up to now, not a clear solution is found to this important problem.

In this context, promising results are being obtained by combining some of these technologies with Electrochemical Advanced Oxidation Processes (EAOPs)⁹⁻¹². Among them, the combination of anodic oxidation with surfactant-aided soil-washing (SASW)³ is particularly interesting, because it helps to obtain good performance in the extraction and destruction of hydrophobic compounds from soil. Soil washing is generally efficient to clean soil. It has been exhaustively studied in our research group in previous works¹³⁻¹⁷, attaining good results in the depletion of target compounds both, from the soil matrix and later from soil washing fluid (SWF) using anodic oxidation. Regarding the SASW process, special care should be taken with the selection of optimal washing fluid composition, volume, mixing rate, temperature and contact time³. The addition of extracting agents (typically surfactants) and their concentration is key to extract pollutants in efficient conditions. Additionally, the recovery of extracting agents once the treatment is carried out is another goal to develop sustainable and cost-effective processes with high removal efficiency.

Once produced the soil washing waste, among the AOPs which can be applied for its removal, electrolysis with diamond electrodes has reached a special level of interest, because of the outstanding performance¹⁸. It has been applied successfully to the

degradation of many types of pollutants, attaining in most cases a very high efficiency¹⁹⁻²².

Perchloroethylene (PCE) is one of the most known chlorinated organic compounds and is among the most common pollutants at industrial sites, because for decades, it has been extensively applied as solvent in metal processing, chemical production and dry cleaning processes. Due to their volatility, it readily escapes from production plants and it is frequently detected in polluted soil and groundwater²³, typically associated to accidental spill of wastes. The United States Environment Protection Agency (EPA) has classified this species as a probable human carcinogen and this has motivated that the maximum level of PCE has been set at 5 µg dm⁻³ under Safe Drinking Water Act (U.S. EPA 2009)²⁴.

The removal of PCE has been faced by lots of authors, using not only biological systems^{4, 25-27}, but also different AOPs such as Fenton process²⁸, oxidation with activated persulfate in a porous media²⁹, sodium percarbonate and iron²⁴ and, recently, through the non-thermal plasma, promoting the generation of highly reactive oxidants in contact with water and gases³⁰. The treatment of this ubiquitous pollutant and possible intermediates can also be obtained by reductive dehalogenation and recent works, in which Zero-valent Iron (ZVI) is used as reductive agent, are of a great interest³¹⁻³⁵. Regarding the application of electrochemical techniques for their removal, there are various previous studies focused on the selection of anodic and cathodic strategies to remove PCE³⁶ and sonoelectrochemical degradation of PCE in aqueous sodium sulphate³⁷ and in absence of background electrolyte³⁸. However, to our best knowledge, studies were not carried out combining this PCE soil-washing with the anodic oxidation of the washing waste obtained.

Therefore, the development of efficient technologies for the remediation of soils polluted with organochlorinated species is still a very important environmental issue and the goal of this work is to evaluate the removal of PCE from spiked soils polluted also with oils (to simulate a real PCE-industrial polluted soil) by using surfactant soil washing and electrolysis with diamond anodes. This treatment was successfully applied for the remediation of soils polluted with clopyralid and lindane in previous works of our group^{16, 39}, two species with very different properties of that exhibited by PCE, which is typically associated to the presence of oils. In this case of the complexity is higher due to the presence of not only soluble species but of micelles of SDS with PCE and oils.

Thus, in this work, the complexity of the treatment is greater because of the presence of oils in the soil, which is a typical case in many industrial polluted sites, because PCE has been commonly used for decades as a solvent to degrease pieces in the metal mechanic industry.

2. Materials and methods

Chemicals. Tetrachloroethylene (C_2Cl_4 , >99%), Sodium Dodecyl Sulphate (SDS) (used as solubilizing agent) and Hexane (Sigma Aldrich, Spain) HPLC grade were obtained from Sigma Aldrich and used for GC-ECD. A hydrophobic lubricant oil Serie FORTE was obtained from Josval (Zaragoza, Spain). Methanol was obtained from VWR. Double deionized water (Millipore Milli-Q System, resistivity: 18.2 M Ω cm at 25°C) was used to prepare soil-washing fluid.

Analytical techniques. To determine tetrachloroethylene concentration in the liquid phase, an L–L extraction process was used before the analytical analysis. This process was carried out in separator flasks of 10 cm³ using hexane as extraction solvent (v/v ratio tetrachloroethylene/solvent 4). After that, all samples extracted from electrolyzed solution were filtered with 0.22 μ m nylon filters before analysis. The removal of

tetrachloroethylene was quantified by Gas Chromatography Electron Capture Detector (GC-ECD) (Thermo Fisher Scientific), using a TG-5MS capillary column (30 m × 0.25 mm 0.25 mm), 63 Ni micro-electron capture detector, a split/splitless injector and ChromCard Software. Under the conditions used, the quantification limit of the GC- ECD was 0.1 mg dm⁻³. The flow rate of gas He was 1.0 cm³ min⁻¹. The temperature of the oven was programmed as follows: 65°C kept for 1 minute, then increased to 140°C at 15°C min⁻¹ followed by another ramp to reach 290°C followed by 2 minutes hold. The temperature of the injector was 260 °C. Particle size was measured using a Mastersizer Hydro 2000SM (Malvern). Measurements of pH and conductivity were measured using a CRISON pH25+ and CRISON CM35+. Zeta potential was also measured for the clarified liquid and the homogeneous sample using a Zetasizer Nano ZS (Malvern, UK). A colorimetric method was used to determine the concentration of the SDS surfactant ⁴⁰. The anions present in the target wastewater were characterized using ion chromatography by means of a Shimadzu LC-20A system¹⁶.

Soil Washing. In this work, samples of 1 Kg of soil were uniformly polluted with tetrachloroethylene (0.02 g) solved in industrial lubricant oil (100 cm³). The main characteristics of the soil are shown in Table 1. Soil washing was carried out in a stirred batch tank as described elsewhere⁴¹.

Table 1. Physico-chemical properties of low permeability soil.

Mineralogy (%)		Particle size distribution (%)	
Kaolinite	26	Gravel	0
Feldspars	15	Sand	4
TiO₂	0.27	Silt	18
Calcite	4	Clay	78
K₂O	0.75	Specific gravity	2.6
SiO₂	7	Hydraulic conductivity (cm/s)	1 × 10 ⁻⁸
Al₂O₃	34.50	Organic content (%)	0

Others	12.48	pH	4.9
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Soil (amount ranging from 100 to 500 g) polluted with 200 mg tetrachloroethylene kg⁻¹ and 1.0 dm³ of SWF (concentration of SDS ranging from 100 to 20,000 mg dm⁻³) were mixed using paddle stirrers ($G \approx 4500 \text{ s}^{-1}$) for 24 hours in order to reach stationary conditions in the reactor. Then, the same tank acted as a settler (for 48 h) to split up the soil from the washing effluent. The soil washing wastes obtained consisted of complex aqueous-oil mixtures of tetrachloroethylene, surfactant and soil, with emulsified micro drops and soluble species.

Electrolysis. The SASW effluents were treated by electrolysis with diamond anodes using a bench-scale electrochemical setup described elsewhere¹⁶. Boron doped diamond (BDD) (Adamant Technologies, Switzerland) and stainless-steel electrodes with a geometric area of 78 cm² were used as anode and cathode, respectively. The characteristics of the BDD used were: sp³/sp² ratio: 225; boron content: 500 ppm; 2-3 μm of BDD coating thickness. The cells cover were made of quartz. The inter-electrode gap between both electrodes was approximately 1.6 mm. The SASW effluent obtained after settling was stored in a thermo-regulated glass tank (600 cm³) and circulated through the cell using a peristaltic pump at flow rate of 60 dm³ h⁻¹. This flow through the cell helps to obtain good mixing (by pumping) and a proper regulation of temperature (very important due to the ohmic losses of electrochemical processes). The electric current was applied using a Delta Electronika ES030-10 power supply (0-30V, 0-10 A). The electrolysis was carried out galvanostatically at 50 mA cm⁻² (which is within the typical range used in literature¹³⁻¹⁷). Prior to use in galvanostatic electrolysis assays, the electrode was polarized for 10 min in a 0.035 M Na₂SO₄ solution at 15 mA cm⁻² to remove any

impurities from its surface. Samples (0.02 dm^3) were collected in the glass tank and temperature was kept constant by means of a thermo-regulated water bath.

3. Results and discussion

Soil washing. The first stage in the remediation of soil polluted with perchloroethylene is the extraction of the pollutant from the soil, in order to transfer it into a liquid that can be further processed by oxidation. To do this, it was evaluated a soil washing process using surfactant solutions as soil washing fluids (SWF). As it is known, solubility of perchloroethylene in water is not very high (150 mg dm^{-3} at 25°C) and because of that, it is necessary to add a surfactant that helps to produce micelles not only from the perchloroethylene but also from the oil contained in the soil, improving the efficiency of the pollutant extraction. So that, a surfactant was chosen taking into account the impact on the soil and previous results of our group in others SW process with also non polar compounds ¹², and the behavior and extraction efficiency of different kind of surfactant (anionic, cationic and non ionic) ¹¹. It was chosen an anionic surfactant, sodium dodecyl sulfate (SDS) and it was used in the range $5\text{-}20 \text{ g dm}^{-3}$ evaluating the efficiency of the washing process at different soil /SWF ratios. Thus, the SWFs used in this work consists of different concentrations of SDS in water in order to determine the best ratio between surfactant and pollutant, capable to extract the chlorinated hydrocarbon efficiently from the soil.

Figure 1 shows the distribution of the organochlorinated pollutant perchloroethylene and the surfactant sodium dodecyl sulfate (SDS) after washing different amounts of a spiked soil (ranging from 100 to 500 g) with 1.0 dm^3 of soil washing fluid (SWF), which contained three different concentrations of SDS (ranging from 5 to 20 g dm^{-3}).

191 In every case, after mixing vigorously the soil with the SWF and letting the system to
192 settle, not two (as expected) but three phases were observed: 1) a volume of clarified
193 liquid at the top of the tank, 2) a dense sludge with most of the treated soil at the bottom
194 and 3) an interphase between both phases in which a significant amount of soil is
195 contained and which can be explained in terms of the strong interactions of the soil
196 particles and the surfactant. As seen in the Part a, concentration of perchloroethylene in
197 the liquid phase is almost negligible and to extract successfully this pollutant it is required
198 to use highly concentrated SDS as SWF, because otherwise the concentrations remaining
199 in the soil after the soil washing procedure are very large. Even with these high
200 concentrations, most of the perchloroethylene is contained in the interphase. In comparing
201 these results with those obtained in the treatment of clopyralid ³⁹ or, more recently, with
202 lindane ¹⁶ using the same technology, it should be remarked that in this case the process
203 is clearly more complicated. Thus, in the first case, the pollutant was released completely
204 to the SWF (without needing a surfactant to improve the efficiency) and in the second
205 case (in which the same surfactant was used), almost no interphase was detected so the
206 clarified liquid contained most of the pollutant after the treatment. As it will be seen later
207 on, the large values of the z-potential will help to explain this observation. For this reason,
208 in this case it was needed to separate the clarified liquid and the interphase all together in
209 order to undergo electrolysis and remove the pollutant.

210 Regarding the surfactant, the strong interactions of SDS with soil can also be seen in Part
211 b of the Figure, where it can be observed that most of the SDS added is retained the soil
212 (even in the bottom or in the interphase) and there is only free SDS in the clarified liquid
213 at low ratios soil /SWF. This result confirms a strong interaction between the SDS and
214 the soil particles.

Figure 1. Pollutant and surfactant distribution after the application of the SASW process among the soil (▨), turbid interphase (■) and clarified liquid (■) during the treatment of soil polluted with 200 mg dm⁻³ of PCE at different SDS/soil ratios. Concentration of SDS used in the raw soil washing fluid: 5.0 g dm⁻³; 10 g dm⁻³; 20 g dm⁻³.

Electrolysis of SWFs. Figure 2 presents the removal of perchloroethylene, oils and SDS from the mixture clarified liquid – soil washing fluid obtained after mixing 200 g of soil with 1 dm⁻³ of SWF during the electrolysis with diamond anodes. As expected, both the perchloroethylene and the oils are completely removed during the electrolysis, being the removal of the perchloroethylene 4-times faster than that of the oils. In addition, the first

decay (organochlorinated pollutant) is exponential while the second (oil pollutant) clearly fits a linear trend. Hence, combination of surfactant soil washing, and electrolysis seems to be a suitable treatment for the removal of these pollutants from SWF.

Figure 2. Electrolysis of soil washing effluent obtained after mixing 200g of polluted soil with 1 L of SWF. PCE (●), oil (■) and SDS (○)

Regarding SDS, its removal is less favoured and, although this molecule undergoes oxidation and the concentration decreases by more than 800 mg dm⁻³ during the test, the removal is only marginal as compared to that of PCE and oils, which are almost completely depleted during the treatment. It is important to point out that the removal of SDS is faster just during the period in which PCE is present in the system, in which more than 500 mg dm⁻³ are removed for charges under 20 k h m⁻³ and then, the rate becomes much slower. This might suggest the more effective oxidation of the micelles with PCE

at the initial moments and that after the removal of these micelles, the removal of SDS that it is interacting with soil should become slower because of some sort of protective role for the soil particles, as it will be pointed out later on.

Focusing on the low removal of SDS, Part a of Figure 3 shows the changes in the distribution of SDS between the clarified liquid (obtained after sedimentation) and the interphase (with most of the soil particles). Additionally, Part b of this Figure indicates the values of the z potential of the total treated liquid and of the clarified phase. In addition, it also gives other relevant information about soils behavior during the electrolysis including the ratio between the clarified and the decanted phases and the total suspended solid concentrations. Both panels of this figure have been coloured with the purpose of marking the complex the periods in which the most important changes occur in the system.

As observed, there are strange changes in the distribution of this surfactant (which it is important to remind that it is not a real pollutant, but it was added to extract the pollutants between the clarified and the interphase), with a sudden and fast transfer of the SDS from the clarified to the interphase, which is later reverted and, then, it continues over the complete electrolysis. They indicate a similar predisposition of SDS to form micelles or to interact with soils. These changes seem to have a protective role on the oxidation of SDS (in particular the interaction with soil particles) which seems to be disfavored in comparison with that of the other organics contained. As seem, the two other parameters shown in the Part b seem to change during this first stage in the same fashion. Z potentials are negative at the beginning of the electrolysis but they become even more negative during this first stage (in particular in the soil) and then, they started to increase recovering at the end of the test the initial value. When the system reached the lowest z potential, the separation of the clarified liquid was less efficient and the concentration of total suspended solid (that initially was not expected to change) exhibits also a lower value,

that can be explained in terms of the disaggregation of colloids from the suspended solids particles.

Figure 3. Part a) Distribution of SDS in the clarified liquid (Δ) and in the interphase (▲) and the evolution of total suspended solids (TSS)(■) with the applied electric charge. Part b) Evolution of zeta potential of the clarified liquid (Δ) and of the interphase (▲) and the ratio of volume clarified and decanted (●) with the applied electric charge.

This behavior was reproducible and it was also obtained in the treatment of other SWFs obtained in this work. Thus, Figure 4 indicates changes in the pH, conductivity, particle size (d_{50} and d_{90}) and SDS measured in the clarified phase during the electrolysis carried out to SWF obtained after treating 200 and 300 g of soil with 1 dm^{-3} of SWF. This latter three parameters are only shown for the first 40 k A h m^{-3} , in order to allow the evaluation of the two first zones, in which most of the relevant changes happens (otherwise data are shown as overlapped). The pH decreases very rapidly in both cases and this change seems to be the driving force for the changes in the SDS concentrations, sedimentability and in the particle size, which follow the same pattern: decreases very rapidly and then increases up to a maximum, from which it finally decreases again down to the average value of the soil particle size. This change indicates a huge change during the electrolysis in the micelles composition obtained after the soil washing. The change can start with the decrease in the pH, which favors the transfer of the surfactant to the soil and allows the

rapid adsorption of anions in order to compensate charges (as will seen with sulfate concentration in the next Figure). Then, the micelles are oxidized and recombined to form again larger micelles, which are oxidized completely at the same time that the perchloroethylene and oils contained in them. SDS released from the attack to micelles is not in the clarified liquid but it strongly interacts with the soil particles and this interaction prevents its oxidation.

Figure 4. Electrolysis of soil washing effluents obtained at ratios soil-surfactant solutions of 200 (full points) and 300 g soil L⁻¹ SWF (empty points). a). Changes in pH (■ □) and conductivity (Δ ▲); b) Changes in the particle size (d₅₀ ● and d₉₀ ■) and SDS (▲) concentration

In order to fully understand the process, the interpretation in the changes in the concentration of other species is important. Figure 5 shows changes in the ion concentrations during the electrolysis. As seen, sulfate undergoes a rapid decrease in its concentration which matches with the decrease in the Z-potential and supports the previous explanation about the redistribution of micelles during the very beginning of the electrolysis. Then, it is observed an increase, which is consistent with the removal of SDS. Chloride increases its concentration in the first stage as a consequence of the degradation of PCE and then, it decreases continuously down to its complete depletion. This anion is

sequentially oxidized to hypochlorite, chlorate and perchlorate. However the concentrations of hypochlorite are much lower than that of oxidants produced. This indicates that in addition to this oxochlorinated anion, other oxidants are being formed in the reaction media, being persulfate the most plausible species as it was also pointed out in the literature (¹⁶).

Figure 5. Evolution of ionic species during the electrolysis of soil washing effluents carried out at soil-surfactant solutions of 200 (full points) and 300 g soil L⁻¹ SWF (empty points). a) O, ● Chloride; ◆, ◇ hypochlorite; b) ■, □ chlorate; △, ▲ perchlorate; c) O, ● sulfate; d) O, ● oxidants.

Figure 6 compares the removal of PCE during the oxidation of the soil washing fluids obtained with ratios soil /SWF 0.3 kg L⁻¹ and 0.2 kg L⁻¹. Except for the higher concentrations drawn in the case of the higher ratio, no differences are observed in the

two electrolysis and the concentration decreases down to very low values. This confirms the robustness of this technology. No intermediates were found by GC in any case.

Figure 6. Removal of PCE during the oxidation of soil washing fluid obtained with ratios $\bigcirc$ 300 g soil L⁻¹ SWF $\bullet$ 200 g soil L⁻¹ SWF. Comparison between the oxidation of these solutions with those of synthetic solution of PCE with 3000 mg dm⁻³ of NaCl ($\blacksquare$) and lindane soil washing solution obtained by using 200 g soil L⁻¹ SWF ($\blacktriangle$).

Regarding kinetics, the results does not fit the expected first order kinetic. Thus, as a consequence of the competition between the removal of perchloroethylene, oils and SDS, the removal rate of perchloroethylene does not perfectly fits a first order kinetic but instead of these two regions are found. This rate is much lower than that obtain during the electrolysis of a synthetic solution containing perchloroethylene in the absence of SDS (also shown in the figure) even in the first faster zone. On the contrary the removal seems

to be more efficient than the removal of lindane obtained by soil washing with the same ratio SDS/pollutant pointing out the good performance of the electrolysis for the treatment of this pollutant ¹⁶. In addition, during that electrolysis of lindane, the same two zones were observed pointing out the similarities between performance of the technology with two very different pollutants.

4. Conclusions

From this work the following conclusions can be drawn:

- Combined soil washing and electrolysis with diamond anodes can be used to remove PCE and oils from soils. High concentrations of SDS are required in the soil washing fluid for an efficient extraction of the chlorinated hydrocarbon and this forces to apply electrolysis not only to the clarified liquid but to also to the interphase, where most of the pollutant is concentrated
- SDS interacts strongly with soil not only during the washing step but also during the electrolysis. This interaction seems to play a protective role against the oxidation of SDS. First moments of the electrolysis are rather complex and there are several processes which modifies importantly the results.
- Removal of PCE is less efficient than that obtained during the electrolysis of synthetic solutions of this chlorinated pollutant. There are two first order kinetic zones, which indicate competition in the electrolysis.

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