Electrodialytic Remediation of heavy Metal polluted Soil – treatment of water saturated or suspended soil

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Electrodialytic soil remediation is a method for removal of heavy metals. Good results have previously been obtained with both treatment of a stationary, water saturated soil matrix and with remediation of a stirred suspension of soil in water. The two different setups have different uses. The first as in-situ or on-site treatment when there is no requirement for fast remediation, as the removal rate of the heavy metals are dependent on the distance between the electrodes (everything else equal) and in such application the electrode spacing must have a certain distance (often meters). In the stirred setup it is possible to shorten the transport route to few mm and to have a faster and continuous process. The present paper for the first time reports a direct comparison of the two options. The remediation of the stirred suspension showed faster than remediation of the water saturated soil even without a short distance between the membranes. The acidification of the suspended soil was fastest and following the mobilization of heavy metals. This may indicate that water splitting at the anion exchange membrane is used more efficiently in the stirred setup.

1. Introduction

Heavy metals can be removed from polluted soil by application of an electric DC field and this forms the base for electrokinetic remediation (EKR) methods. Heavy metals are most often adsorbed to the soil particles or precipitated, and as the transport mechanism for heavy metals in the applied electric field is mainly electromigration (transport of ions in a liquid phase in a applied electric field), desorption of the heavy metals is crucial for a successful remediation. An acidic environment promotes desorption of heavy metals. During EKR the soil is acidified by electromigrating H^+ ions from the anode reaction, and the heavy metals are subsequent mobilized and transported to the electrodes (positive ions towards the negative electrode and opposite). A comprehensive theoretical description of EKR can be found in (Yeung, 2006) and a review of results obtained with industrially polluted soil is given in (Ottosen et al., 2008). A major advantage of EKR is the possibility to treat fine grained soils where other methods tend to fail (Yeung, 2006).

Electrodialytic soil remediation (EDR) is one electrokinetic method for removal of heavy metals from soil (and particulate waste products). In EDR, ion exchange membranes are separating soil and processing solutions, while passive membranes are used in other EKR techniques. Remediation of suspended soil is possible when using ion exchange membranes, because they hinder direct mixing of ions from processing solutions and in the soil suspension. There are thus two options for application of EDR: (A) to treat the soil as a stationary, wet matrix (in-situ or on-site) or (B) to treat the soil in a

suspension (with the possibility for combining EDR with soil washing and only treat the fine fraction with EDR) (On-site). Which option is the best in a specific case depends on both site and soil characteristics. One example is a calcareous soil, where the site owner wishes a fast remediation. Addition of enhancement solution to the soil for desorption of heavy metals might be necessary, because in calcareous soils the acidic front progresses very slowly, hampering fast remediation (Ottosen et al., 2005). Here option B is the best. The enhancement solution if necessary can be well mixed into the soil fines when suspended, and as the membranes can be placed closer than in the stationary case, the distance for electromigrating heavy metal ions is shorter. Another example could be remediation of a site where the upper half meter is polluted, the groundwater level is deep and there is no specific request for fast remediation. Here in-situ treatment (option A) with electrode units placed directly in the soil could be the best option from an economic point of view.

In the present work, for the first time, lab experiments are conducted with the aim of a direct comparison of electrodialytic remediation of a compacted soil and soil suspended in water. The experiments are conducted with three different industrially soils polluted with Cu and Pb.

2. Materials and methods

2.1 2.1 Experimental soils and analytical

Three industrially polluted soils were used in this investigation: *Soil A*: was sampled at an abandoned wood preservation site (in the depth of 10 - 25 cm). *Soils B and C* were sampled from piles of polluted soil, which had previously to the sampling been excavated at two different polluted sites. The soils were sieved through a 4 mm sieve before use in the experiments.

Concentration of Cu and Pb in soil was measured after pre-treatment of the soil as described in Danish Standard 259 "Determination of metals in water, sludge and sediments – General guidelines for determination by atomic absorption spectrophotometry" where 1.0 g of dry soil and 20.0 mL (1:1) HNO_3 are heated at 200 kPa (120 °C) for 30 min. The liquid was separated from the solid particles by vacuum through a 0.45 μm filter and diluted to 100 mL. The concentrations of Cu and Pb were measured with ICP. *Soil pH* was measured by suspending 10.0 g dry soil in 25 mL 1.0 M KCl. After 1 h of contact time pH was measured using a Radiometer pH electrode. *Organic matter* The content of organic matter was found as a loss of ignition after 30 min at 550 °C. *Carbonate content* was determined volumetrically by the Scheibler-method and calculated assuming that all carbonate present is calcium carbonate. Five measurements of each of the analysis on the initial soil were made. On the treated soil three analyses were made.

2.2 Electrodialytic remediation experiments

The electrodialytic experiments were conducted in pairs of two: one experiment with stationary soil and one with stirred soil (Figure 1). All other parameters were kept the same within each set. The cylindrical cells were made from polymethyl methacrylate and had an internal diameter of 8 cm. The ion exchange membranes were from Ionics (anion exchange membrane AR204 SZRA B02249C and cation exchange membrane CR67HUY N12116B). Platinum coated electrodes from Permascand were used. A power supply (Hewlett Packard E3612A) was used to maintain a constant current.

The electrode compartments were 5 cm long and in each were circulated 500 mL 0.01 M $NaNO_3$ (adjusted to 2 with HNO_3) between the compartment and a reservoir flask. The soil compartment in the experiments with stationary soil was 1.5 cm long, whereas the length of the central compartment in the stirred soil suspension was 5 cm. The soil was kept suspended during the experiments by constant stirring with a plastic-flap attached to a glass-stick and connected to an overhead stirrer (RW11 basic from IKA). The suspension reached initially to about 3 cm below the hole where the stirrer was placed, but the height differed slightly during the experiments. Five sets of experiments (one stirred and one stationary) were conducted and the characteristics for each set are shown in Table 1.

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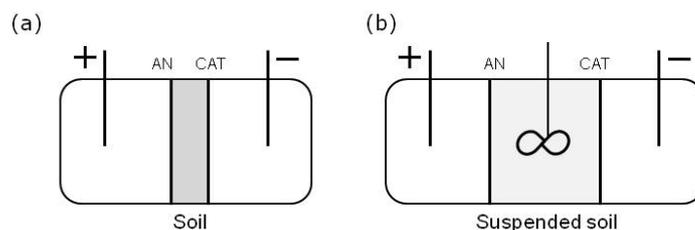
Figure 1: Schematics of the experimental cells (a) soil compacted and water saturated and (b) soil suspended in distilled water and stirred to keep in suspension during experiments.(AN = anion exchange membrane, CAT = cation exchange membrane)

Table 1: Overview of electrodialytic remediation experiments (an experimental set covers one experiment with suspended soil and one with stationary soil)

Experimental set	Soil	Current (mA)	Duration (days)	Charge transfer (C)	Soil weight (g)
A1	A	5	14	6050	144
B1	B	5	21	9070	146
B2		15	21	27,200	136
C1	C	10	14	12,100	149
C2		15	16	20,800	148

3. Results and discussion

3.1 Soil characteristics

Some characteristics of the three soils are shown in Table 2 together with the Danish limiting values for the most sensitive land use. The soils all had elevated concentrations of Cu, but only soil A and C exceeded the limiting value. In both soil B and C the Pb concentration exceeded the limiting values with more than a factor 10 (soil A was not polluted with Pb). The three soils vary greatly in the soil characteristics of major importance to EDR; carbonate content, loss on ignition and fine fraction.

Table 2: Characteristics of the soils and the Danish limiting values for the most sensitive land use

	Soil A	Soil B	Soil C	Limiting value
Cu conc. (mg/kg)	1030 ± 46	390 ± 39	1140 ± 144	500
Pb conc. (mg/kg)	-	420 ± 34	550 ± 25	40
pH_{KCl}	6.6 ± 0.1	7.8 ± 0.03	7.2 ± 0.1	
Conductivity (mS/cm)	0.1 ± 0.06	0.4 ± 0.02	2.5 ± 0.3	
Carbonate content (%)	1.6 ± 0.1	10.9 ± 1.0	7.9 ± 0.3	
Loss on ignition (%)	1.8 ± 0.6	3.1 ± 0.03	2.9 ± 0.3	
Fine fraction (< 63 µm) (%)	28	45	63	

3.2 Overall results from electrodialytic experiments

The overall results from the EDR experiments are shown in Table 3. The voltage range for each experiment is given. The recovery is defined as the ratio between the sum of mass found in the different parts of the cell at the end of the experiment and the initial mass calculated on basis of the mean initial concentration. The removal in percentage is calculated as mass of the heavy metal not in the soil (and solution in the central compartment in the stirred experiments) divided by the total mass found in all parts of the cell at the end of the experiment. The recovery was between 77 % and 111 % and the variation is due to the inhomogeneous distribution of the pollutants in the industrially polluted soils.

Table 3: Overview of electrodialytic remediation results (*max voltage of power supply, current dropped to 3 mA)

	Voltage range (V)	Recovery Cu / Pb (%)	Removed Cu / Pb (%)	Soil pH$_{KCl}$
A1-sus	31 – 87	99 / -	77 / -	3.4
A1-sta	6 – 34	102 / -	70 / -	3.3
B1-sus	2 – 7	83 / 85	3 / 2	7.1
B1-sta	2 – 4	96 / 97	1 / 1	7.6
B2-sus	4 – 26	103 / 90	41 / 31	6.1
B2-sta	2 – 15	77 / 85	4 / 4	6.7
C1-sus	2 – 4	85 / 89	2 / 1	6.7
C1-sta	3 – 84	106 / 111	2 / 1	6.6
C2-sus	3 – 24	94 / 89	30 /4	5.0
C2-sta	4 – 138*	95 / 79	4 / 1	6.2

3.3 Comparison between stirred and stationary remediation

In both experiments A1 Cu was removed successfully as the removal percentage was 77 % and 70 % (Table 3) in experiment A1-sus and A1-sta, respectively. The corresponding final Cu concentrations were 290 mg/kg and 330 mg/kg for. Thus the Cu concentration meets the limiting value at the end of both experiments. From the two calcareous soils very little Cu and Pb were removed during the experiments (series B1 and C1, Table 3), even though the charge transfer was higher than in the A1 experiments. Previously it has been shown for other soils that both Cu and Pb were removed at a higher pH in a calcareous soil than in a non-calcareous soil during EDR (Ottosen et al., 2001). This because a fraction of the heavy metals are co-precipitated in the calcareous part of the soil and are mobilized when the carbonates are dissolved during acidification. The pH$_{KCl}$ should though be less than about 6 before this mobilization started (Ottosen et al., 2001). In the experiments in series B1 and C1 the pH$_{KCl}$ was still above 6.5 and at this pH Cu and Pb were not mobile for electromigration.

In the experiments in series B2 and C2 a clear difference in the removed percentage of Cu between the stirred and the stationary experiment is seen (Table 3). In both cases the stirred experiment showed a significantly higher removal percentage than the stationary. The same trend is seen for Pb in series B2. From the carbonate content in the soil at the end of the different experiments (Figure 2) it can be seen that in every case, the carbonate content was lower in the suspended experiment than in the stationary, and this is likely the reason for the better removal percentage. A larger fraction of the carbonates have been dissolved and hereby more Cu (and Pb in C2) was mobilized for electromigration. The final concentrations in experiment B2-sus was though still 270 mg Pb/kg, which exceeds the limiting value (Cu was already initially below this value before the experiment), and in experiment C2-sus the Cu concentration was 790 mg/kg also exceeding the limiting value, so even longer treatment is needed to meet the goal. For the stationary EDR the remediation of the calcareous soils is very time consuming as less than 1.5 cm was remediated in 2and 3 weeks for soil C and B, respectively. Up-scaling the stirred setup to have a very short distance between the membranes and thus transport route for the heavy metal ions can be obtained as described in (Kirkelund et al., 2010), where EDR treatment of fly ash is conducted in pilot scale in a electrodialysis stack with thicker spacers (2 mm) than normally for treatment of solutions. It is possible (and sometimes necessary) to combine EDR with soil washing and only treat the slurry of soil fines by EDR after the unpolluted coarser fractions have been removed in the washing process. Previously, Pb polluted soil fines in suspension were remediated successfully using EDR (Jensen et al., 2006). The combined technique allows for EDR as a continuous process.
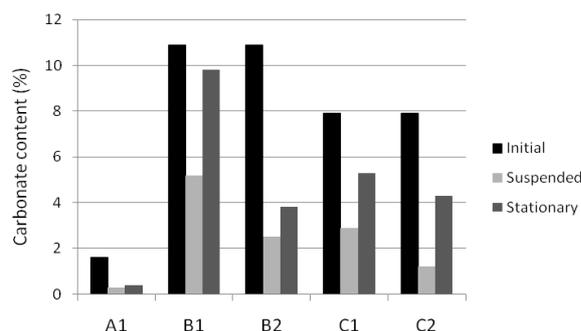
Figure 2: Carbonate content in the soil initially and at the end of the EDR experiments

The faster acidification of the stirred experiments (seen from the lower carbonate content and the slightly lower soil pH) can have different causes. A recent review on current transfer in membrane systems concluded that even though an essential increase in understanding has been gained during the last years there are still many open questions (Nikonenko et al., 2010), and thus a full theoretical explanation on the finding of the complex system with soil in the desalination compartment cannot be given. However, some overall considerations follow. When a direct current is applied to an electrodialysis cell perpendicular to the membranes (as in the experiments here), the difference in transport numbers in the solution and the membranes causes a concentration decrease near the membrane in the desalination compartment (Nikonenko et al., 2010) - the soil compartment in EDR. In the case, where the current density is so high, that the concentration reaches zero at the membrane surface (i.e. an overlimiting current is applied), water splitting will occur and generate H^+/OH^-, which are then major current carriers. In EDR with a stationary soil, an overlimiting current is applied in relation to the anion exchange membrane, but not for the cation exchange membrane. This means water splitting at the anion exchange membrane only, and by this an acidic front will develop into the soil (Ottosen et al., 2000). It important to choose a current density between the limiting current density for the anion echange membrane and the cation exchange membrane as an alkaline front from the cation exchange membrane hinder efficient removal of heavy metals (both in the stationary case (Ottosen et al., 2001) and in the stirred case (Jensen et al., 2007)). In the stirred EDR system, the electrolyte concentration is much diluted as the ionic conductivity of the solution (in which the soil is suspended) is much less than the ionic concentration in the pore solution of the stationary soil. The electrolyte concentration affects the limiting current of the membranes (lower limiting current at lower concentrations for same current density). Another difference is that the solution is stirred instead of stationary, and at overlimiting currents Kim et al. (2011) found for liquid electrodialysis that an increase in flow rate of the solution was more efficient in relation to improvement of ionic separation than increasing the applied potential. In the present investigation EDR of a steady soil solution is compared to a stirred suspension, and from the finding of Kim et al.(2011), the stirred system may give the best treatment, which was also seen in the present investigation. Kirkelund et al. (2009) compared EDR of harbor sediment with different stirring velocity and found the best removal of Pb and Cu at the highest stirring velocity of the tested. In addition to the differences in acidification of the soil/soil suspension by water splitting there may also be a higher interdiffusion over the cation exchange membrane in the stirred cell, where H^+ ions from the acidic catholyte can exchange with other cations in the liquid in which the soil is suspended.

Table 3 shows the voltage range for the different experiments. During the experimental sets with soils A and B the voltage was higher in the stirred cell than in the stationary. For soil C on the contrary the voltage in the suspended experiment was lowest. As the current was constant in all experiments this means that the energy consumption for the treatment was following the voltage. Sun et al. (2012) showed experimentally with a soil from the same site as soil A that the voltage over the stirred cell was significantly lower when treating soil fines only compared to treating the soil with original grain size distribution (at the same liquid to solid ratio). This may explain why soil C differs from soil A and B, as soil C had the largest fine fraction. Moreover soil C was dewatered by electroosmosis during

experiment C2-sta to a final water content of only 6.8 % whereas it was more than 16 % in the remaining stationary experiments. This is probably the cause for the high voltage in this experiment as good electric contact especially between membranes and soil is difficult to obtain at such low water content.

4. Conclusions

Electrodialytic soil remediation can be used for remediation of stationary, water saturated soils (in-situ) or suspended soil (ex-situ). In the present investigation a direct comparison based on laboratory experiments was made of the two systems. Faster remediation or faster dissolution of carbonates indicating a faster remediation were obtained in the stirred system. The cause for this is not yet fully explained as there are different effects influencing the two systems. It is suggested that suspending the soil means dissolution which lowers the limiting current density for water splitting increasing the extent. Also the stirring itself is important as the transport route for the heavy metals is shortened.

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