Electrodialytic remediation of harbour sediment in suspension—Evaluation of effects induced by changes in stirring velocity and current density on heavy metal removal and pH

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ABSTRACT

Electrodialytic remediation was used to remove heavy metals from a suspension of dredged harbour sediment. The studied metals Cu, Pb, Zn and Cd are normally strongly bound in anoxic sediment. Six electrodialytic laboratory remediation experiments were made, lasting 14 days and under oxic conditions. The influence on the metal removal was investigated by changing current densities and stirring velocity of the sediment suspension. Using a current density of $1.0\,mA/cm^2$ gave the highest metal removal. The sediment suspension was partly oxidised when mixed into a suspension for the electrodialytic remediation experiments and was further oxidised during the experiments. Even at low stirring velocities, oxic conditions were obtained. The metal removal was dependent on the achieved pH in the sediment and the highest metal removal and corresponding low pH was obtained by using a current density of $1.0\,mA/cm^2$ and a stirring velocity of the sediment suspension of 1000 rpm. The highest removal obtained was 98% Cd, 78% Zn, 65% Pb and 44% Cu after 14 days of remediation. The metal removal was more dependent on the stirring velocity than on the current density. When manually stirring the sediment suspension or using a stirring velocity of 60 rpm the sediment deposited, which led to a slightly higher pH in the sediment and keeping all the sediment in suspension is essential for a successful remediation.

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1. Introduction

Accumulated harbour sediment is generally anoxic if the sediment is not suspended into the overlaying oxygen rich water by wind, current or ship traffic. Available dissolved oxygen in the water is consumed by microbial respiration in the top layer of the sediment, which can be oxic. Thereafter other electron acceptors (e.g. NO_3^- and SO_4^{2-}) in the sediment are consumed for microbial respiration in the underlying sediment. When SO_4^{2-} is used as oxygen source, sulphides are formed (H_2S, FeS, FeS_2, MeS_2) and the sediment is anoxic. In sulphidic anoxic sediment, stable metal sulphides (MeS_2) are usually dominating the metal speciation. Consequently, metals are generally not very mobile or bioavailable in anoxic sediment [1].

However, when sediment is dredged, it is suspended and exposed to air or water rich in dissolved oxygen. Aeration of anoxic sediment generally increases the availability of metals due to changed redox potentials and pH during oxidation [2–5]. Changes in redox potential in sediment generally lead to production of hydrogen ions by oxidation of sulphides and thus, pH in weakly buffered

sediment will decrease when the redox potential is changed [2]. Dredged sediment is often disposed of; hence, further changes in redox potential and pH can occur by drying and oxidation [6,7].

Extraction experiments have been made to compare pH dependent desorption in anoxic and oxic sediment samples. Tack et al. [4] used highly buffered sediment and showed that the solubility of Cd, Cu, Pb and Zn was significantly higher at low pH in oxidised sediment compared to anoxic sediment. Fe and Ca solubility decreased when the sediment was oxidised, while no significant differences were observed for Mn, Ni and Co. Calmano et al. [2] showed increased pH dependent solubility of metals in weakly buffered sediment when oxidised, although the solubility difference between anoxic and oxic sediment was more significant for Cu and Pb, compared to Cd and Zn.

Redox potential (E_H) in sediments can be measured by electrodes. Due to the complex nature of sediments and the presence of several redox couples, the redox potential measured is probably a mixed potential rather than a true equilibrium potential for all the redox couples [8]. At measured redox potential above 300 mV, oxygen is generally present, while NO_3^- is reduced between 300 and 200 mV and Mn^{4-}, Fe^{3+} and SO_4^{2-} are reduced thereafter [4].

Heavy metal mobilisation caused by oxidation during disposal of dredged sediment can be a problem if the sediment is not stabilised. However, if heavy metals are to be extracted from sediment as a
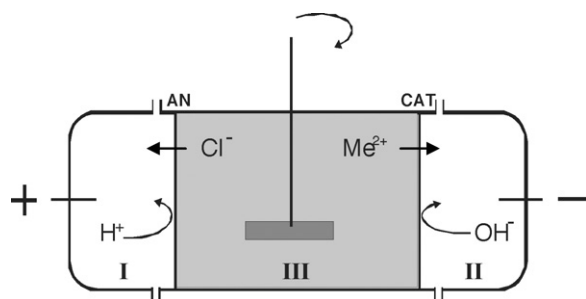

Fig. 1. The electrodialytic laboratory cell. AN—anion exchange membrane; CAT—cation exchange membrane.

remediation method, oxidation and mobilization of metals can be a great advantage.

Electrodialytic remediation has shown potential as a remediation technique for dredged contaminated harbour sediment [9]. A laboratory cell for electrodialytic remediation is seen in Fig. 1. In compartment III, a sediment suspension is placed. Compartment III is separated from the electrolyte compartments I (anolyte) and II (catholyte) by ion exchange membranes. When the electric field is applied, the anions migrate towards the anode and the cations towards the cathode. By electrode processes, H^+ is produced at the anode and OH^- at the cathode. The selectivity of the ion exchange membranes ensure that ions are only removed from compartment III and not added from the electrolyte compartments. The available fraction of metals in the sediment are released by acidification due to water splitting ($H_2O \rightarrow H^+ + OH^-$) at the anion exchange membrane [10,11]. Water splitting occurs at the anion exchange membrane when the limiting current of the membrane is exceeded, which normally happens at the current densities used in electrodialytic remediation. The produced OH^- is transported over the anion exchange membrane and the produced H^+ enters the sediment suspension, migrating towards the cathode, while acidifying the sediment in compartment III. The removed metals concentrate in the electrolyte compartments and cations can precipitate at the cathode. The metals in the electrolytes can be further concentrated by electrodeposition. Thus, the volume of contamination can be reduced significantly.

In this study, electrodialytic remediation was used to remove heavy metals from wet, reduced, dredged sediment. The experiments were made under oxic conditions, because the sediment should preferably be oxidised during the experiments to increase the metal availability. There were two objectives: (1) to study the influence on the metal removal by variations in current density and stirring velocity of the sediment suspension and (2) to evaluate if the stirring velocity influenced the acidification and oxidation of the sediment during remediation.

2. Materials and methods

2.1. Experimental harbour sediment

Norwegian harbour sediment from Haakonsvern, Bergen was used in this study and the heavy metals of interest were Cu, Zn, Pb and Cd. The harbour sediment was dredged by NCC Norway with a special dredging device for removing only the finer, polluted material (<5 mm). The sediment was wet, black and smelled of H_2S when received. The wet sediment was frozen until use.

2.2. Analytical methods

Heavy metal concentrations in the sediment were determined after pre-treatment according to Danish Standard DS 259 [12]:

Table 1
Experimental conditions.

Experiment	Current density (mA/cm^2)	Stirring speed (rpm)
1	0	1000
2	0.6	1000
3	1.0	1000
4	1.4	1000
5	1.0	Manually
6	1.0	60

1.0 g dry sediment and 20.0 ml (1:1) HNO_3 were heated at 200 kPa (120 °C) for 30 min. The liquid was separated from the solid particles by vacuum through a 0.45 μm nucleopore filter and diluted to 50 ml. The heavy metals were thereafter measured by flame or graphite furnace AAS (atomic absorption spectrometry). The concentration units used in this paper are mg/kg dry material.

Organic matter was measured by loss of ignition at 550 °C for 1 h. The carbonate content was determined by a volumetric calcimeter method as described in Loeppert and Suarez [13]. The pH was measured in 1 M KCl at a liquid-to-solid ratio (L/S) of 5 (wet sediment) and after 1 hour of agitation, pH was measured by a Radiometer Analytical pH electrode. Redox potential was measured with a Radiometer Analytical redox electrode. Redox potentials were measured in the original sediment directly, i.e. inserting the electrode in the sediment and waiting for a stable reading. Redox potential was measured directly after the frozen sediment was thawed.

2.3. Electrodialytic experiments

A sketch of the laboratory cell is shown in Fig. 1. The cells were made of Plexiglas and the internal diameter of all cell parts was 8 cm. The length of compartment III was 10 cm and 240 g wet harbour sediment (approximately 80 g dry matter) and 260 ml distilled water was mixed in compartment III. The *L/S* ratio was approximately 5 in the experiments. Six experiments were made and the descriptions are seen in Table 1. All the electrodialytic experiments lasted 14 days.

The electrolyte in compartment I and II was 500 ml 0.01 M $NaNO_3$, which was adjusted with HNO_3 to pH < 2 during the experiments. The ion exchange membranes were obtained from Ionics (anion exchange membrane 204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). Platinum coated titanium electrodes from Permascand were used as working electrodes and a power supply (Hewlett Packard E3612A) was used to maintain a constant DC current. Magnetic pumps from Pan World were used to circulate the electrolytes, with a flow rate of 2.6 L/min. An IKA stirrer RW 11 basic "Labegg" with adjustable rotation velocity of 0–2000 rpm (in solution) was used to stir the sediment suspension. The stirrer was a plastic flap fastened to a glass spatula. The total length of the plastic flap was 6.5 cm and 0.6 cm wide. The hole in the experimental cell (compartment III) for the stirrer was 1.5 cm in diameter.

In experiments 1–4, the rotation velocity of the stirrer was set to 1000 rpm (fully suspended sediment). In experiment 5 the sediment suspension was manually stirred with a glass spatula every morning and afternoon for 10 s and in experiment 6 the stirring velocity was set to 60 rpm. In experiment 5, the sediment quickly sedimented creating a sediment and a liquid phase, but all the sediment was in suspension while manually stirring. In experiment 6, not all the sediment was in suspension at the low stirring velocity and a small fraction of the sediment deposited near the ion exchange membranes. Several digestions for heavy metal measurements were made on the sediment after experiment 5 and 6 to investigate if there had developed concentration differences in the sediment.

Table 2
Sediment characteristics.

Characteristic	Value
Cu (mg/kg DM)	45.3 ± 2.4
Zn (mg/kg DM)	117.4 ± 8.4
Pb (mg/kg DM)	53.5 ± 3.3
Cd (mg/kg DM)	2.1 ± 0.23
pH	7.5
Organic matter (%)	26
Carbonate content (%)	12
E_H (mV)—top layer	45
E_H (mV)—bottom layer	−110

pH and electrical conductivity were measured daily in the sediment suspension. The first measurements were made before applying the current and the suspension was mixed for 5 min before sampling. The sample was taken by turning the stirrer off and allowing the sediment to settle for 15 min. In experiment 5, with manual stirring, the sample was taken before the stirring. pH and electrical conductivity were measured with electrodes from Radiometer Analytical. In experiment 3, 5 and 6 redox potential was also measured by a Radiometer Analytical electrode. The samples were replaced in compartment III after the measurements and the stirring resumed.

At the end of the electrodialytic experiments, the membranes and the stirrer were treated with 1 M HNO_3 to extract the heavy metals that were adsorbed within the membrane or on the stirrer. The electrodes were rinsed in 5 M HNO_3. The harbour sediment suspension was filtered through a 45 μm filter. Both the liquid and the sediment solids were analysed for heavy metals. The electrolytes and the filtered liquid from compartment III were preserved by adding concentrated HNO_3 in a 1:4 ratio and heated at 200 kPa (120 °C) for 30 min. All the samples were measured by AAS (flame or graphite furnace).

3. Results and discussion

The sediment characteristics (Table 2) showed that the sediment had a high carbonate content (12%) and a high content of organic matter (26%). The redox potential was measured directly in the top and bottom layer of the thawed sediment. The sediment was reduced and the bottom layer anoxic, suggesting that the sediment was anoxic when frozen. However, the thawing process seemed to slightly oxidise the sediment in the top layer. The sediment was not kept in an oxygen free environment, since this was not the purpose of this study. The electrodialytic experiments were made directly after the sediment thawed otherwise the sediment was kept refrigerated in sealed containers until use.

Previous investigations of pH dependent desorption on oxidised Haakonsvern sediment showed a desorption order of Cd > Pb ~ Zn > Cu [11]. Cd started desorbing below pH 7, Pb and Zn between pH 4 and 6 and Cu only started desorbing below pH 1. Another leaching experiment made with fresh, reduced Haakonsvern sediment showed 5% Cu, 20% Pb, 40% Zn and 52% Cd extraction after 14 days at pH 2.8 [14].

3.1. Electrodialytic experiments

The metal removal was defined as the amount of metal found in the electrolytes (I and II), the membranes and electrodes, compared to the total metal amount measured in the cells after remediation. The metal removal after application of different current densities is seen in Fig. 2 and after different stirring velocities in Fig. 3. The metals were removed mostly to the catholyte and cathode, as metal cation species. Table 4 shows the final metal concentrations in the sediment along with the metal recovery in each experiment. The metal recovery is defined as the total amount of metal found in
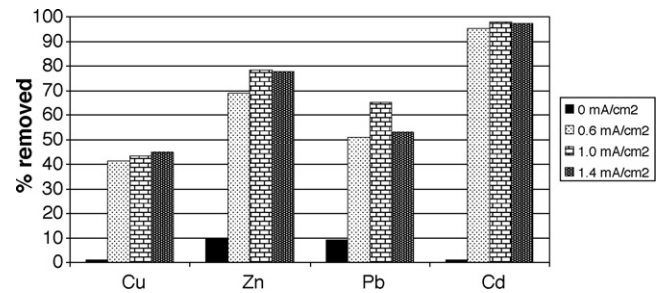

Fig. 2. The metal removal influenced by increasing current density while stirring is constant (1000 rpm).
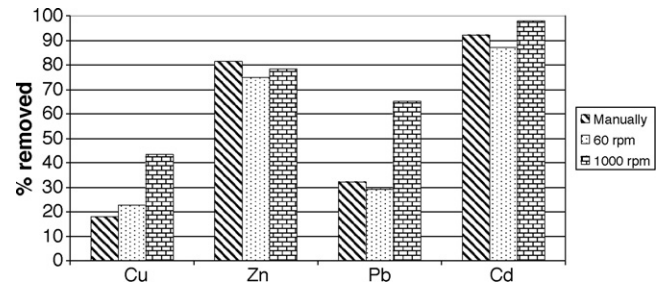

Fig. 3. The influence of stirring velocity of the sediment suspension on the metal removal while current density is constant (1.0 mA/cm^2).

the sediment and liquid in compartment III, electrolytes, membranes and electrodes after remediation, compared to the initial metal amount in the sediment. pH, electrical conductivity (EC) and redox potential (E_H) in the suspension in compartment III is shown in Fig. 4.
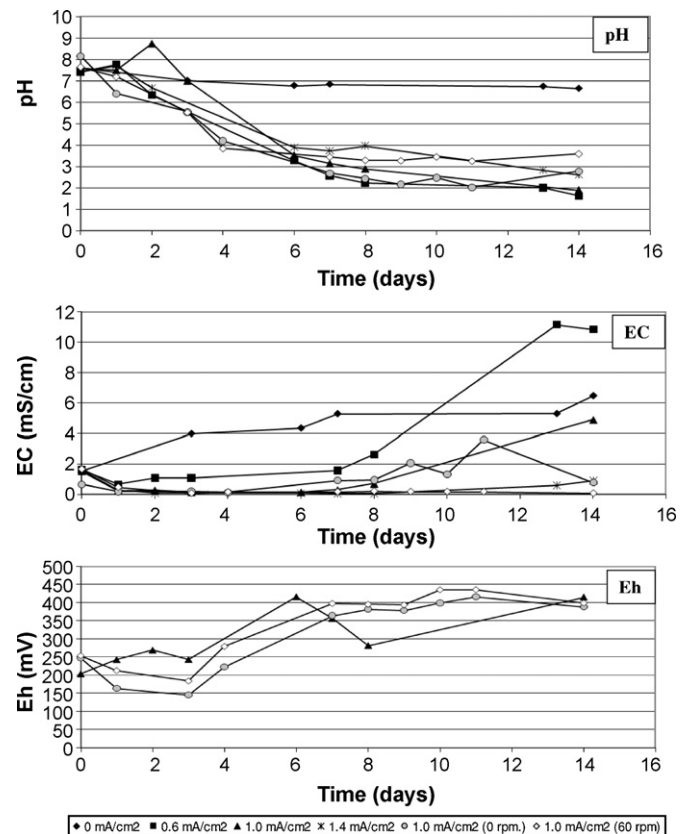

Fig. 4. pH, EC and redox potential in the sediment suspension.

Table 3
pH in the sediment and sediment mass loss after remediation.

Experiment	Final pH in sediment	Sediment mass loss (%)
1 (0 mA/cm^2, 1000 rpm)	6.9	20
2 (0.6 mA/cm^2, 1000 rpm)	2.1	26
3 (1.0 mA/cm^2, 1000 rpm)	2.1	21
4 (1.4 mA/cm^2, 1000 rpm)	2.5	28
5 (1.0 mA/cm^2 manually)	2.6	28
6 (1.0 mA/cm^2, 60 rpm)	2.8	29

The sediments were acidified during the electrodialytic remediation experiments, as seen in a decrease in pH in the sediment (Table 3). Due to acidification, a decrease in the sediment mass was observed due to dissolution of salts, carbonates and other acid soluble minerals. The mass loss in experiment 1 (pH 6.9) was also likely to result from dissolution of salts and carbonates. This is supported by electrodialytic soil remediation experiments where it was observed that carbonates dissolved at pH 7 and resulted in soil mass loss during experiments [15].

3.2. Metal removal

3.2.1. Current density

The removal increased significantly when applying an electric field to the sediment (Fig. 2). Even though, removal of Zn and Pb (<10%) was observed in the experiment without current, both to the catholyte and the anolyte, probably by inter diffusion [16] over the membranes. The sediment in this experiment was acidified compared to the initial pH (Table 2), which suggests that there was an increase in the redox potential in the sediment suspension or diffusion of H$^+$ over the ion exchange membranes from the acidic electrolytes. The redox potential was not measured in the sediment suspension during this experiment.

Of the tested current densities, the highest removal was found at 1.0 mA/cm^2, where 44% Cu, 78% Zn, 65% Pb and 98% Cd were removed, which was only slightly higher than at 0.6 mA/cm^2 and higher removal than was seen in extraction experiments without current at low pH [14]. Increasing the current density to 1.4 mA/cm^2 did not increase the removal further and the Pb removal was even lower at 1.4 mA/cm^2. pH in the sediment was slightly higher at 1.4 mA/cm^2, which could be the reason for the lower Pb removal. Previous experiments with remediation of harbour sediment also showed less efficient metal removal at current densities above 1.0 mA/cm^2 [11]. This suggests that there is an optimal current density for efficient metal removal and that higher current densities could cause water splitting at the cation exchange membrane, resulting in pH increase in compartment III, which was also indicated for remediation of soil fines suspension by Jensen et al. [17]. For the experimental conditions and sediment used here, the current density of 1.0 mA/cm^2 resulted in sufficient low pH for the highest removals.

The metal concentrations in the sediment (Table 4) decreased compared to the initial concentrations when electrodialytically

treated and the lowest concentrations were found in experiment 3. In experiment 1 (0 mA/cm^2) the metal concentrations increased compared to the initial concentrations, because of the sediment mass reduction.

3.2.2. Stirring velocity

The stirring velocity influenced the removal of Cu and Pb, whereas Zn and Cd were less affected (Fig. 3). The highest stirring velocity (1000 rpm) resulted in the highest removals and the Cu and Pb removals were 20% and 35% higher than at the lower stirring velocities. The removal of Zn, Pb and Cd was slightly lower at 60 rpm than for the manually stirring, which was also reflected in the metal concentrations. The final pH in the sediments was higher with lower stirring velocity than at 1000 rpm, which probably caused the difference in metal removal. The sediment suspension was oxidised during the experiments, regardless of the stirring velocity (Fig. 4).

pH in the sediment was 2.6 in experiment 5 (manually stirring) compared to 2.1 in experiment 3 (1000 rpm). The electromigration rate is higher in a solution than in the pore water of a stationary porous medium. Hydrogen ions produced by water splitting at the anion exchange membrane thus moves faster in the solution than in deposited sediment. This could explain the lower voltage over the cell when the sediment is not mixed in a suspension. The sediment was not stirred in experiment 5 before the measurements. Mixing the sediment before sampling might have given slightly higher pH readings, since the produced H$^+$ would react with the sediment constituents during stirring and the sediment's buffer capacity would affect the pH.

Generally in the stirred cell, the equilibrium between the amount of dissolved metals in the solution and the amount of metal in the sediment will be shifted as metals are removed. Thus, metals can be continuously released from the sediment during electrodialytic remediation, since equilibrium is not reached. In the experiment with manual stirring, the sediment separated from the liquid phase during the experiment. Thus, the conditions changed in cycles between being mixed and sedimentated in the cell. During the cycles when the sediment was separated from the liquid phase, the metal ions may have migrated in the sediment phase towards the cathode as well as being released to the overlaying liquid phase and removed here. However, this release from the sediment to the liquid could be limited by a low diffusion rate in the sediment. When the sediment was mixed, metals were probably released directly into solution, if the pH and redox conditions favoured a release. Despite the separation of the sediment and liquid in experiment 5, and sediment deposits in experiment 6, homogenous metal concentrations were found in the sediments. The mixing was probably frequent (experiment 5) and vigorous (experiment 6) enough to avoid pH and metal concentration gradients to form in the deposited sediment.

In experiment 6 (60 rpm), pH in the suspension and the sediment was higher than under the other stirring conditions, which probably caused the lower metal removal. The voltage was also higher in this experiment than at the other stirring velocities, thus there was higher electrical resistance in the cell. This could be caused by the small sediment deposits close to the ion exchange membranes, resulting in membrane fouling, which may have reduced the efficiency of the anion exchange membrane.

3.3. Sediment suspension

Fig. 4 shows pH, electrical conductivity and redox potential in the sediment suspension as a function of time.

The sediment suspensions redox potentials (E_H) were between +200 and +250 mV at the beginning of the experiments. This shows

Table 4
Final metal concentrations in the sediment and metal recovery in the electrodialytic experiments.

Exp. no	Final metal concentration (mg/kg)				Metal recovery (%)			
	Cu	Zn	Pb	Cd	Cu	Zn	Pb	Cd
1	55.9	144.9	52.8	2.39	98	117	90	88
2	38.5	37.6	26.6	0.10	113	81	88	133
3	31.2	35.5	22.1	0.06	106	143	97	116
4	31.6	35.7	27.0	0.08	91	102	82	122
5	47.8	35.6	40.0	0.32	89	109	74	122
6	45.0	42.4	47.2	0.39	87	112	82	100

that the sediment was oxidised while mixing the sediment as preparation of the experiments, and that this oxidation happened quickly. After 7 days of remediation the sediment suspensions were oxidised and the redox potentials stabilised at around +400 mV. The readings of the redox potential showed a decrease between days 6 and 8 in experiment 3 (fully stirred) and between days 0 and 3 in experiments 5 (manual stirring) and 6 (low stirring). The reason for this was unclear, but could be due to analytical errors. No significant difference was seen in the redox potential caused by the different stirring processes, which indicates that the stirring of the suspension was vigorous enough to obtain oxidative conditions during the experiments. However, the redox potential was measured in the sediment suspension and in the experiments with lower stirring, sediment deposited at the bottom of the cell. Thus, different redox potentials could be present in the deposited sediment phase. This, together with the higher pH in the sediment, could explain the lower removal of Cu and Pb in the experiments with lower stirring velocity, since metal solubility of Cu and Pb was reported more susceptible to redox and pH changes than Zn and Cd [2].

pH decreased in the sediment suspensions and the main acidification generally occurred before 6 days of remediation. The produced acid at the anion exchange membrane due to water splitting was buffered by the carbonates in the sediment, which caused the delayed acidification. The changes in redox potential could also result in a decrease in pH, but the decrease is generally small in highly buffered sediments [4,5]. However, this most likely happened in experiment 1, without current, where a slight decrease in pH (from 7.6 to 6.8) was observed in the sediment suspension within 4 days. A further decrease in the pH was not observed after the redox potential stabilised at +400 mV after 7 days of remediation. pH decreased faster and was lower in all the experiments with applied current, which indicates that the main process for acidifying the sediment was water splitting induced by the current rather than changes in the redox potential. Final pH in the sediment suspensions was below 2 in experiments 2 ($0.6 \, mA/cm^2$) and 3 ($1.0 \, mA/cm^2$) with full stirring. In experiment 4 ($1.4 \, mA/cm^2$) and experiment 5 (no stirring) the final pH was below 3 and in experiment 6 (low stirring) the final pH in the sediment suspension was 3.6. These pH values were slightly different than the pH measured on the sediments after the experiments (Table 3). In experiment 5 an increase in pH was seen between days 11 and 14.

The electrical conductivity (EC) varied over time for the different experimental conditions. In the experiments with 0 and $0.6 \, mA/cm^2$, the EC increased all through the experiments. In the other experiments the EC was lower, especially in experiment 4 ($1.4 \, mA/cm^2$) and 6 (low stirring) where the EC was below 1 mS/cm throughout the experiments. In experiment 3 ($1.0 \, mA/cm^2$) and 5 (no stirring), the EC started at the same low level as in experiment 4 and 6 but increased after 7 days of remediation. In experiment 3 the EC coincided with the lowest pH in the sediment suspension. A decrease in EC in experiment 5 was seen together with an increase in pH between days 11 and 14. In experiment 1 ($0 \, mA/cm^2$) the sediment was slightly acidified, which was sufficient to dissolve easily soluble species, which resulted in increased EC. Since the ions could not electromigrate, the amount of dissolved ions in compartment III and the EC increased. In experiment 2 ($0.6 \, mA/cm^2$) the current strength did not seem efficient in removing all the released ions from the sediment. In the other experiments, the current strength seemed efficient in removing dissolved ions and the EC was generally less than 0.9 mS/cm. Nevertheless, the EC increased in experiment 5 (manually stirring), which indicates slower release processes due to the limited stirring or due to lower pH and easier transport of H^+ in the liquid phase.

The voltage between the electrodes was generally high, in agreement with the low electrical conductivity. The voltage was highest in the experiment 6 (60 rpm) of the three experiments with different stirring velocity, probably due to clogging of the ion exchange membranes.

4. Conclusion

Electrodialytic remediation was used to remove heavy metals from anoxic contaminated harbour sediment. The highest removal obtained was 98% Cd, 78% Zn, 65% Pb and 44% Cu at $1.0 \, mA/cm^2$. In anoxic sediment metals are usually present as immobile metal sulphides. However, the sediment was partly oxidised when first mixed in the electrodialytic cell and further during the electrodialytic experiments, which change the metal speciation and the availability. The sediment suspension was oxidised after 7 days of remediation and this was not dependent on the stirring velocity.

Acidification of sediment was observed in all the electrodialytic experiments, including an experiment without applied current. Changes in redox potential could acidify this sediment, however acidification resulting from redox changes was less significant compared to the acidification caused by water splitting at the anion exchange membrane in the experiments with applied current density.

The Cu and Pb removal was dependent on the stirring velocity of the sediment suspension, where the highest velocity resulted in the highest removals. The metal removal was less dependent on the applied current density. It seemed crucial for the remediation potential for all metals to keep the sediment in suspension to obtain low pH in the sediment. For operational conditions it is also important to keep all the sediment in suspension to avoid deposits and high voltage levels.

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