Integrating ZVI-dehalogenation into an electrolytic soil-washing cell

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Abstract

Combination into a single electrochemical reactor of soil washing, ZVI dehalogenation and anodic oxidation can be used to degrade directly the clopyralid contained in spiked soil. Treatment is efficient, achieving the complete removal of chlorinated organics as well as the complete mineralization of the liquid waste produced. However, this combined process does not seem to improve the efficiency with respect to a system operated without addition of iron. Results show that the dechlorinated intermediates formed are less reactive than the parent pollutants, being particularly important the formation of oxalic acid, because its combination with iron (II) helps to explain the decrease in the overall rate of mineralization. This negative impact on the efficiency of the electrochemical process is not completely undesirable, because the toxicity of the waste decreases importantly in the very early stages with the use of iron, opening the possibility of a combination with biological treatments. Again, the accumulation of oxalate intermediates helps to explain this conclusion. Results point out the important effect of the size of iron particles used on the treatment and the complexity of the mechanisms that develop in the cell, which are explained in terms of the different parameters monitored.

Keywords

Soil washing; clopyralid; electrolysis; diamond anodes; ZVI

Highlights

- ZVI dehalogenation can be combined with the integrated soil-washing electrolysis
- Impact of combination is under expectation from the viewpoint of efficiency
- Dehalogenation leads to a less reactive mixture with lower toxicity
- Key role of oxalic acid on the combined process performance

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Introduction

The combination of soil washing with electrolysis has demonstrated to be extremely promising in the search of novel treatment technologies that could be applied for the remediation of soils polluted with chlorinated hydrocarbons. It is highly effective in the depletion of the pollutants from the soil and its cost is not very high, in particular if compared to that of other competing technologies [1, 2]. One important point looked for in this technology is the fast reduction in the hazardousness of the waste, which in the case of soils polluted with chlorinated hydrocarbons can be attained just by dechlorinating the pollutants during the soil washing process [3].

Reaction with zero-valent iron (ZVI, Fe^0) is one of the most promising technologies to achieve this dechlorination [4]. The overall dehalogenation reaction by ZVI is represented by eq. 1, where in R indicates a hydrocarbon group and X a halogen atom contained in the chlorinated hydrocarbon. As seem, during the process, chloride and ferrous ions are released to the wastewater, while acidity is consumed. Typically, ferrous ion will undergo many transformations depending on the matrix of the wastewater, being the most important its transformation into iron (III) species. This feature may have a great relevance in case of combining this technology with oxidative processes, because it can promote the formation of very powerful oxidation reagents (such as the Fenton reagent in case of dosing hydrogen peroxide).

The relevance of the ZVI dechlorinating technology is supported by the high number of scientific works published in the last decade, in which the ZVI has been intensively studied for the remediation of water and soil polluted with a wide range of contaminants,

including not only chlorinated organic compounds [4-8] but also inorganic hazardous pollutants such as arsenic, and heavy metals [9-13]. According to these works, the main drawback of this process is the slow kinetics of this reaction, which is aimed to be improved with the use of nanoscale ZVI (nZVI, <100 nm)[13-15]. The specific surface area of the nanoparticle (10-100 nm) is several times larger than that of a micro-scale particle and, hence, the reactivity seems to be significantly enhanced with their use.

When accidental spills occurs, soil washing can be a very good technology, because it can be applied rapidly avoiding the diffusion of the pollution. Depending on the solubility of the pollutants, the soil washing fluid used can consist simply of water or it has to be a more complex formulation containing surfactants [16-19]. After the soil washing, pollution is transferred from the soil to the soil washing fluid, becoming into a soil washing waste that has to be treated. A very important objective is the reduction of the pollution in this effluent down to limits that permit its recovery and reuse in the soil washing process. Previous works of our group have demonstrated the good performance of this technology for many different types of pollutants and the feasibility of its combination with anodic oxidation with diamond anodes for the treatment of the soil washing wastes produced [20]. Even, we have demonstrated that we can integrated both technologies in the same reactor, carrying out at a time the soil washing and the depletion of the pollutant in the same electrochemical cell [21]. At this point, it is work to highlight that anodic oxidation with diamond electrodes is a very efficient technology, capable to mineralize almost any type of pollutant with an outstanding efficiency [22-26].

In this work, we aim to compare a novel approach: combination of ZVI dechlorination with the integrated soil washing-electrolysis technology, in order to elucidate if there are clear advantages (or not) with the addition of the dechlorination stage. To do this, we have integrated in the same electrochemical cell prototype, the three stages of the

treatment: soil washing, iron dechlorination and electrolysis. Two types of iron have been compared: nano-ZVI in which the average size of the iron particle added is 1.07 micrometer and iron granules at which the average size is 568 micrometers. The same mass of iron has been used in the tests with the two iron species in order to allow comparison of results.

Materials & Methods

Chemical reagent. Kaolinite obtained from Manuel Riesgo (Spain) was selected as soil model [27, 28]. Clopyralid (99%) from Sigma Aldrich was selected as a model of organic pollutant to evaluate the technology. Two types of iron were tested: micro iron ($\geq 99\%$), reduced, powder (fine) purchased from Sigma Aldrich and Nanofer Star (NanoIron, Czech Republic), which is a dry air-stable nZVI powder used as received. Methanol HPLC grade and formic acid (Sigma-Aldrich, Spain) were used for the mobile phase of the HPLC technique. Sulfuric acid (98%) (Scharlab, Barcelona) were used to regulate the pH. Double deionized water (Millipore Milli-Q system, resistivity: $18.2\text{M}\Omega\text{cm}$ at $25\text{ }^{\circ}\text{C}$) was used to prepare all solutions.

Analytic Techniques. The samples were collected at selected time intervals and were filtered with $0.22\text{ }\mu\text{m}$ Nylon Supelco filters before analysis. The concentration of the clopyralid and their dehalogenated aromatic intermediates were quantified by HPLC (Agilent 1200 series) using a ZORBAX Eclipse Plus5 C18 analytical column. The mobile phase consisted of 30% methanol / 70% water with 0.1% of formic acid (flow rate: $0.8\text{ cm}^3\text{ min}^{-1}$). The DAD detection wavelength was 280 nm, the temperature was maintained $25\text{ }^{\circ}\text{C}$ and the injection volume was $20\text{ }\mu\text{L}$. The short-chain intermediates (aliphatic acids) were quantified also by HPLC using a Hi-Flex H, $300\times 7.7\text{mm}$ analytical column. The mobile phase consisted of H_2SO_4 solution (5mM) (flow rate: $0.5\text{ cm}^3\text{ min}^{-1}$). The DAD

detection wavelength was 210 nm, the temperature was maintained 35°C and the injection volume was 100 µL.

The Total Organic Carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytic Jena analyser. Measurements of pH and conductivity were obtained using a CRISON pH25+ and CRISON CM35+, respectively. The anions were characterized using ion chromatography by means of a Shimadzu LC-20A system. Particle size was monitored using a Malvern 2000 analyser (Malvern Instruments). Toxicity was determined along the different stages of the electrochemical pre-treatment by means of a BioTox™ Kit supplied by Aboatox. The inhibitory effect of the sample on the light emission of luminescent bacteria, *Aliivibrio fischeri*, formerly *Vibrio fischeri* [29], is measured with a luminometer (Junior LB 9509 of Berthold Technologies). This test provides a rapid, easy to use method for measuring toxicity of aqueous samples. The sample toxicity was evaluated as EC50 by measuring the effective concentration at which 50% of the light is lost due to the toxicity [30, 31].

Experimental set-up. The soil washing and the electrochemical oxidation process were simultaneously carried out in the same setup, which consists of one electrochemical cell and one soil-washing and dehalogenation tank, in which the wastewater was continuously recycled during the experiment. The soil-washing and dehalogenation tank consists of a rigid silicon tube 1 m of length and 69 mm of diameter, which was filled with the soil and the fixed amount of iron (Figure 1).

Figure 1. Scheme of soil washing and oxidation reactor.

It stores around 2 L of solution and ends into a metallic mesh (0.5 mm diameter) placed to avoid the loss of soil and iron particles. The electrochemical reactor was a commercial single compartment DiaCell ® Type 101 equipped with a Boron doped diamond (BDD) (WaterDiam, Switzerland) as anode and stainless steel as cathode. The electrodes were circular with a geometric area of 78 cm². The diamond coating was deposit on a p-Si as support and contained a boron concentration of 500 mg dm⁻³, and it had a thickness of 2.50 and sp³/sp² ratio of 225. The electrode gap between anode and cathode was 1.8 mm. The electric current was provided by a Delta Electronika ES030-10 power supply (0-30V, 0-10A). The current density applied was 25 mA cm⁻² in a galvanostatic mode, according with previous results obtained [21]. The temperature was kept at 40 °C using a thermostated bath. A pump continuously recirculates the wastewater throughout of the two operations at 40 dm³ h⁻¹.

Results and Discussion

Figure 1 shows the changes in the concentration of TOC during the combined treatment studied in this work, at which (as already described) the soil washing with iron particles and electrolysis were simultaneously performed in the same cell. Results are compared to

those obtained in a conventional combined soil washing-electrolytic process, in which no iron is added.

As expected, release of the pollutant from the soil to the soil washing fluid (electrolyte) is almost instantaneous and from the first moment, the maximum concentrations of pollutants in the liquid are obtained. This result is in agreement with our previous results obtained in the evaluation of a prototype for the combined soil-washing and electrolytic treatments, which demonstrated that this novel technology may exhibit several advantages, as compared to the sequential application of the two treatments [21]. It is important to state that initial time in the plots corresponds to the moment in which the current was started to be passed throughout the electrochemical cell. It was performed in this form due to operative reasons because the mixture soil, water and iron must be previously in contact for 15 minutes to guarantee its homogeneity. This explains that the values of the different parameters when current was started to be applied, were not nil. At the same time, it is important to note that the iron catalyst (granules or nanoparticles) has significant superficial-area which allows the adsorption of clopyralid, as a previous conversion step, in its surface. For this reason, a variation in the initial TOC values was attained, for each one of the experiments performed (see, Fig. 1). This variation can be increased by the adsorption of clopyralid onto the growing iron hydroxide precipitates, formed after the oxidation of the iron (II) formed during the dehalogenation to iron (III). After the fast initial release, the TOC decreases with a rate that depends on the amount of iron added to the reactor as well as its surface (granules and nanoparticles). In the case of iron granules, there are no great differences in the two tests carried out, suggesting that the dose of iron used is not limiting the process. However, the initial TOC values were around $10\text{-}12\text{ mg dm}^{-3}$, which indicates that the clopyralid in solution is rapidly transformed (by dehalogenation with iron granulates and by electrolysis) when the current

is applied, but TOC decreases slower. Meanwhile, higher initial TOC values were achieved when iron nanoparticles were used and it could be related to the effective transformation of clopyralid when this catalyst is used, generating byproducts that are difficult to be oxidized by electrolysis (when the current starts to pass throughout the cell). By electrolysis without iron catalyst in solution, TOC decays rapidly, showing better performances than with the other process. Nevertheless, a total decontamination is attained in all tests carried out.

As already commented, many potential reactions are promoted, which may be occurring simultaneously in the electrolyte. In addition, several of them can be contradictory from the viewpoint of the treatment, transforming the electrolyte into a very complex reactive system. Thus, in addition to the oxidation promoted by the diamond anode [2] and by the Fenton processes (consequence of the cathodic production of hydrogen peroxide and of the generation of iron (II) with the dehalogenation)[32]; there are other important processes like:

- dehalogenation reductive chemical processes catalyzed by the iron particles (heterogeneous catalytic reaction including adsorption stages) which can lead to the formation of 3-chloropicolinic acid, 6 chloropicolinic acid (eq.2) or fully dechlorinated picolinic acid (eq.3)

- cathodic hydro-dehalogenation reactions, which should lead to the formation of the same intermediates but without iron (II) production (eqs. 4 and 5)

- mediated oxidation carried out by oxidants produced on the anode surface and activated by the iron (II), which occur by homogenous catalytic reactions.

Among these processes, and because of the presence of large concentration of iron particles, chemical dehalogenation is one of the most important reactions expected. In fact, this dehalogenation consists of a reductive process which promotes the formation of less oxidizable compounds than the initial clopyralid, as revealed by TOC evolution. So, what seems to be more important is that, opposite to what it could be expected, addition of iron does not seem to have a positive effect on the mineralization of the soil washing fluid but very negative. In fact, complete TOC removal (complete mineralization) is obtained in the test without addition of any type of iron particles with less than two times of the current charge required for the others approaches. In addition, the less efficient process from the mineralization point of view corresponds to the test in which with the higher surface available of ZVI was used (nanoparticles), and this behavior may be explained in terms of the formation of more refractory byproducts, as already commented above.

Figure 2. TOC removal during the combined soil washing- iron dechlorination and electrolysis treatment. Experimental conditions: 25 mA cm⁻² and 40°C. Iron granules: ▲ 48 g, ▲ 72 g; Iron nanoparticles: ◆ 48 g; Without iron: ×.

Although this result can be discouraging and negative from the viewpoint of using electrolysis as final treatment, it can be positive for the combination of dehalogenating soil-washing with other type of final treatments like the biological oxidation and the information obtained can help to develop many other processes. This alternative can be a good possibility that it is starting to be studied in our lab. For this reason, in order to know more about this mineralization, it is important to discuss the changes in the concentration of the different intermediates produced.

Release of clopyralid from soil is almost instantaneous and consequently, concentration of clopyralid increases very rapidly in the electrolyte, just after the startup of the tests, as it is shown in Figure 2 (it is important to indicate that initial time corresponds to the beginning of the electrolysis, after 15 min of homogenization of solution). As explained before, this clopyralid should undergo several processes simultaneously, including electrochemical oxidation, reduction and iron dehalogenation. Competition in the oxidation between the clopyralid and these intermediates may explain the lower oxidation rate observed for this molecule when iron is present in the treatment. It is important to note that there is not a good agreement between the changes in the concentration of TOC and clopyralid, being the profiles very different in the case of the system in which the ZVI nanoparticles are added. However, the clopyralid decay is very related for the tests by using iron catalysts, which may indicate that this organic compound suffers a rapid conversion in other intermediates in short times (minor than those achieved to remove the total carbon concentration in solution, mainly when iron nanoparticles was used). Meanwhile, by electrolysis, the elimination of clopyralid seems to be fast, confirming that this approach appears to be more efficient.

Figure 3. Clopyralid removal during the combined soil washing- iron dechlorination and electrolysis treatment. Experimental conditions: 25 mA cm^{-2} and 40°C . Iron granules: ▲ 48 g, ▲ 72 g; Iron nanoparticles: ◆ 48 g; Without iron: ×.

Thus, the most important differences are observed in the dehalogenated species produced during the treatment (Figure 4). As seen, the production of picolinic acid is important and it is promoted with the addition of iron, although there are no important differences between the tests carried out with 48 and 72 g of iron granules. There are also no differences when iron granules or nanoparticles are used. This result is in agreement with the clopyralid decay reported in Fig. 3. It is important to point out that no 6-chloropicolinic acid or 3-chloropicolinic acid are detected by HPLC (only traces), which indicates that these intermediates are rapidly reduced to picolinic acid or electrochemically oxidized once formed, because the dehalogenation with ZVI is known to proceed through two sequential steps and there is not a direct one step conversion mechanism.

Figure 4. Trends of the main intermediates formed during the combined soil washing-iron dechlorination and electrolysis treatment: a) picolinic acid, b) oxalic acid. Experimental conditions: 25 mA cm⁻² and 40°C. Iron granules: ▲ 48 g, ▲ 72 g; Iron nanoparticles: ◆ 48 g; Without iron: ×.

Another important point to be highlighted is that picolinic acid is a less hazardous pollutant than clopyralid, so its formation can be seen initially as positive. However, this compound seems to be more refractory to the electrochemical treatment than the clopyralid and, although it is oxidized, according to the experimental results, the rate is much slower. In addition, it contributes to make slower the elimination of organic compounds in solution (e.g.: TOC decay (see, Fig. 2)) because it competes for the oxidants produced on the electrodes during the electrolysis by the recombination of hydroxyl radical (eq. 6), by the reaction of this radical with oxygen (eq. 7) or by oxidation of ions present in the solution (as will be explained later).

However, the most important difference shown in Figure 4 is not in the picolinic acid concentration but in other intermediate detected by HPLC, the oxalic acid. It behaves as a very important species in the case of the process with nano-ZVI iron and less important

(although it also occurs) in the case of the tests in which the granular ZVI was used and, also, in the process with not external iron was added. It is clearly the main responsible of the slower mineralization (TOC decay) in the presence of iron nanoparticles because it is present in the solution when the current is applied. Thus, the slower mineralization observed in this approach can be explained in terms of the formation of iron(II) oxalate complexes, which are known to be difficult to be oxidized.

No other organic were detected during the treatment, being this observation consistent with the results obtained in previous works focused on the degradation of organics at very low concentrations by electrolysis with diamond anodes [33, 34]. In those works, it was demonstrated that this process behaves as a sort of electrochemical cold combustion for which once the pollutant molecules start to be oxidized, they are fully converted into carbon dioxide without the occurrence of appreciable concentrations of intermediates [35].

In order to see if the speciation observed has an influence on the hazardousness of the soil washing waste (and then to initially appreciate the perspectives of a combination with biological treatments), the toxicity of three samples was measured in the treatment without iron addition and in one of the treatments with each type of iron (before electrolysis, after a low electric charge passed and after the treatment). Figure 5 presents the evolution of the EC_{50} along the electrolytic treatment. This parameter indicates the concentration causing and inhibition over the 50% of the individuals and in the plot it was expressed as the mL of the soil washing waste electrolyzed needed to deactivate 50% of the light produced by the *Aliivibrio fischeri*. It can be seen that initially, before the application of current, the toxicity is slightly reduced simply with the addition of iron particles, being the most important decrease observed with the nanoparticles. This observation may be related to the initial dehalogenation of the clopyralid and is in

agreement with the speciation observed. However, the most important changes are developed with the application of current. In the test carried out without addition of iron, toxicity decreases initially but then it came back to the initial value. However, in the other two test (with iron) there is an initial negative effect of current which is then reverted and leads to a treated solution with a much lower toxicity, in agreement with the speciation observed and that suggests that combination with biological treatments can be a good choice.

Figure 5. Changes in the EC₅₀ during the electrolysis of washing fluid in a set-up with no iron (○), macro zero valent iron particles (◐) and nano zero valent iron particles (●).

Regarding other species with interest to understand the process, chlorine species are expected to be the most important, because they are expected to be released 1) from the soil during the washing (mainly by ion exchange), 2) from the clopyralid by chemical and electrochemical hydrodehalogenation and, because of the electrochemical process, they can undergo many different transformations. In particular, because of the use of diamond anodes, it is expected the oxidation of chloride to chlorate and perchlorate, which is a non-desired process, typically associated with diamond electrolysis.

Figure 6 shows the concentrations reached at the end of the tests carried out. As seen, they differ significantly. There is almost no chloride in the case of the test carried out without iron and although concentrations in the test with granular iron are low (below 2 ppm), they become much more relevant in the case of using nanoparticles because in that case the concentration rises up to 8 ppm. Initially, this higher concentration can be explained by a more efficient dechlorination of clopyralid, because of the larger surface area of this iron reagent, which makes it more active towards dechlorination.

On the other hand, in the test without addition of iron, it can be observed a very high concentration of hypochlorite (<6 ppm), which is much lower in the cases of the tests carried out with iron (< 1 ppm). To explain this observation it has to be taken into account that chlorine formed electrochemically can react with iron according to eq. 1 producing ferric chloride. This reaction cannot occur in the case of the system without iron particles and this explains the higher concentration of hypochlorite and also the important concentrations of chlorate and particularly of perchlorate in that case.

Solubility of iron chloride is high and this means that iron (III) is going to be present in the system. Iron (III) is known to form many different species by water electrolysis

including insoluble iron hydroxide, which may act as solid that retains chlorides, helping to explain the lower concentration of chlorates and perchlorates when iron is present [36].

It can also be reduced cathodically to iron (II). However, this reaction seems to be not efficient in the case of dosing iron nanoparticles and this observation can be explained because of the formation of iron (II) and iron (III) oxalate salts and complexes, which do not exhibit any protecting role for the chloride against the oxidation to chlorate and perchlorate and support their high concentrations in the system because they protect the oxalate against oxidation.

Figure 6. Final concentration of chloro-species after the combined soil washing- iron dechlorination and electrolysis treatment. Experimental conditions: 25 mA cm⁻² and 40°C.

These results are consistent with the changes in the pH and conductivity of the system, which are globalizing parameters whose value is related to all species contained in the system. The decrease in the value of the pH (acidification) in the case of the tests carried out with iron can be explained in terms of this formation of iron hydroxide (which as

shown in eq. 1 produces H^+). This is the only reaction that supports this pH decrease, which obviously is not observed in the test in which no iron is added because it cannot develop, as iron chloride cannot be formed. At this point, it is important to take into account that dechlorination reactions do not tend to diminish the pH but to increase it. Release of inorganic ions from soil and pH changes explain the changes in the conductivity. The only discrepancy is seen in the system with nanoparticles of iron (both in the pH and conductivity) and it can be explained by the sequestration of iron by oxalate, which is consistent with both the changes in the pH and conductivity. Thus, a reversion of the trend is observed for approximately 3 h of electrolysis just the moment in which the oxalate concentration starts to decrease.

Figure 7. Trends of pH (a) and conductivity (b) during the combined soil washing- iron dechlorination and electrolysis treatment. Experimental conditions: 25 mA cm^{-2} and 40°C . Iron granules: ▲ 48 g, ▲ 72 g; Iron nanoparticles: ◆ 48 g; Without iron: x.

The production of oxidants is a very important point to understand the process, because it is known that typically the performance of electrolysis with diamond anodes of organics at low concentration relies on it. Figure 8 shows the concentration of oxidants capable to oxidize iodide to iodine and it indicates that there are not important differences in the amount of oxidants which remains in the electrolyte, regardless of the addition of iron

and of the formation of hypochlorite. This concentration remains almost constant during the four tests, suggesting that mediated oxidation is having a similar role always, which does not seem to be very important, because of the high residual concentration, which may indicate that oxidants produced are not effective for the degradation of the organics. Initially, because of the release of sulfate during soil washing, it is expected that the primary oxidant in the system is peroxodisulfate, which can be electrogenerated according to eqs. 17 and 18).

Figure 8. Trend of the oxidant concentration during the combined soil washing-iron dechlorination and electrolysis treatment. Experimental conditions: 25 mA cm⁻² and 40°C. Iron granules: ▲ 48 g, ▲ 72 g; Iron nanoparticles: ◆ 48 g; without iron: ×.

Conclusions

From this work, the following conclusions can be drawn

- A combined soil washing – ZVI dehalogenation- electrolytic systems can be used to treat soils polluted with clopyralid. The system can attain the complete mineralization of the waste,

- Extraction of the pollutant from soil is very rapid and electrochemical interaction leads to rapid transformation of the pollutants contained in the soil washing waste,
- Iron dehalogenation has a very important impact on the efficiency of the process. It leads to less hazardous (from the viewpoint of toxicity) waste but at the same time, the intermediates formed are less oxidizable than the chlorinated parents. This results in a less efficient process from the viewpoint of mineralization, and
- Oxalic acid and its combination with iron (II) has a key role in the performance of the system and its accumulation helps to explain the lower mineralization efficiency and toxicity, which is particularly important in the case of using iron nanoparticles.

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References

- [1] R. Lopez-Vizcaino, C. Saez, P. Canizares, M.A. Rodrigo, The use of a combined process of surfactant-aided soil washing and coagulation for PAH-contaminated soils treatment, *Separation and Purification Technology*, 88 (2012) 46-51.
- [2] M. Muñoz-Morales, M. Braojos, C. Sáez, P. Cañizares, M.A. Rodrigo, Remediation of soils polluted with lindane using surfactant-aided soil washing and electrochemical oxidation, *Journal of Hazardous Materials*, 339 (2017) 232-238.
- [3] M.A. Rodrigo, N. Oturan, M.A. Oturan, Electrochemically Assisted Remediation of Pesticides in Soils and Water: A Review, *Chemical Reviews*, 114 (2014) 8720-8745.
- [4] C.M. Dominguez, S. Rodriguez, D. Lorenzo, A. Romero, A. Santos, Degradation of Hexachlorocyclohexanes (HCHs) by Stable Zero Valent Iron (ZVI) Microparticles, *Water Air and Soil Pollution*, 227 (2016).
- [5] C.M. Dominguez, J. Parchao, S. Rodriguez, D. Lorenzo, A. Romero, A. Santos, Kinetics of Lindane Dechlorination by Zerovalent Iron Microparticles: Effect of Different Salts and Stability Study, *Industrial & Engineering Chemistry Research*, 55 (2016) 12776-12785.

- [6] X. Zhao, W. Liu, Z. Cai, B. Han, T. Qian, D. Zhao, An overview of preparation and applications of stabilized zero-valent iron nanoparticles for soil and groundwater remediation, *Water Research*, 100 (2016) 245-266.
- [7] C. Lei, Y. Sun, E. Khan, S.S. Chen, D.C.W. Tsang, N.J.D. Graham, Y.S. Ok, X. Yang, D. Lin, Y. Feng, X.-D. Li, Removal of chlorinated organic solvents from hydraulic fracturing wastewater by bare and entrapped nanoscale zero-valent iron, *Chemosphere*, 196 (2018) 9-17.
- [8] M. Velimirovic, M. Auffan, L. Carniato, V. Micic Batka, D. Schmid, S. Wagner, D. Borschneck, O. Proux, F. von der Kammer, T. Hofmann, Effect of field site hydrogeochemical conditions on the corrosion of milled zerovalent iron particles and their dechlorination efficiency, *The Science of the total environment*, 618 (2018) 1619-1627.
- [9] C.-H. Weng, Y.-T. Lin, T.Y. Lin, C.M. Kao, Enhancement of electrokinetic remediation of hyper-Cr(VI) contaminated clay by zero-valent iron, *Journal of Hazardous Materials*, 149 (2007) 292-302.
- [10] C. Yuan, T.-S. Chiang, The mechanisms of arsenic removal from soil by electrokinetic process coupled with iron permeable reaction barrier, *Chemosphere*, 67 (2007) 1533-1542.
- [11] L.-N. Shi, Y. Zhou, Z. Chen, M. Megharaj, R. Naidu, Simultaneous adsorption and degradation of Zn²⁺ and Cu²⁺ from wastewaters using nanoscale zero-valent iron impregnated with clays, *Environmental Science and Pollution Research*, 20 (2013) 3639-3648.
- [12] S.R. Kanel, H. Choi, Removal of Arsenic from Groundwater by Industrial Byproducts and Its Comparison with Zero-Valent Iron, *Journal of Hazardous Toxic and Radioactive Waste*, 21 (2017).
- [13] X. Xia, Y. Hua, X. Huang, L. Ling, W. Zhang, Removal of Arsenic and Selenium with Nanoscale Zero-Valent Iron (nZVI), *Acta Chimica Sinica*, 75 (2017) 594-601.
- [14] Y. Liu, G.V. Lowry, Effect of particle age (Fe-o content) and solution pH on NZVI reactivity: H₂ evolution and TCE dechlorination, *Environmental Science & Technology*, 40 (2006) 6085-6090.
- [15] H. Kim, H.-J. Hong, J. Jung, S.-H. Kim, J.-W. Yang, Degradation of trichloroethylene (TCE) by nanoscale zero-valent iron (nZVI) immobilized in alginate bead, *Journal of Hazardous Materials*, 176 (2010) 1038-1043.
- [16] R. Semer, K.R. Reddy, Evaluation of soil washing process to remove mixed contaminants from a sandy loam, *Journal of Hazardous Materials*, 45 (1996) 45-57.
- [17] M.I. Kuhlman, T.M. Greenfield, Simplified soil washing processes for a variety of soils, *Journal of Hazardous Materials*, 66 (1999) 31-45.
- [18] A. Giannis, E. Gidarakos, Washing enhanced electrokinetic remediation for removal cadmium from real contaminated soil, *Journal of Hazardous Materials*, 123 (2005) 165-175.
- [19] J. Gomez, M. Teresa Alcantara, M. Pazos, M. Angeles Sanroman, Soil washing using cyclodextrins and their recovery by application of electrochemical technology, *Chemical Engineering Journal*, 159 (2010) 53-57.
- [20] S. Cotillas, L. Canizares, M. Munoz, C. Saez, P. Canizares, M.A. Rodrigo, Is it really important the addition of salts for the electrolysis of soil washing effluents?, *Electrochimica Acta*, 246 (2017) 372-379.
- [21] S. Cotillas, C. Saez, P. Canizares, I. Cretescu, M.A. Rodrigo, Removal of 2,4-D herbicide in soils using a combined process based on washing and adsorption electrochemically assisted, *Separation and Purification Technology*, 194 (2018) 19-25.
- [22] A. Uranga-Flores, C. de la Rosa-Juarez, S. Gutierrez-Granados, D.C. de Moura, C.A. Martinez-Huitle, J.M. Peralta Hernandez, Electrochemical promotion of strong oxidants to degrade Acid Red 211: Effect of supporting electrolytes, *Journal of Electroanalytical Chemistry*, 738 (2015) 84-91.
- [23] J.H. Bezerra Rocha, A.M. Sales Solano, N.S. Fernandes, D.R. da Silva, J. Manuel Peralta-Hernandez, C.A. Martinez-Huitle, Electrochemical Degradation of Remazol Red BR and Novacron Blue C-D Dyes Using Diamond Electrode, *Electrocatalysis*, 3 (2012) 1-12.

- [24] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, Single and Coupled Electrochemical Processes and Reactors for the Abatement of Organic Water Pollutants: A Critical Review, *Chemical Reviews*, 115 (2015) 13362-13407.
- [25] I. Sires, E. Brillas, Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review, *Environment International*, 40 (2012) 212-229.
- [26] I. Sires, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza, Electrochemical advanced oxidation processes: today and tomorrow. A review, *Environmental Science and Pollution Research*, 21 (2014) 8336-8367.
- [27] R. Lopez-Vizcaino, J. Alonso, P. Canizares, M.J. Leon, V. Navarro, M.A. Rodrigo, C. Saez, Electroremediation of a natural soil polluted with phenanthrene in a pilot plant, *Journal of Hazardous Materials*, 265 (2014) 142-150.
- [28] R. Lopez-Vizcaino, J. Alonso, P. Canizares, M.J. Leon, V. Navarro, M.A. Rodrigo, C. Saez, Removal of phenanthrene from synthetic kaolin soils by electrokinetic soil flushing, *Separation and Purification Technology*, 132 (2014) 33-40.
- [29] H. Urbanczyk, J.C. Ast, M.J. Higgins, J. Carson, P.V. Dunlap, Reclassification of *Vibrio fischeri*, *Vibrio logei*, *Vibrio salmonicida* and *Vibrio wodanis* as *Aliivibrio fischeri* gen. nov., comb. nov., *Aliivibrio logei* comb. nov., *Aliivibrio salmonicida* comb. nov. and *Aliivibrio wodanis* comb. nov, *International Journal of Systematic and Evolutionary Microbiology*, 57 (2007) 2823-2829.
- [30] N.A. Salles, F. Fourcade, F. Geneste, D. Floner, A. Amrane, Relevance of an electrochemical process prior to a biological treatment for the removal of an organophosphorous pesticide, phosmet, *Journal of Hazardous Materials*, 181 (2010) 617-623.
- [31] V. Sarria, S. Parra, N. Adler, P. Péringer, N. Benitez, C. Pulgarin, Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds, *Catalysis Today*, 76 (2002) 301-315.
- [32] C.M. Dominguez, N. Oturan, A. Romero, A. Santos, M.A. Oturan, Optimization of electro-Fenton process for effective degradation of organochlorine pesticide lindane, *Catalysis Today*, 313 (2018) 196-202.
- [33] M.A. Rodrigo, P. Canizares, A. Sanchez-Carretero, C. Saez, Use of conductive-diamond electrochemical oxidation for wastewater treatment, *Catalysis Today*, 151 (2010) 173-177.
- [34] M. MuñozMorales, C. Sáez, P. Cañizares, M.A. Rodrigo, A new strategy for the electrolytic removal of organics based on adsorption onto granular activated carbon, *Electrochemistry Communications*, 90 (2018) 47-50.
- [35] P. Canizares, C. Saez, J. Lobato, R. Paz, M.A. Rodrigo, Effect of the operating conditions on the oxidation mechanisms in conductive-diamond electrolyses, *Journal of the Electrochemical Society*, 154 (2007) E37-E44.
- [36] E. Lacasa, P. Canizares, C. Saez, F. Martinez, M.A. Rodrigo, Modelling and cost evaluation of electro-coagulation processes for the removal of anions from water, *Separation and Purification Technology*, 107 (2013) 219-227.