Electrolysis with diamond anodes of the effluents of a combined soil washing – ZVI dechlorination process

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Abstract

In this work, a new soil washing process in which Soil-Liquid extraction technology is enhanced by adding iron particles (zero valent iron nanoparticles or granules) was investigated to remove clopyralid from spiked soils. This novel approach can be efficiently used to extract chlorinated hydrocarbons from soil and aims to obtain soil-washing wastes with low content of hazardous chlorinated species. The iron particles used were subsequently removed from the treated soil using magnetic fields. Then, the complete mineralization of the produced soil washing effluents was successfully achieved by applying anodic oxidation with diamond anodes in an electrochemical flow cell. Results demonstrated that, opposite to what it was initially expected, no improvements in the efficiency of the electrochemical process were observed by adding iron particles during the soil washing. This behavior is explained in terms of the lower electrochemical reactivity of the dechlorinated derivatives produced. Although results are not as promising as initially expected, it does not mean a completely negative outcome for the use of ZVI during washing, because the hazardousness of the pollutants is rapidly decreased in the initial stages of the soil-washing, opening the possibility for the combination of this technology with other processes, such as biological treatment

Keywords

Soil washing; clopyralid; electrolysis; diamond anodes; ZVI dehalogenation

Highlights

- Combination of ZVI dehalogenation and soil washing in a single stage is feasible
- The type and concentration of iron used determine the soil washing composition
- Anodic oxidation is an efficient treatment for soil washing wastes
- Dechlorinated species in the waste leads to lower efficiency in the electrolysis

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1. Introduction

The combination of soil-washing and anodic oxidation for removing chlorinated hydrocarbons and other species from soil has received a great deal of attention [1-3]. Results shown in different works indicate that the combined technologies can be considered as an alternative for the remediation of acute accidental pollution in small confined amounts of soil [4-10], especially when the electrolysis with diamond electrodes is used, because of the high efficiencies reached always, which highlight the outstanding performance of the diamond coatings as electrocatalytic material [11-14].

In this context, the toxicity and hazardousness of wastes can be expected to decrease significantly by the dehalogenation of the pollutants contained. Because of that, the development of zero-valent iron (ZVI) dehalogenation processes has been recently investigated. In this process, chlorinated hydrocarbons (RCl) are transformed into less halogenated molecules (RH), with the release of chloride and ferrous ions and the consumption of acidity (eq. 1).

$$Fe^0 + RCl + H^+ \rightarrow Fe^{2+} + RH + Cl^- \qquad (1)$$

This slow heterogeneous process is developed on the surface of iron particles and, hence, its kinetic rate can be increased by using tiny iron nanoparticles (nZVI), with average diameter below 100 nm [15, 16]. These nanoparticles have a larger specific surface area than that of the more conventionally-used granule particles. Thus, the rate of the dehalogenation is expected to be significantly enhanced with their use, when the same mass dosages of iron are compared.

The application of nZVI has been extensively evaluated over the last two decades to treat halogenated compounds [17, 18], such as trichloroethylene (TCE) [19, 20], perchloroethylene (PCE) [21] and polychlorinated biphenyls (PCBs) [22, 23]. Also, this technology has been used to treat other contaminants, namely pesticides [24], herbicides

[25, 26], nitroaromatic compounds [27], a variety of metal ions including Cr(VI) and Pb(II) [28, 29], and arsenic [30, 31], among many others. Results are very promising but although ZVI dehalogenation is efficient as decontamination process, it is not a final treatment and, because of that, it is frequently combined with other technologies in order to enhance its effectiveness [32].

In order to develop methods that can rapidly remove the hazardousness associated to the occurrence of chlorinated hydrocarbons in soil, the combination of soil washing and iron dehalogenation is proposed as promising treatment in this work. This novel approach aims to obtain soil-washing wastes with low content of hazardous chlorinated species. Then, these spent soil washing fluids can be electrolytically treated, regenerating the soil-washing fluid for further use. In order to reach this objective, there are two possibilities: integrating soil washing and electrolysis in the same reactor or applying the two technologies sequentially. The first approach was recently evaluated in another work of our group[33], while the evaluation of the second is the main objective of this work. In this frame, the treatment of soil polluted with clopyralid (as a model of soluble chlorinated hydrocarbon) is going investigated by soil washing dehalogenation process with ZVI particles.

Clopyralid (3,6 dichloro-2-pyridinecarboxilic acid) is a widespread herbicide used to control broadleaf weeds. It is highly soluble in water and its volatilization is considered negligible because of its low vapor pressure (0.002 Pa at 298.15 K) [34, 35].

The soil washing wastes obtained are going to be treated by electrolysis with diamond anodes. It is aimed to determine if the dehalogenation has a positive impact on the overall treatment results, as initially it could be expected by considering the lower hazardousness of the non-halogenated pollutants.

2. Materials & Methods

2.1 Chemical reagents. The material selected as model soil was the kaolinite, which is characterized by its inertness, low cation exchange capacity, low hydraulic conductivity and zero organic content [36, 37]. Clopyralid (99%), purchased from Sigma Aldrich, was selected as a model of organic compound. Two types of iron were studied: 1) micro iron (≥99%) reduced, powder (fine) purchased from Sigma Aldrich at which the average size is 568 µm 2) dry air-stable nZVI purchased from Nanofer Star (NanoIron, Czech Republic) that was used as received which the average size of the iron particle added is 1.07 µm. Methanol HPLC grade and formic acid (Sigma-Aldrich, Spain) were used for the mobile phase. Sulfuric acid (98%) (Scharlab, Barcelona) were used to control pH. Double deionized water (Millipore Milli-Q system, resistivity: 18.2MΩcm at 25 ºC) was used to prepare all solutions.

2.2 Preparation of polluted soil. In the lab-scale studies, the contamination method frequently used to evaluate the remediation technologies is the spiking soil sample with organic compounds [9, 38]. For this reason, a solution was prepared by dissolving clopyralid in Milli-Q water and subsequently, this was mixed with clay soil to obtain the samples of polluted soil. The excess of water was evaporated when the polluted soils were aerated for 1 day. Then, the clopyralid was homogeneously distributed into the soil, obtaining a concentration after the pollution procedure of 0.1 g kg^{-1} of soil.

2.3 Soil washing procedure with ZVI. Samples of 300 g of polluted soil were placed in bottles. For each one, selected doses of nZVI and micro ZVI were added (30 and 45 g/L) and then, these were filled with 1 L of water and close with a plastic cap. Then, bottles containing soil, water and iron particles were shaken on a mechanical stirrer for 72 h at a stirring rate of 500 rpm, keeping a temperature of 40 °C. After stirring, the tanks were allowed to stand (for 24 h) to split up the soil from the washing effluent generated during the soil washing process. Iron was removed simply by using a lab-magnet and it was characterized after the treatment.

2.4 Electrochemical treatment of soil washing effluents. Anodic oxidation experiments were carried out in a bench-scale plant by using an undivided electrochemical flow cell (inter-electrode gap was about 1.8 mm) for treating the soil washing effluents (Figure 1). Two monopolar electrodes were used: Boron doped diamond (BDD) (WaterDiam, Switzerland) and stainless steel was used as anode and cathode, respectively. A BDD circular electrode with a geometric area of 78 cm^2, boron concentration of 500 mg dm^{-3}, a thickness of 2.50, sp^3/sp^2 ratio of 225 and p-Si as support. The soil washing effluents were stored in a thermo-regulated glass tank with a capacity of 1.0 L and circulated through the cell using a peristaltic pump at a flow rate of 50 L h^{-1}. The electric current was provided by a Delta Electronika ES030-10 power supply (0-30V, 0-10A), and the electrical current density applied was 25 mA cm^{-2}. Temperature of the system is kept constant (25ºC) by means of a thermostatised bath (JP Selecta, Digiterm 100) and a heat exchanger.

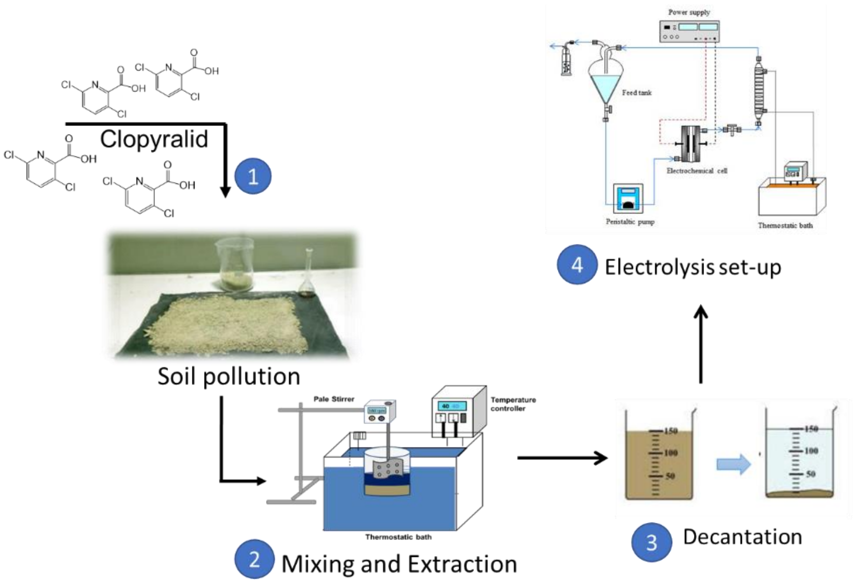

Figure 1. Scheme of the experimental procedure followed from the soil pollution to the electrochemical treatment of the washing effluents generated. 1. Pollution of soil with clopyralid. 2. Mixing and extraction of pollutant to the washing fluid. 3. Decantation process. 4. Electrolysis with BDD electrodes of polluted liquid phase.

2.5 Analytical Techniques. During the soil washing and the oxidation of the soil washing effluent, several samples were taken at selected time intervals, shorter in the first day (8 hours) and longer after the following days (10 hours). They were filtered with 0.22 µm Nylon Supelco filters before analysis. The concentrations of the clopyralid and intermediates were quantified by HPLC (Agilent 1200 series) as described elsewhere [39]. Dehalogenated intermediates of clopyralid also were analyzed with the same HPLC procedure optimized to identify the parental compound. The use of the same method avoids new measurements of the same samples with the unnecessary use of additional resources. A Multi N/C 3100 Analytic Jena analyzer was used for monitoring the total organic carbon (TOC) concentration. Measurements of pH and conductivity and anions were carried out as described elsewhere [1]. Size range of ZVI particles was measured using a Malvern 2000 analyser (Malvern Instruments).

3. Results and Discussion

The changes in the concentration of clopyralid in the soil washing fluid (SWF) during the washing process are shown in Figure 2.

To start with, a sudden increase in the concentration of clopyralid in the washing fluid it is observed (in presence or in absence of iron particles). This behavior is related to the chemical properties of the carboxylic group that make it high soluble in water. Additionally, the soil composition has a paramount importance because the kaolinic soil has a low cation exchange capacity that explain the nearly instantaneous extraction in the early beginnings.

Then, when the iron particles were used during soil washing treatment, a gradual decrease in the clopyralid concentration was attained up to a constant value. This behavior may be related to the dechlorination process, which is known to be carried out in several consecutive steps, including not only reactive stages but also the adsorption of the chlorinated species onto the iron catalyst surface and onto the growing iron hydroxide precipitates formed.

Another important observation is that the extraction of clopyralid from soil is not only fast, but it is also quantitative. This result was also observed in previous studies in which the simpler conventional soil-washing technology was evaluated [1, 2]. Opposite, the dechlorination reactions are much slower and seem to be more complex. Thus, no significant differences are observed between the two dosages of iron used, just a slightly faster decrease in the clopyralid concentration when using nanoparticles of ZVI. This observation suggests that the process depends on the active area of the iron particles in contact with the chlorinated hydrocarbon pollutant, which is more significant at nZVI, although there is not a linear dependence between both parameters.

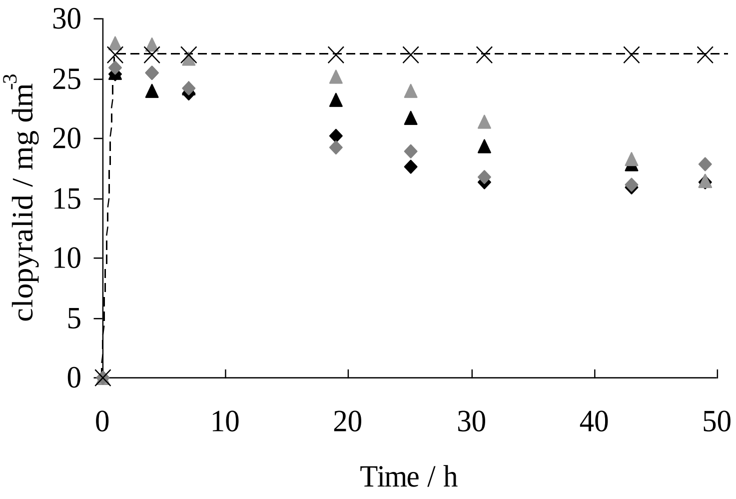

Figure 2. Changes in the concentration of clopyralid during the soil washing with the addition of granular iron (▲30 g kg^{-1}, ▲45 g Kg^{-1}), ZVI nanoparticles (◆30 g kg^{-1},◆45 g kg^{-1}) and no iron (×).

In order to understand the processes that develop during the electrochemical conversion of clopyralid, the identification and quantification of the dehalogenated derivatives formed during the soil washing process was carried out (Figs. 3 and 4). As can be observed, clopyralid is transformed into 6-chloropicolinic acid, 3-chloropicolinic acid and the fully dehalogenated picolinic acid, according to eqs. 1 and 2.

$$Fe^0 + C_6H_3Cl_2NO_2 + H^+ \rightarrow Fe^{2+} + C_6H_4ClNO_2 + Cl^- \qquad (1)$$

$$Fe^0 + C_6H_4ClNO_2 + H^+ \rightarrow Fe^{2+} + C_6H_5NO_2 + Cl^- \qquad (2)$$

Based on these observations, the soil-washing process cannot be considered only as a simple solid-liquid extraction, but it is confirmed that it behaves as a more complex reactive process, because the clopyralid is converted in several intermediates by the heterogeneous catalytic-dechlorination reactions carried out onto the iron catalyst surfaces (granular and nanoparticles). In addition, the reactivity seems not to be the same when soil-washing is carried out with iron nanoparticles or iron granules. In the former case, the main products are the monohalogenated derivatives: 3-chloropicolinic acid and 6-chloropicolinic acid. Conversely, the fully-dehalogenated picolinic acid is mainly produced, in the latter case.

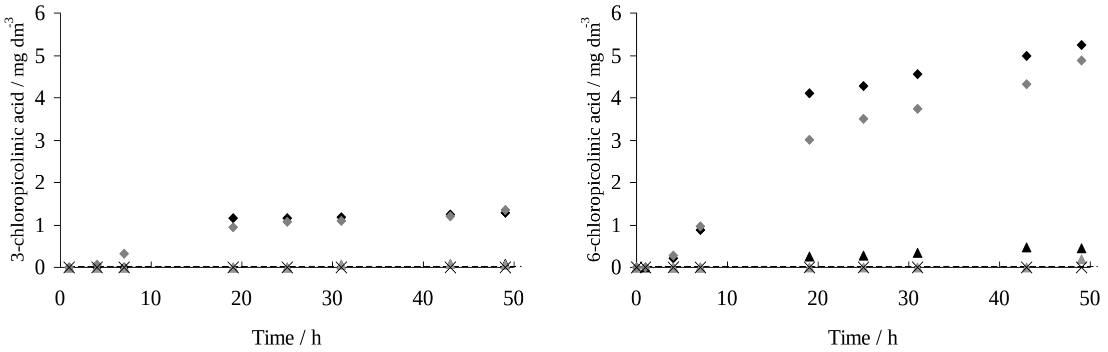

Figure 3. Changes in the concentration of monohalogenated derivatives of clopyralid during the soil washing with the addition of granular iron (▲30 g kg^{-1}, ▲45 g Kg^{-1}), ZVI nanoparticles (◆30 g kg^{-1},◆45 g kg^{-1}) and no iron (×).

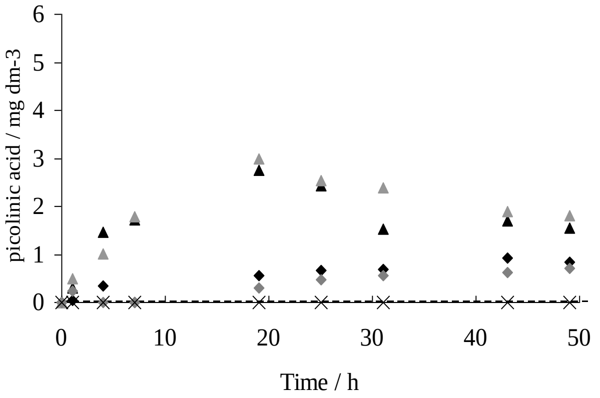

Figure 4. Changes in the concentration of picolinic acid during the soil washing with the addition of granular iron (▲30 g kg^{-1}, ▲45 g Kg^{-1}), ZVI nanoparticles (◆30 g kg^{-1},◆45 g kg^{-1}) and no iron (×).

Another aspect that must be remarked is that no important differences were observed, in terms of elimination of clopyralid when different dosages of iron were used (30 and 45 g kg^{-1} of soil), suggesting that the heterogeneous catalytic process is not limited by the iron content, at least within the concentrations range used in this work.

As indicated previously, the soil-washing is applied as first step to remove clopyralid from the soil. Results confirms that this extraction is efficiently performed due to the fast transfer of the pollutants from the soil to washing fluid. However, soil washing is not a final treatment but just an operation in which the pollution is transferred from the soil to a liquid and additional treatments are necessary to achieve complete removal of the pollutants [32] from the washing wastewater produced.

Therefore, the effluent was electrochemically treated by applying anodic oxidation with BDD anodes. In order to discuss results, it is important to indicate that, with the procedure applied in this work, the soil-washing fluids may contain small amounts of iron particles not completed separated during the soil washing process and they may have an impact on the results of the electrolysis. This is more important in the case of the soil washing with the nZVI, because of the very small size of the particles which disfavor its complete separation using magnetic fields.

Regarding the SWF obtained after the washing process, Fig. 5 shows that the initial TOC concentrations are different in each test. The initial lower values of TOC in the washing fluids produced during treatment with iron may be explained by the different adsorption/reaction steps attained when iron catalysts are used in solution. Among them, it is important to highlight the adsorption of pollutant molecules onto the growing iron (III) hydroxide precipitate (that it is formed after the release of iron (II) and its further oxidation with oxygen) in the soil washing fluids (SWFs). In addition, when iron materials were introduced, reaction steps are performed, transforming clopyralid into other byproducts (dehalogenation reactions are attained), as already confirmed by the results reported in Figs. 3 and 4.

In the onset of Fig. 5 it can be noted that there is a faster depletion of TOC in the electrolysis of SWFs obtained without addition of iron. Lower coefficient of determination (R^2) has been obtained with granular iron because of the higher heterogeneity of active surface in comparison with the nano-ZVI particles. This indicates that more persistent pollutants are produced when iron catalysts are used. On the other hand, a first order kinetic decay is confirmed for all tests carried out, as it could be expected for the mineralization of low concentrated organics using anodic oxidation with diamond anodes [40, 41]. However, the mineralization rates reached during the anodic oxidation are not affected by the different dosages of iron used in the SWFs. Then, even when the SWFs contain persistent pollutants, which are difficult to be mineralized, there is no direct relationship between the concentration of iron used in the soil washing step and the decrease in the mineralization rate by anodic oxidation.

In this frame, the changes in the concentration of clopyralid and dehalogenated derivatives were evaluated in order to understand the electrochemical mineralization treatment of this spent SWF. It is important to highlight that no other byproducts were detected by chromatography during electrolysis with BDD. This can be explained in terms of the low initial concentrations of organics contained in the SWF. In this range of concentrations, the intermediates formed electrochemically in the nearness of the electrode surface are known to be rapidly oxidized and, hence, they are almost not detected by chromatography as it has been pointed out many times in the literature [42-44].

The changes in the concentration of clopyralid and the three dehalogenated derivatives in the five tests are reported in Figs. 6 and 7. As can be seen, a complete electrochemical mineralization is always achieved. In the case of clopyralid, its rapid oxidation supplements the previous dehalogenation process achieved during the soil washing treatment and it results in its complete removal from the SWF. Picolinic acid is also completely depleted for very low current charges, as it could be initially expected because of its very low initial concentration.

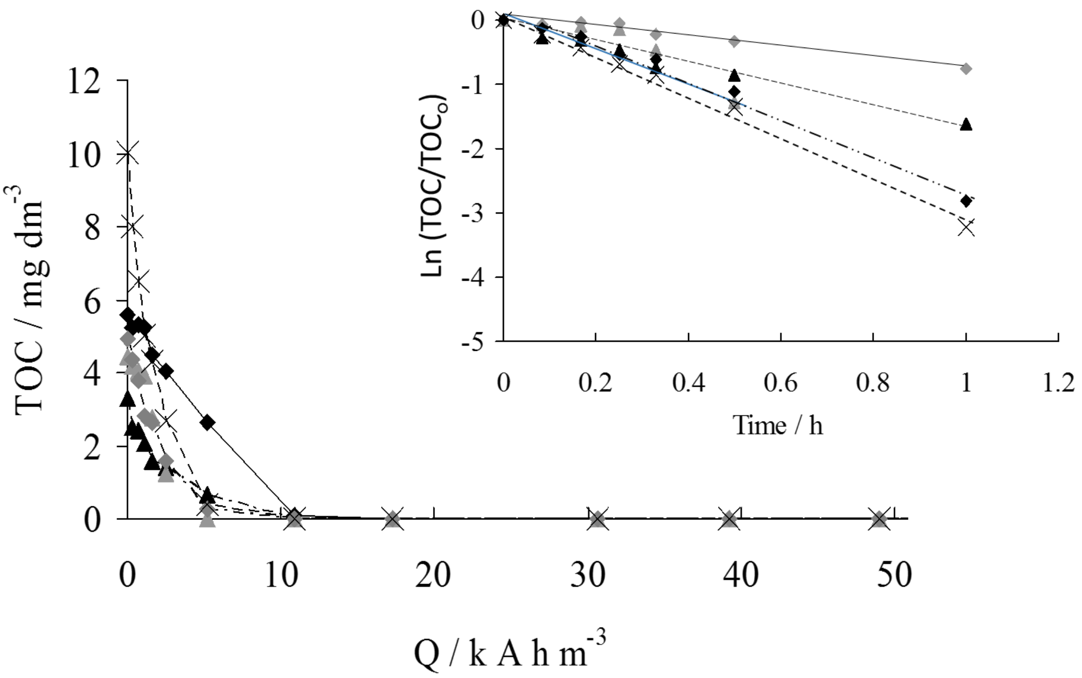

Figure 5. Changes in the TOC concentration during the electrolysis of the waste obtained with the addition of granular iron (▲30 g kg^{-1} r^2=0.892, ▲45 g Kg^{-1} r^2=0.868), ZVI nanoparticles (◆30 g kg^{-1}, r^2 = 0.982,◆45 g kg^{-1}, r^2= 0.981) and no iron (×, r^2 = 0.991) during the soil-washing process. Onset: representation in semi-logarithmic and normalized plot for kinetics evaluation purpose.

Meanwhile, the elimination of the mono-halogenated derivatives produced during the soil washing with iron is completely different. For the experiment without iron, these by-products are not present in the SWF and the mineralization behavior is associated to the electrochemical combustion of clopyralid, being a fast process. Conversely, in the tests where the iron catalysts were used, the mono-halogenated derivatives are degraded more slowly than the initial clopyralid. In fact, the removal rate for the 6-chloropicolinic acid is much slower than that of the clopyralid. This result is particularly relevant for the post SWFs treatment, because the concentration of the dechlorination intermediates in the effluents is very high (especially in the effluent treated with nZVI) and this process requires more than a 3 times higher current charge to deplete these species. Then, the lower efficiency in the mineralization of these wastes can be explained in terms of the difficulties in the oxidation of these molecules and it is a negative point for the combination of technologies.

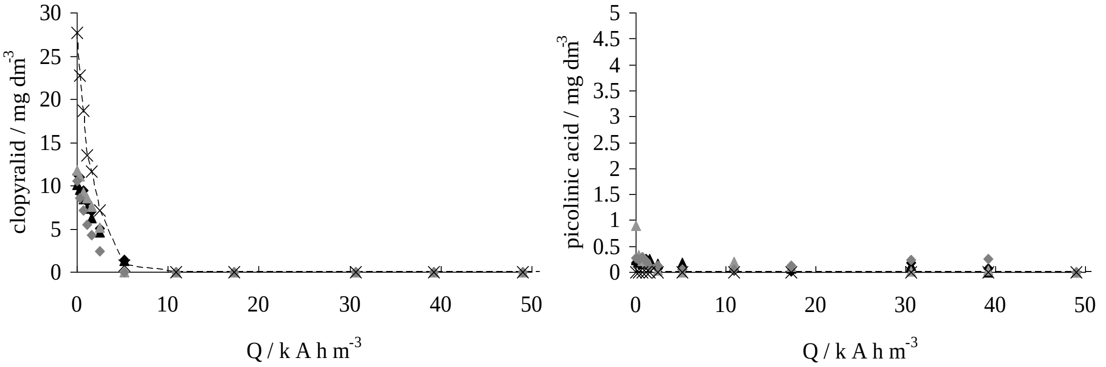

Figure 6. Changes in the concentration of clopyralid and picolinic acid during the electrolysis of the waste obtained with the addition of granular iron (▲30 g kg^{-1}, ▲45 g Kg^{-1}), ZVI nanoparticles (◆30 g kg^{-1},◆45 g kg^{-1}) and no iron(×) during the soil-washing process.

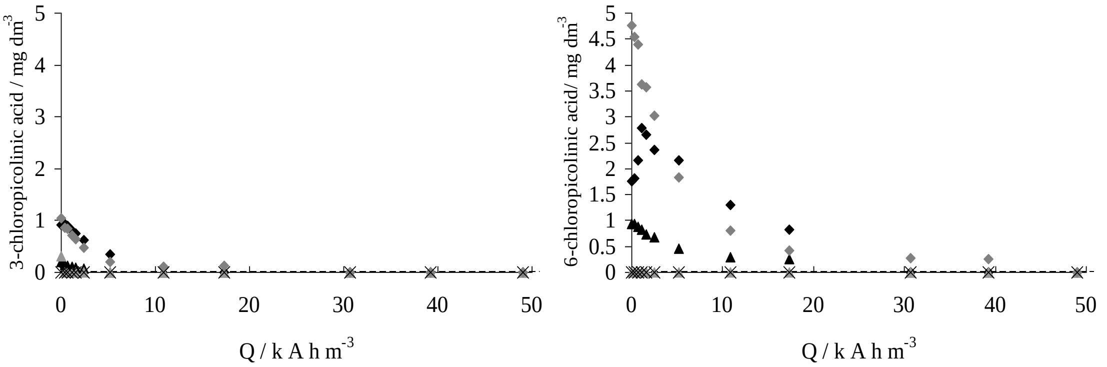

Figure 7 Changes in the concentration of mono-halogenated derivatives of clopyralid during the electrolysis of the waste obtained with the addition of granular iron (▲30 g kg^{-1},▲45 g Kg^{-1}), ZVI nanoparticles (◆30 g kg^{-1},◆45 g kg^{-1}) and no iron (×) during the soil-washing process.

The evolution of inorganic species is also important in order to fully understand the process, because the electrogeneration of oxidants can be promoted from the ions release during the oxidation of the organics or simply from the ions contained in the SWF. For this reason, the concentration of chloride, in the effluents of the soil washing processes in which iron is added, was followed to understand the processes. As expected, significant concentrations of chloride were detected in the SWFs. As seen in Figure 8, these concentrations are higher when granular iron was used. This can be explained in terms of the most extended dehalogenation treatment, which is supported by the final byproducts obtained (picolinic acid instead of 6-chloropicolinic or 3-chloropicolinic acids). Meanwhile, lower concentration of chloride was determined when no iron catalyst was used. It indicates that in that case the initial concentration of chloride only comes from the ionic exchange of the SWF with the soil.

Another interesting feature worth to be commented is that the maximum chloride concentration is attained at the beginning in the tests carried out to SWF obtained with iron. This means that the dehalogenation is also one of the first step during electrolysis. This dehalogenation is not an anodic, but a cathodic process and it also stands for the small increase observed at the beginning of the tests in the concentration of monochlorinated derivatives.

The decrease on the chloride concentration is due to the formation of higher oxidation oxochlorinated anions, such as hypochlorite, chlorate and perchlorate, which, as already known, is one of the drawbacks associated to the use of anodic oxidation with diamond anodes [45-48].

A last interesting point to be discussed in this work is the comparison of the changes in the pH and conductivity (Figure 9). As can be seen, the electrolysis for both SWFs, treated with nZVI or granular iron, are completely different. In the first case, there is almost no changes in the conductivity and the decrease of the pH is limited. In the other case, there is a change of more than 5 pH units, pointing out the development of different processes, as already indicated by the intermediates contained in the SWF.

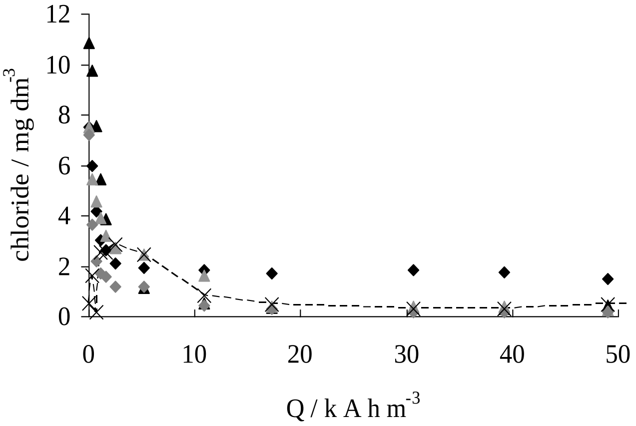

Figure 8. Changes in the chloride concentration during the electrolysis of the waste obtained with the addition of granular iron (▲30 g kg^{-1}, ▲45 g Kg^{-1}), ZVI nanoparticles (◆30 g kg^{-1},◆45 g kg^{-1}) and no iron (×) during the soil-washing process.

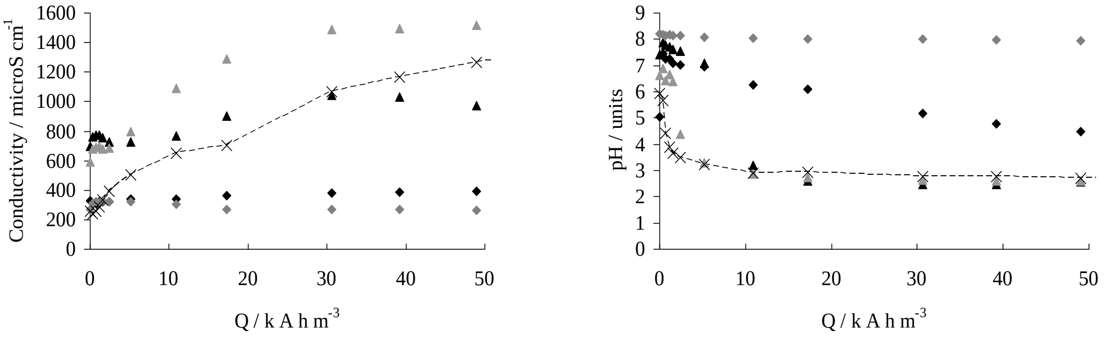

Figure 9. Changes in the conductivity and pH during the electrolysis of the waste obtained with the addition of granular iron (▲30 g kg^{-1}, ▲45 g Kg^{-1}), ZVI nanoparticles (◆30 g kg^{-1},◆45 g kg^{-1}) and no iron (×) during the soil-washing process.

Hence, the promotion of iron dehalogenation during the soil washing does not result in any relevant advantage from the viewpoint of the mineralization of the waste. On the contrary, the system becomes less efficient and this can be explained because of the lower electrochemical oxidazability of mono-halogenated derivatives. Anyhow, because of the lower hazardousness of the non-chlorinated intermediates, this can be a good option for combined biological electrochemical process. Further studies are being conducted in order to confirm this point.

4. Conclusions

Based on the results obtained, we can conclude that is possible to combine ZVI and soil washing in a single treatment. Clopyralid is efficiently removed from soil but the composition of the SWFs is markedly different depending on iron particles used. In all cases, the release of the pollutant from soil to the SWF is very rapid and effective, as also observed in previous studies in which the simpler conventional soil-washing technology is applied. 6-chloropicolinic, 3-chloropicolinic and picolinic acids are the final products found in the soil washing with iron particles and the speciation depends on the type of iron added during the soil washing process. However, this process is not a final treatment but just an operation in which the pollution is transferred from the soil to a liquid and additional treatments are necessary to achieve complete removal of the pollutants. Thus, the complete degradation of the pollutants in the SWFs was possible by using anodic oxidation with diamond electrodes, and a first order kinetic decay (in terms of mineralization) was confirmed for all tests carried out. Opposite to what it could be expected, the oxidation of non-chlorinated species is not favored with respect to the electrolysis of the raw effluent of the soil washing (only clopyralid is contained in the solution) and the overall remediation process is less efficient from the viewpoint of the current charge required. Anyhow, with this process the hazardousness of the waste is decreased from the very beginning, making promising the combination of this technology with biological treatments.

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