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Treatment of a suspension of PCB contaminated soil using iron nanoparticles and electric current

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ABSTRACT

Contaminated soils and sediments with polychlorinated biphenyls (PCB) are an important environmental problem due to the persistence of these synthetic aromatic compounds and to the lack of a cost-effective and sustainable remediation technology. Recently, a new experimental setup has been proposed using electrodialytic remediation and iron nanoparticles. The current work compares the performance of this new setup (A) with conventional electrokinetics (setup B). An historically contaminated soil with an initial PCB concentration of 258 μg kg^{-1} was treated during 5, 10, 20 and 45 d using different amounts of iron nanoparticles in both setups A and B. A PCB removal of 83% was obtained in setup A compared with 58% of setup B. Setup A also showed additional advantages, such as a higher PCB dechlorination, in a shorter time, with lower nZVI consumption, and with the use of half of the voltage gradient when compared with the traditional setup (B). Energy and nZVI costs for a full-scale reactor are estimated at 72 € for each cubic meter of PCB contaminated soil treated on-site, making this technology competitive when compared with average off-site incineration (885 € m^{-3}) or landfilling (231 € m^{-3}) cost in Europe and in the USA (327 USD m^{-3}).

Highlights

- High PCB removal (83%) was achieved with the new electrodialytic setup.
- Short times and less nanoparticles were needed using the new electrodialytic setup.
- Hepta and hexa chlorinated congeners were also degraded.
- Direct current enhanced dechlorination in the conventional setup through pH change.
- The new setup is competitive compared with incineration and landfilling.

Keywords

Electrokinetics (EK); electrodialytic remediation (EDR); nZVI; polychlorinated biphenyls; PCB

1. INTRODUCTION

Polychlorinated biphenyls (PCB) are a family of 209 congeners, classified as persistent organic pollutants (POP), carcinogenic and recalcitrant, which strongly adsorb to soils and sediments. Despite the environmental concern regarding PCB ecotoxicity and accumulation in the food chain, there is no quantification of the total volumes of PCB contaminated soils and sediments worldwide. A review of remediation technologies available for PCB-contaminated soils and sediments identified the need to find cost-effective and more sustainable alternatives than the commonly adopted “dig and dump” and “dig and incinerate” solutions (Gomes et al., 2013a).

Electroremediation comprises a group of technologies that has evolved over the last decades with the incorporation of enhancement techniques and the combination with other remediation technologies, targeting a wide range of contaminants. Electrodialytic remediation – a method based on the combination of the electrokinetic movement of ions in soil with the principle of electrodialysis – was used successfully in different matrices such as mine tailings (Hansen et al., 2007), soils *ex situ* (Ottosen et al., 2009b), different types of fly ashes (Ferreira et al., 2005; 2008), wood waste (Ribeiro et al., 2000), sewage sludge (Pazos et al., 2010), freshwater sediments and harbor sediments (Kirkelund et al., 2009). Electrodialytic remediation of suspended soil has proven to be a faster process to be used *ex situ* for the removal of heavy metals (Ottosen et al., 2013; Sun et al., 2012) and polycyclic aromatic hydrocarbons (PAH) (Lima et al., 2012).

Zero valent iron nanoparticles (nZVI) were considered a promising alternative for PCB dechlorination in aqueous solutions (He et al., 2010; Lowry and Johnson, 2004; Wang and Zhang, 1997; Zhuang et al., 2011). In general, the dechlorination can be expressed by the following reaction (Zhang et al., 1998):

$$C_xH_yCl_z + zH^+ + zFe^0 \rightarrow C_xH_{y+z} + zFe^{2+} + zCl^- \qquad (1)$$

in which iron acts as a reductant (electron donor) for the removal of chlorine. This reaction is similar to the process occurring during iron corrosion, with the beneficial effects of transforming chlorinated pollutants. Still a 95% PCB dechlorination in soils was just achieved at high temperatures (300 ºC) (Varanasi et al., 2007) and a removal efficiency of 98% with 100 mg of nZVI was obtained at 600 °C (Liu et al., 2014). In field applications, nZVI can be injected in the aquifers through injection wells, or incorporated to topsoil to adsorb or degrade pollutants (Crane and Scott, 2012). Results in aquifers show that nZVI have limited mobility, ranging from 1 m (Kocur et al., 2014) to 6-10 m (Zhang and Elliott, 2006).

One of the methods tested to enhance nZVI mobility was the use of low-level direct current (DC) (Jones et al., 2010; Pamukcu et al., 2008; Yang et al., 2007), using the same principles of electrokinetic remediation (EKR). Electroremediation and nZVI were combined by Fan et al (2013) and they obtained a 20% PCB removal from soils after 14 d using Fe/Pd bimetallic nanoparticles in conjunction with surfactants.

In a recent work (Gomes et al., 2014a), we presented a new experimental setup for on-site or *ex-situ* electrokinetic treatment of PCB contaminated soils in which the soil is kept in suspension with the simultaneous addition of nZVI and surfactants (saponin and Tween 80). In the current work the main objectives were to: i) assess the effectiveness for the dechlorination of PCB by nZVI of the new setup in comparison with the traditional cell used in electrokinetic setups; ii) test if longer EKR experiments with nZVI could increase PCB dechlorination; and to iii) evaluate the effect of using direct electric current

2. MATERIALS AND METHODS

2.1. Chemicals and solvents

PCB standards were analytical grade, obtained from Fluka, Sigma-Aldrich (PCB28, 52, 101, 138, 153, 180 and 209) and Ultrascientific (PCB30; PCB65 and PCB204). The solvents hexane and acetone were Pestinorm (VWR BDH Prolabo). Hydrochloric (37.6%), nitric (65%) and sulfuric (95-7%) acids were trace metal grade. Anhydrous Na_2SO_4, $KMnO_4$, NaCl, and silica gel (silicic acid) were lab grade. Silica gel was cleaned up before use according to the USEPA method 3630C. The water was deionized with a Milli-Q plus system from Millipore (Bedford, MA, USA). A polyacrylic acid (PAA) slurry-stabilized suspension of zero valent iron nanoparticles (NANOFER 25S, NANO IRON, s.r.o., Rajhrad, Czech Republic) was used in the experiments, with 50 nm average particles size, an average surface area of 20-25 $m^2 g^{-1}$, a particle size distribution of 20-100 nm and iron content in the range of 80-90 wt. %.

2.2 Soil characterization

The contaminated soil used in the experiments was provided by a hazardous waste operator in Portugal and is a mixture of contaminated soils from industrial sites with transformers oils spills. The soil characterization methods used were described in Jensen et al (2007). The elemental analysis were made using Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP) on an Agilent ICP-OES Varian 720-ES equipment. Table 1 presents the physical and chemical characteristics of the soil used in the experiments. According to the United States Department of Agriculture Natural Resources Conservation Service, this soil is classified as “very strongly alkaline” and this alkaline pH can be due to the presence of strong basis of industrial origin. The soil tested is a mixture of industrial contaminated soils, so it is also possible to have in the mixture fly ashes from coal fired boilers or power plants, rich in calcium oxide (CaO), which readily dissolves in water to form

$Ca(OH)_2$ (Lopareva-Pohu et al., 2011). The PCB concentrations measured are above the guidance values for total PCB in Denmark, even though only the most common congeners in environmental samples were measured. In Denmark, the limit for soil quality is 0.02 mg kg^{-1} total PCB and if the concentration exceeds 50 mg kg^{-1} the soil is classified as hazardous waste (Jensen, 2009). The soil was homogenized, air dried and sieved, and only the particles with size < 2 mm were used in the experiments.

Table 1. Physical and chemical characteristics of the soil.

Parameter	
Soil particles (%)	
Coarse sand (200 < Ø < 2000 µm)	19.1
Fine sand (20 < Ø < 200 µm)	67.3
Silt (2 < Ø < 20 µm)	12.7
Clay (Ø < 2 µm)	0.9
Textural classification	Loamy sand
pH (H_2O)	12.2
Conductivity (mS cm^{-1})	18.76
Exchangeable cations ($cmol_{(c)}$ kg^{-1})	
Ca^{2+}	83.75
Mg^{2+}	3.2
K^+	26.88
Na^+	9.37
Sum of exchangeable cations ($cmol_{(c)}$ kg^{-1})	123.2
Calcium carbonate (%)	18.0
Organic matter (%)	16.46
Total PCB[a] (μg kg^{-1})	258 ± 24
Metals[b] (mg kg^{-1})	
Al	20980 ± 590
As	8.6 ± 2.0
Cd	0.68 ± 0.14
Cr	51.66 ± 2.69
Cu	141.73 ± 94.62
Fe	13162 ± 301
Ni	31.98 ± 1.26
Pb	45.43 ± 3.31
Zn	2155 ± 40

[a] Sum of PCB28, 30, 52, 65, 101, 138, 153, 180, 204 and 209

[b] Acid digestion with HNO_3 according to the Danish Standard DS259.

2.3 PCB analysis

For PCB analysis, the soil extraction method used was the USEPA method 3550C, in which 10 g of soil was extracted with 3 × 30 mL of acetone-hexane (1:1) in a glass vial by ultrasonication (20 kHz) for 60 min. After vacuum filtration and concentration, the extracts were cleaned following the USEPA methods 3665A and 3630C. Aqueous samples (soil filtrate and catholyte) were extracted according to the method used by Lowry and Johnson (2004), after adjusting the pH of the acid samples to pH 7 with NaOH. The PCB congeners were analyzed by gas chromatography (GC) with an ECD detector (HP 6890 Series, Hewlett-Packard, Palo Alto, California, USA). The column used was a TRB–5–MS with 30 m × 0.25 mm i.d. and 0.25 μm film thickness (Phenomenex, Torrance, CA, USA). The oven temperature was programmed starting at 70 ºC for 2 min, increased to 150 ºC at a rate of 25 ºC min^{-1} and then increased 4 ºC min^{-1} to 200 ºC, 8 ºC min^{-1} to 280 ºC where it holds for 4 min and finally 10 ºC min^{-1} to 300 ºC, where it holds for 2 min. Pure nitrogen was used as the carrier gas. The injector was splitless set at 260 °C. The injections of 1.00 μl were performed manually.

2.4 Electroremediation experiments

The electroremediation experiments were carried out in two different cylindrical Plexiglas-cells. The electrodialytic cell (setup A) had two compartments [Figure 1 a)]. In one compartment (L = 10 cm, Ø = 8 cm) the anode was placed directly into the soil slurry and the plastic-flaps attached to a glass-stick overhead stirrer (Lab-egg Bie&Bernsten, Denmark, ~350 rpm) maintained the soil in suspension during the treatment. A cation-exchange membrane (CAT, GE Water & Process Technologies Bvba - ED, Cation, CR67, MKIII, Blank) separates this compartment from the cathode compartment (L = 5 cm, Ø = 8 cm) [Figure 1 b)]. The catholyte was recirculated by a mechanical pump (Plastomec magnet pump, model P05) between the chamber and a glass bottle.

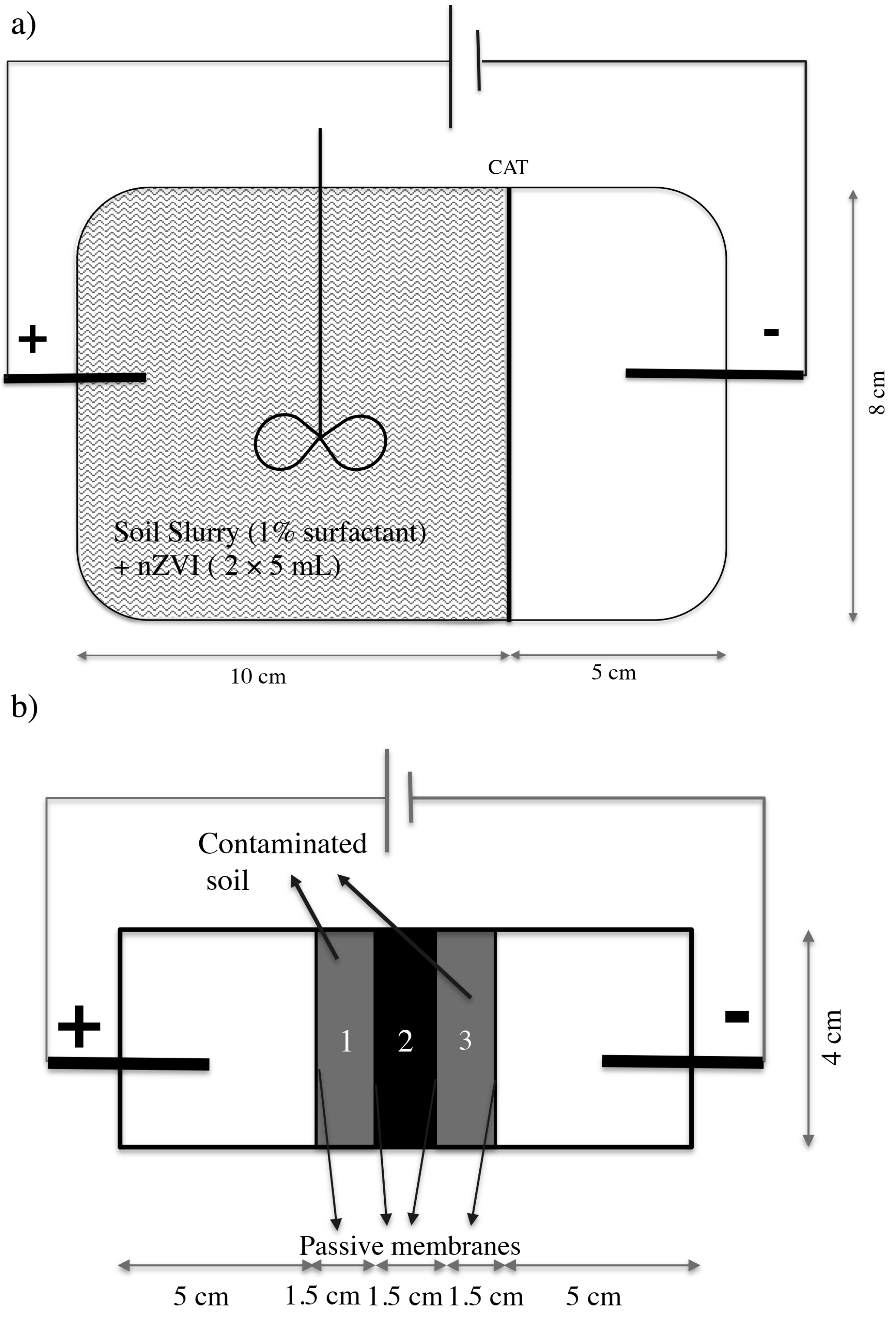

Figure 1. Schematic representation of the experimental setups used in the experiments: a) setup A - new electrodialytic cell (CAT – cation exchange membrane); b) electrokinetic cell (setup B).

The electrokinetic cell (setup B) consists of three compartments: two electrode compartments (L = 5 cm, internal diameter Ø = 4 cm) and a central compartment. The central compartment subdivided in three parts (L = 1.5 cm each, total of 4.5 cm, Ø = 4 cm). The nZVI were placed in the middle part (2) and the soil in the other two [1 and 3, Figure 1 b)]. The soil was saturated with deionized water before the experiments. Cellulose filters (passive membranes) were used to assure the separation between the soil and electrolytes, and the soil and the iron nanoparticles.

In both setups, a power supply (Hewlett Packard E3612A, Palo Alto, USA) was used to maintain a constant voltage and the current was monitored (Fluke 179 multimeter). The electrodes were platinized titanium bars, with a diameter of 3 mm and a length of 10 cm in setup A and 5 cm in setup B (Permascand®).

Six different laboratory experiments (A–F) were carried out, according to the experimental conditions presented in Table 2, in order to compare the two setups and to evaluate the effect of a variable duration in setup B (as the maximum duration of the experiments in the literature was 14 d (Fan et al., 2013)). The iron nanoparticles were placed in the center of both cells. In setup B (experiments A, B, C and D), the central reservoir was filled at the beginning of the experiments with nZVI. In experiment C more nZVI was added (2 mL), in days 7 and 9, to test if the addition of fresh nanoparticles could enhance the PCB dechlorination. In setup A (experiments E and F), two injections of 5 mL nZVI were made at 24 and 48 h, when the soil suspension pH was neutral. The electrolyte used in all experiments was 10^{-2} M NaCl. In the electrodialytic setup (experiment F), the catholyte pH was manually maintained approximately at 2 by the periodic addition of HCl 5 M to avoid alkaline pH in the catholyte.

Table 2. Summary of experimental conditions.

Exp.	nZVI (mL)	Type of injection	Setup	Voltage (V cm^{-1})	Soil (g, dry weight)	Duration (d)
A	13	Unique (in the beginning of experiment)	B	2	65.30	10
B	13	Unique (in the beginning of experiment)	B	0	49.84	10
C	20	Repeated (additional iron in days 7 and 9)	B	2	67.50	20
D	13	Unique (in the beginning of experiment)	B	2	69.94	45
E	10	2 injections of 5 mL at 24 and 48 h	A	0	50.01	5
F	10	2 injections of 5 mL at 24 and 48 h	A	1	50.05	5

The current between electrodes, the soil suspension pH and in the electrolytes were measured every 24 h. In setup A at the end of the experiments, the suspension from the central compartment was filtered by gravity through 0.45 μm filter paper. In setup B samples from the anode and the cathode side were collected separately. Subsamples were prepared for humidity measurements. For both setups, the soil was air-dried and crushed slightly in a mortar before the PCB extraction and pH measurements. At the end of the experiments the Fe contents in the different parts of the cell (membranes, soil, solutions, and electrodes) were determined. The Fe contents in the CAT membranes and at the electrodes were measured after extraction in 1 M HNO_3 and 5 M HNO_3, respectively. The Fe was extracted from soil by the sodium dithionite-citrate-bicarbonate method (Mehra and Jackson, 1960) and from the passive membranes with concentrated HCl.

3. RESULTS AND DISCUSSION

3.1 Comparison between the two experimental setups

Setup A shows PCB removal percentages of 83% with direct current and 29% without, as shown in Figure 2. The best removals are higher than in previous studies with conventional electrokinetics (Fan et al., 2013), higher than batch tests without current (Chen et al., 2014), and also higher than in previous experiments using this setup with different surfactants (Gomes et al., 2014a). The suspension and stirring of the soil enhances the PCB dechlorination by nZVI, probably due to an increase in desorption from soil and/or to a higher contact and reaction between nZVI and PCB. In the traditional electrokinetic setup (setup B), the iron has to be transported across the compacted saturated soil to reach the contaminants. Even a low proportion of carbonate minerals may cause an increase in the deposition of PAA-nZVI particles and aggregates, due to a weaker negative surface charge (Laumann et al., 2013). As the soil used in the experiments has high carbonate content (18%), the limited dechlorination (12-58%) observed in setup B (Figure 2) can be due to this soil characteristic.

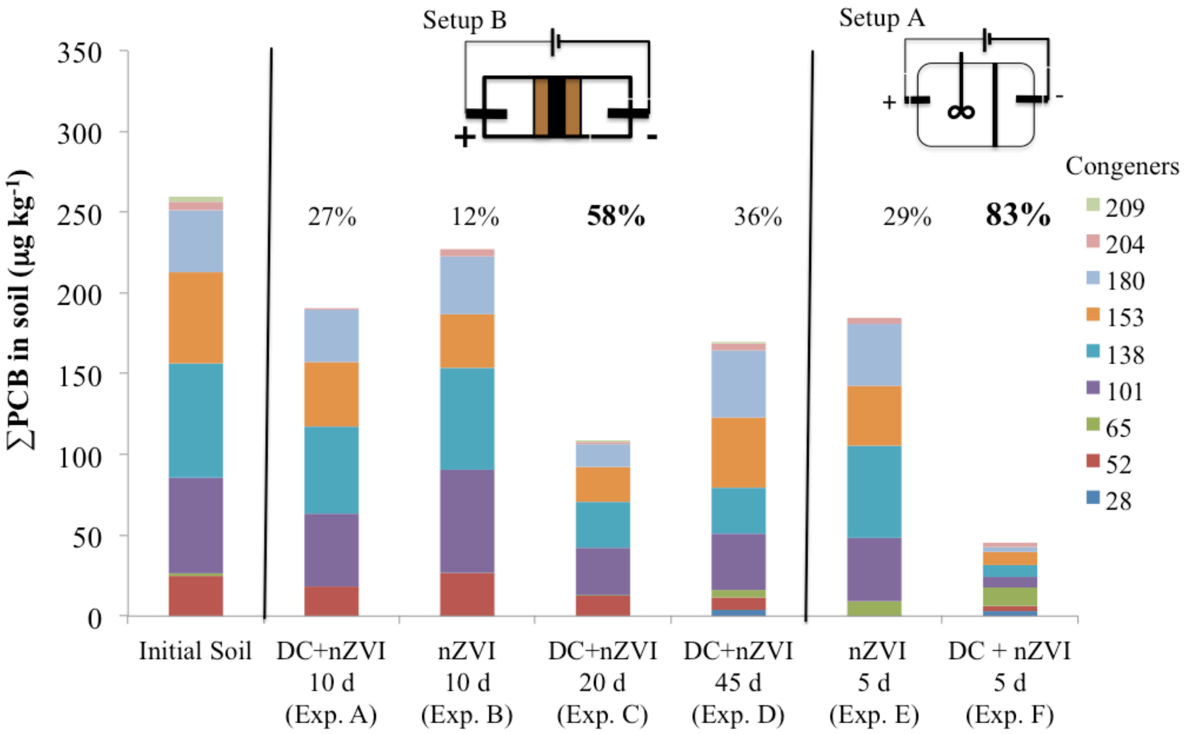

Figure 2. Average concentration of the sum of PCB congeners (PCB28, 52, 65, 101, 138, 153, 180, 204 and 209) in soil before and after the experiments using conventional electrokinetics (setup B) and the new electrodialytic setup (A). Percentages on the top of each column represent PCB removal regarding the sum of congeners analyzed in the initial soil. PCB – polychlorinated biphenyls, DC – Direct Current, nZVI – zero valent iron nanoparticles.

In both setups, there are chemical reactions that deplete the Fe^0 reductant power (Tosco et al., 2014; Zhang, 2003) and are occurring in the cell center compartment due to the presence of water, oxygen, H^+ from water electrolysis, and carbonates from the soil:

$$2Fe^0_{(s)} + 4H^+_{(aq)} + O_{2\,(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \tag{2}$$

$$Fe^0_{(s)} + 2H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)} + 2OH^-_{(aq)} \tag{3}$$

$$Fe^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow FeCO_{3(s)} \tag{4}$$

Also, the presence of transformer oil was found to adversely affect the PCB degradation (Chang et al., 2010). Despite the introduction of H^+ (resultant of hydrolysis in the anode) and the atmospheric O_2 dissolved by the slurry stirring that promotes Fe^0 oxidation, a higher PCB removal is obtained in the electrodialytic setup (A) compared with the conventional eletrokinetic setup (B). In both setups, in none of the aqueous samples (electrolyte and filtrates) PCB were detected. The electrokinetic setup (B) is more prone to nZVI aggregation and settling, as other experiments with molinate contaminated soils showed (Gomes et al., 2014c).

In other remediation techniques (Beckingham and Ghosh, 2011; Li et al., 2013; Vasilyeva et al., 2010; Wu et al., 2012), lower chlorinated congeners (tri and tetrachlorobiphenyls) were the ones with highest removal. In this study, lower chlorinated congeners were degraded, namely PCB28, PCB52 and PCB65 (particularly in setup B), but higher chlorinated congeners were also degraded (Experiment F). In some experiments an increase of PCB65 occurred (two, five and six times more the initial amount in the experiments D, E and F, respectively) likely due to the dechlorination of higher chlorinated congeners, such as PCB204. In setup B removal percentages for each congener are lower than in setup A. The dechlorination pathways of congeners by nZVI were proposed by Chen et al. (2014) for PCB153 and by Gomes et al (2014a) for PCB138 and PCB180.

3.2 Different duration experiments

The experiments using the conventional electrokinetic setup (B) had different durations to assess if longer times would increase PCB dechlorination. Comparing the 10 d experiment (A) with the 45 d experiment (D), the PCB removal has a small increase (27% vs. 36%) (Figure 2). Although the removal percentages are higher than in previous studies with 14 d experiments (Fan et al., 2013), their values are not encouraging for a scale up of the process (pilot and full scale) for the remediation of PCB contaminated soils and sediments. The higher dechlorination in experiment C is related with the additional nZVI injected at days 7 and 9, not with the exposure duration. Comparing the congeners concentrations obtained in the soil (duplicate samples), we observed that they are not statistically different in the three experiments (A, C and D) at a 0.05 level of significance [one-way ANOVA, F(2,20) = 2.14, p = 0.14]. This means that PCB dechlorination in setup B does not increase over time.

3.3 Experiments with and without direct current

Direct current can be used to enhance nZVI transport in different porous matrices or model soils (Gomes et al., 2013b) but, in the electrodialytic setup (A), the contact between the nanoparticles and the contaminated soil is ensured by the stirring so the current may not be needed for PCB dechlorination. However, results show that the experiment with direct current (exp. F) had a much higher PCB removal (83%) than the experiment just with the iron nanoparticles (exp. E) (29%). We believe that due to the high pH and buffer capacity of the soil (Table 1 and Figure 3) in the experiment without current (exp. E) the soil kept a constant alkaline pH that promoted the passivation of the iron nanoparticles. On the contrary, in the experiment with current (exp. F) water electrolysis (eq. 5 and 6) produces H^+ in the anode, thus lowering the pH of the soil slurry

$$2H_2O - 4e^- \rightarrow O_{2(g)} + 4H^+ \qquad E_0 = -1.229 \text{ V (anode)} \qquad (5)$$

$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-$ $E_0 = -0.828$ V (cathode) (6)

A slightly acidic pH (4.90–5.10) increases the dechlorination of PCB by nZVI and nZVI/Pd (Wang et al., 2012). The effect of the acidification of the soil slurry favors the PCB dechlorination when a direct current is used, explaining the higher removals obtained in exp. F compared with exp. E. Table 4 shows the pH values after the experiments. Only in experiment F a lower pH is obtained due to the high buffer capacity of the soil.

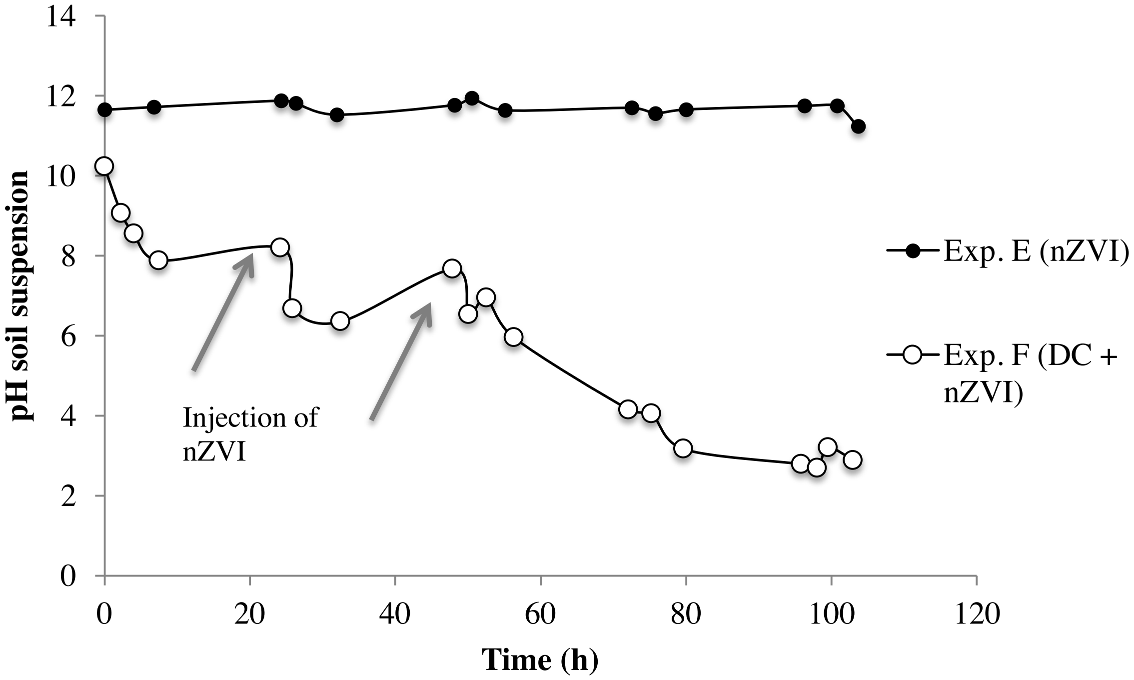

Figure 3. Evolution of pH in the soil suspension during the experiments using the new electrodialytic setup (A). DC – direct current, nZVI – zero valent iron nanoparticles.

Table 4. Soil pH at the end of the experiments in both setups. Initial soil pH is 12.2.

Setup A		**Setup B**		
Exp.	**Soil pH**	**Exp.**	**Anode side**	**Cathode side**
		A	11.28	12.18
E	9.47	B	12.25	12.07
F	5.70	C	11.60	11.83
		D	11.21	11.69

Figure 4 shows the current values measured in the experiments, using both cells. The highest current values were measured in setup A and are related to the high metal content of the tested soil. When the metals are dissolved or desorbed by the H^+ generated at the anode, the conductivity of the suspension increases. In setup B (Figure 4), the current values reached a peak immediately after the experiment start, when the quantity of ions in the pore solution was higher due to the dissolution of salts associated with soil particles. The current dropped abruptly in the first hours and stabilized thereafter, with little oscillations, in all experiments. The H^+ generated at the anode can solubilize transition metals such as Fe and Ni from soil, that can degrade PCB via catalytic hydrodechlorination with H_2 successively removing chlorine atoms from PCB generating biphenyl, according to the general chemical equation (Wu et al., 2012):

$$C_{12}H_{(10\text{-}m)}\,Cl_m + nH_2 \rightarrow C_{12}H_{(10\text{-}m+n)}Cl_{m\text{-}n} + nHCl,\ m \geqq n \qquad (7)$$

Although this hydrodechlorination has been reported for aqueous or organic solvents, in the tested setup there are all the needed conditions for it to occur. However, further research is needed to evaluate the importance of this dechlorination process, to assess how iron (natural and manufactured) and other metals act as catalysts.

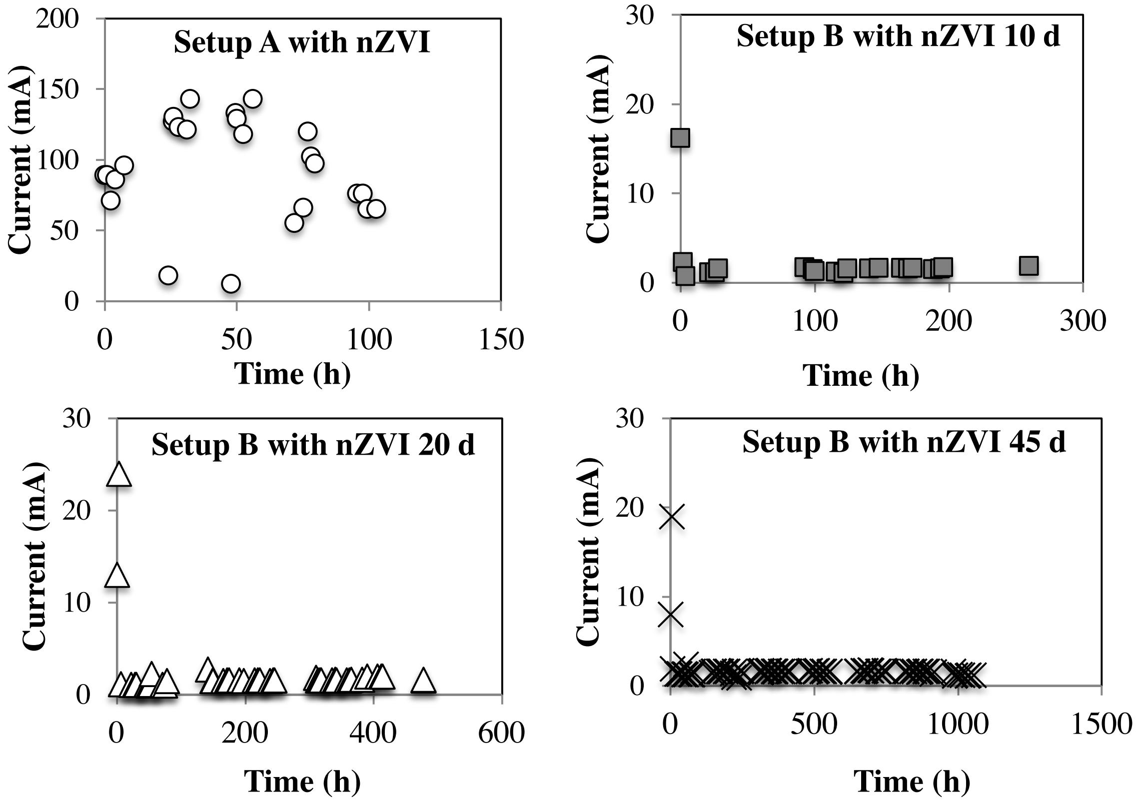

Figure 4. Current variation during the experiments.

3.4 Upscale of the new electrodialytic setup (A)

Based on the preliminary results obtained in this work, a rough estimate of the operation cost of using the new electrodialytic setup (A) for *ex situ* remediation of PCB contaminated soil was made. Basically, considering the energy consumption for the stirring and electrodialytic remediation of a full-scale reactor for a cubic meter of contaminated soil and the nZVI costs (at current commercial prices 61 € kg^{-1}), the costs are 72 €. The energy consumption was extrapolated from the lab scale cell (0.88 Wh g^{-1}). For the calculation of the energy costs, we considered the average cost of energy in the European Union (EUROSTAT 2011). If we are only dealing with organic contaminants that can be completely degraded, there is no need to treat and dispose the anolyte after separation from the solids. Even adding the excavation and transport costs, this solution is competitive when compared with the off-site incineration average costs (885 € m^{-3}) and off-site landfilling costs (231 € m^{-3}) in Europe (Summersgill, 2006) and the off-site landfilling costs for hazardous waste in the USA (327 USD m^{-3}, approximately 239 € m^{-3}) (Ram et al., 2013).

4. CONCLUSIONS

In summary, the new electrodialytic setup tested in this work allowed PCB dechlorination from contaminated soil *ex situ* at a higher percentage, in a shorter time, with lower nZVI consumption, and with the use of half of the voltage gradient when compared with the traditional electrokinetic setup. In addition, there is no need to treat and dispose of the anolyte. However, additional testing with different soils, repeated application of the technique on the same material (also with different duration experiments), testing of enhancement methods and further optimization and scale up of the process are needed to prove the versatility of the electrodialytic setup.

The results show that the soil characteristics are important and affect the reactions between nZVI and the target contaminant, especially pH and carbonate content. Direct current can enhance dechlorination in this new electrodialytic setup.

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