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An optimised method for electrodialytic removal of heavy metals from harbour sediments

Kristine B. Pedersen^a, Pernille E. Jensen^b, Lisbeth M. Ottosen^{b1} and Tore Lejon^{*a}

*Corresponding author: e-mail tore.lejon@uit.no; tel. +47 776 44736; fax. +47 776 44765

^a Department of Chemistry, University of Tromsø, The Arctic University of Norway, Postbox 6050 Langnes, N-9037 Tromsø, Norway.

^b Arctic Technology Centre, Department of Civil Engineering, Technical University of Denmark, Building 118, 2800 Lyngby, Denmark

Abstract

A 2-compartment electrodialytic cell set-up for treatment of solid materials has in many respects proven superior to other types of cells in removing heavy metals from sediments. Most notably, remediation times were shorter, energy consumption was lower and higher removal efficiencies were observed. By employing multivariate modelling and investigating additional experimental variables, the relative importance of variables effecting remediation was determined and response surfaces for heavy metal removal were calculated. Employing optimal conditions it was possible to remove targeted metals (Pb, Cu, Zn), by 73 – 96 %, and remediation objectives could be met in a large region of the studied experimental domain.

Keywords: Electrokinetics, Chemometrics, Sequential extraction, Heavy metals, Harbour sediments

¹ ISE member

1. Introduction

Electrodialysis has previously been used to remove heavy metals from solid materials [1-7]. The method is based on the principles of electrokinetic remediation (EKR) in which an electric field of low level current is applied to the polluted material, conducted by the pore water or suspension liquid in the solid material. In uncontrolled EKR, the electrolysis reactions at the electrodes result in the formation of an acidic front at the anode (generated protons) and an alkaline front at the cathode (generated hydroxyl ions). In the zone between the acidic and alkaline fronts water is generated, the pH changes from acidic to alkaline, resulting in precipitation, e.g. of cations from the acidic front. Since electromigration, which is the transport of ions and ionic complexes from the material treated, dominates the transport process of ions and the effective ionic mobility of the proton is nearly twice as high as for the hydroxyl ion, the acidic front dominates the system. Acidic conditions cause the heavy metals adsorbed to particles in the solid material to desorb and be transported to the cathode. The rate of acidification of the polluted material depends on the physical and chemical properties of the polluted material as well as the experimental settings. A high buffering capacity will for instance retard the acidification as may high contents of organic species and salts [8-10].

Electrodialysis was introduced as a measure of controlling the transport of ions to and from the polluted solid material in the 1990s. In the electro-dialytic set-up, ion-exchange membranes separate the electrodes and electrolytes from the polluted material. Several cell designs have been employed, containing 3 to 5 compartments [6]. In the original 3-compartment cell, the polluted material is placed in the center compartment. An anion exchange membrane is placed adjacent to the anode and likewise a cation exchange membrane is placed adjacent to the cathode, thus preventing acidic and alkaline fronts from entering the polluted material. Acidification of the polluted material necessary for desorption and mobilisation of the metals is however still achieved, mainly due to water splitting at the anion exchange membrane [11] and the hydroxyl ions generated will be transported across the membrane to the anolyte while the protons will advance towards the cathode. Protons supplied to the polluted material will cause the metals to desorb and be transported by electromigration towards the cathode [8, 9].

In order to control which ions are in contact with the electrodes, 4- and 5-compartment cells have been introduced. In these designs an extra compartment is added between the electrode compartment and the polluted material with alternating ion exchange membrane, which means that anions and cations transported from the polluted material to the first electrolyte compartment on either side will not reach the electrodes. This is a means of preventing generation of chloride gas at the anode (especially relevant for harbour sediments) and precipitation of metals on the cathode. Even though the 5-compartment cell was more efficient in some respects, the 3-compartment design became the choice for most applications and was in addition the foundation for scaling up efforts to stack designs that facilitate remediation of larger quantities. The basis for the design remaining the same [12, 13], i.e. to apply ion exchange membranes to separate the polluted material from the circulating electrolytes.

It has been well established that applying a stirred rather than a stationary electrochemical cell set-up significantly improves removal efficiencies of heavy metals from soil [14], harbour sediment [15] and fly ash [5]. For harbour sediment it was in addition shown that the stirring rate influenced Cu and Pb removal, while not significantly influencing the removal of Cd and Zn [16]. Other experimental variables that influence the removal efficiencies of heavy metals in the traditional 3-compartment cell set-up include current density, remediation time and the liquid-solid ratio (L/S) of the sediment suspension [6, 15, 17].

Figure 1: The 2-compartment electrochemical remediation cell.

A new cell design was developed at The Technical University of Denmark in 2011 and a patent was applied for in 2013 (EU 13183278). The set-up consists of a 2-compartment cell; one compartment containing the sediment suspension and the anode, while the electrolyte is circulated in the second compartment (figure 1). A cation exchange membrane separates the two compartments, preventing advancement of an alkaline front due to the electrolysis reaction at the cathode. Acidification is caused by protons via the electrolysis reaction at the anode and hence occurs faster in the 2-compartment than in the 3-compartment cell set-up resulting in a higher conductivity as observed in a recent study [18]. In addition, the final pH and voltages were observed to be lower in the 2-compartment cell. These

results were confirmed when comparing different cell designs in a screening study and it was in addition observed that the removal of metals were generally more efficient in the 2-compartment cell, attributed to the faster acidification and higher content of protons [19].

In the study the influence of a limited number of experimental variables were investigated employing Projections onto Latent Structures (PLS) [20-22]. Among the advantages of PLS are that it copes with co-linearity between variables and provides plots of the data compressed to fewer dimensions than the original dataset [20-23]. The results may then be presented in different ways, e.g. as Variable Importance in the Projection (VIP) plots. These plots will reflect the relative importance of the model parameters included. The liability of PLS in predicting experimental conditions for specified remediation has also been published elsewhere [24].

Sequential extraction is a method widely used for investigating metal partitioning in soils and sediments. For harbour sediment studies in relation to EKR and electrolysytic remediation, the most commonly investigated sediment fractions are exchangeable, reducible, oxidisable and residual phases. The distribution of metals in the sediment fractions can be used for assessing metal availability.

Ribiero *et al.* showed that electrolysytic remediation accelerates weathering of the soil making metals in all soil fractions more available [25]. Studies of harbour sediments have shown that the heavy metal content quantitatively decreased in all sediment fractions during electrolysytic remediation or EKR [26-28]. The removal of heavy metals from the oxidisable fraction was attributed to oxidation of the sediment during electrolysytic remediation. It was speculated whether the removal from the residual fraction was due to deviations in the sequential extraction method, i.e. whether some of the organic matter had not been oxidised hence leaving part of the oxidisable fraction in the residual fraction [28]. A study of 10 soils of organic content up to 21%, however, showed that replicating the oxidation step of sequential extraction did not significantly change the results of metal partitioning in the soil [29].

Since previous results revealed the 2-compartment cell to be most effective it was decided to extend the study by investigating other parameters that might influence remediation, using the 3-compartment cell as reference. Experimental variables included *remediation time, current density, L/S, stirring rate,*

and in addition *suspension liquid* to test the comparative influence of applying tap water rather than distilled water, and the influence of *light* for operating in areas with periods of limited daylight (as would be the case in the Arctic region). The difference in efficiency between the two cells was investigated and included evaluation of the experimental variable importance, clean-up levels, energy consumption and heavy metal removal in relation to the original distribution of these in the sediment fractions. After identifying relevant variables, the objective was to calculate optimal remediation conditions for the 2-compartment cell.

2. Experimental

2.1 Experimental sediments

Sediments from Sisimiut, Greenland were sampled from the top 10 cm of the seabed using a Van Veen grab and were kept frozen during transport and stored in a freezer until analysed or treated.

2.2 Sediment analyses

Major elements and heavy metal concentrations (Al, Ca, Fe, K, Mg, Mn, Na, V, Cr, Cu, Ni, Pb, Zn) were measured based on digestion (Danish standard DS259). Sediment dried at 105°C (1.0 g) and HNO₃ (9 M, 20 mL) were autoclaved (200 kPa, 120 °C, 30 minutes). Solid particles were subsequently removed by vacuum filtration through a 0.45 µm filter and the liquid was diluted to 100 mL. Metal concentrations in the liquid were measured by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) and are given as mg metal per kg dry matter.

Chloride content was measured by agitating sediment (10 g) dried at 40 °C with Millipore water (40 mL) on a horizontal shaker for 20 hours. Solid particles were removed by vacuum filtration (0.45 µm filter) and the chloride concentration was measured by ion chromatography.

Carbonate content was determined by treating dried sediment (5.0 g) with HCl (3 M; 20 mL) and the CO₂ developed was measured volumetrically in a Scheibler apparatus, calibrated with CaCO₃.

Organic content was based on loss of ignition of dried sediment (2.5 g) being heated at 550 °C for an hour.

pH (KCl). Dried sediment (5.0 g) was agitated with KCl (1M, 12.5 mL) for an hour and pH was subsequently measured using an analytical radiometer electrode.

Conductivity. Dried sediment (5.0 g) was agitated with distilled water (25 mL) for an hour and the conductivity was subsequently measured using an analytical radiometer electrode.

Grain size distribution was determined by wet sieving. Wet sediment (75 g), distilled water (350 mL) and Na₄P₂O₇ (0.1 M, 10 mL) were agitated for 24 hours. The slurry was subsequently sieved through a 63 µm sieve to determine the fraction above and below 63 µm.

Sequential extraction was made in four steps based on the improvement of the three-step method [30] described by Standards, Measurements and Testing Program of the European Union. Air-dried sediment (0.5 g) was first extracted with acetic acid (0.11 M, 20 mL) for 16 hours; secondly extracted with hydroxylammonium chloride (0.1 M, 20 mL) for 16 hours; thirdly extracted with hydrogen peroxide (8.8 M, 5 mL) for 1 hour, then extracted at 85 °C for 1 hour, followed by evaporation of liquid at 85 °C, subsequently the cooled solid fraction was extracted with ammonium acetate (1 M, 25 mL, pH 2) for 16 h; and fourthly digestion of the remaining solid particles (as described above).

pH dependent extraction experiments were made by agitating 8 samples of dried sediment (5 g) with HNO₃ (25 mL) in varying concentrations (0.01-1 M). Extractions with distilled water were made as a reference. All the samples were agitated for a week on a horizontal shaker. Subsequently samples settled for 15 minutes and the pH was measured. The sediment suspensions were vacuum-filtered through a 45 µm filter and digested (as described above).

2.3 Electrodialytic remediation experiments

2.3.1 Materials

The 2-compartment and 3-compartment cells used in the study were designed using the same materials and sizes. The 3-compartment cell consisted of a centre compartment and two adjoining electrode and electrolyte compartments. An anion exchange membrane was placed between the anode- and centre compartment, while a cation exchange membrane separated the cathode- and centre compartment. In comparison the 2-compartment cell excluded the anode compartment and anion exchange membrane (Figure 1). The cell compartments were manufactured from Plexiglas and the dimensions were: length of electrolyte compartments 3.5 cm; length of sediment suspension compartment 10 cm; inner diameter of all compartments 8 cm. Ion exchange membranes were from Ionics (anion exchange membrane 204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). The electrolyte used was NaNO_3 (0.01 M) adjusted to pH 2 by HNO_3 (7 M). The electrolyte liquids (350 mL) were circulated via Pan World pumps with flow rates of 30 mL/min. Platinum coated titanium electrodes were used in each electrolyte compartment and a power supply (Hewlett Packard E3612A) maintained a constant DC current. The sediment suspension was stirred by an RW11 Basic lab-egg (IKA 2830001) with a stirrer consisting of plastic flaps (4 cm x 0.5 cm) fastened to a glass rod. No light conditions in selected experiments were obtained by covering the electrodialytic cell in tin foil.

After the experiments the sediment suspensions were gravitational filtered and the heavy metal concentration in both the suspension liquid and solids were measured. The stirrer, membranes and electrodes were rinsed in HNO_3 (5 M) overnight and the heavy metal concentrations in the rinsing liquids as well as with the electrolyte liquids were measured by ICP-OES.

2.3.2 Experimental design

An experimental design was made for testing the comparative influence of experimental variables in the two different cell set-ups including a total of 7 experimental variables in the design. The continuous variables were *current density*, *remediation time*, *L/S* and *stirring rate*. The discrete variables were *cell set-up*, *suspension liquid* (distilled water/tap water) and *light/no light*. Undertaking a complete two-level factorial design would entail conducting 2^7 (128) experiments. By assuming that the interaction effects are negligible compared to the main effects, the amount of experiments could be reduced to a 2^{7-4} fractional factorial design consisting of 8 experiments (1-8) based on a three-variable matrix from a complete 2^3 factorial design. In addition 4 experiments (9-12) equivalent to the centre point of the continuous variables were conducted. In order to ensure that maximum variation in the experimental domain was covered, MODDE 7 software was used for the design.

A second design was made for assessing variable influence of the same experimental variables in the 2-compartment cell by using experiments 5-8 and adding 4 experiments (13-16) to complete a 2^{6-3} fractional factorial design. Experiments 11 and 12 represented the centre point of the continuous variables.

The experimental settings are given in table 1.

Table 1: The experimental designs

Experiment	Time after acidification/h	Current density/ mA/cm ²	L/S/ ml/g	Stirring rate/rpm	Cell set-up	Suspension liquid	Light/no light	Design
1	48	0.04	2	1300	3C	Tap water	Light	1
2	444	0.04	12	100	3C	Distilled	Light	1
3	48	1.0	12	1300	3C	Distilled	No light	1
4	444	1.0	2	100	3C	Tap water	No light	1
5	48	0.04	2	100	2C	Distilled	No light	1,2
6	444	0.04	12	1300	2C	Tap water	Light	1,2
7	48	1.0	12	100	2C	Tap water	Light	1,2
8	444	1.0	2	1300	2C	Distilled	Light	1,2
9	246	0.52	7	700	3C	Distilled	Light	1
10	246	0.52	7	700	3C	Distilled	No light	1
11	246	0.52	7	700	2C	Distilled	Light	1,2
12	246	0.52	7	700	2C	Distilled	No light	1,2
13	48	0.04	2	1300	2C	Tap water	Light	2
14	444	0.04	12	100	2C	Distilled	Light	2
15	48	1.0	2	1300	2C	Distilled	No light	2
16	444	1.0	12	100	2C	Tap water	No light	2

The clean-up levels were calculated as the percentage of the given metal/heavy metal removed compared to the initial amount in the sediment.

The power consumption in Wh (E) was calculated as:

$$\int_{t=0}^t E = VI dt$$

where V is the voltage between the electrodes (V), I is the current (A) and t is the remediation time (h).

2.4 Multivariate analysis – PLS modelling

In this study SimcaP11 software was used for PLS modelling based on the 16 experiments in table 1. The X matrix consisted of the experimental variables and the Y matrix consisted of the clean-up levels (%) of the metals/heavy metals in the sediment. In order to include the discrete variables in the modelling, they were arbitrarily set to -1 or 1.

VIP plots were used to assess the variable importance in the calculated models, expressed in absolute values. In order to establish whether a given variable has a positive/negative influence on the model, coefficient plots were used. Contour plots were used for assessing the removal of metals/heavy metals as a function of the experimental variables.

3. Results

3.1 Sediment characteristics

The sediment characteristics (table 2) revealed a low buffer capacity (low content of carbonate and organic matter). Triplicate determinations of metal concentrations were made prior to all 16 experiments and the high standard deviation of Ca indicates that it is not as evenly distributed in the sediment as the other elements. Since Ca is associated with carbonate in the sediment, this implies that the content of carbonate may also be unevenly distributed in the sediment. The heavy metals Cu, Pb and Zn (table 3) also have high standard deviations, which may be attributed to uneven distribution of the contamination.

Table 2: Sediment characteristics.

Characteristic	Units	Value
<i>Carbonate</i>	%	1.7 ±9%
<i>Organic matter</i>	%	6.4 ±1.5%
<i>pH</i>		7.49±0.2%
<i>Grain size <63µm</i>	%	19.0
<i>Chloride</i>	mg/kg	7951±9%
<i>Al</i>		3828±9%
<i>Ca</i>		9593±29%
<i>Fe</i>		9263±12%
<i>K</i>		1365±9%
<i>Mg</i>		3077±8%
<i>Mn</i>		71±11%
<i>Na</i>		4742±13%
<i>V</i>		26.8±15%

Sediment quality guidelines currently do not exist for Greenland, so the concentrations of heavy metals in the sediment are compared to guidelines for OSPAR and relevant Arctic countries in table 3. OSPAR has two sets of background criteria; background concentrations (BC) and background assessment concentrations (BAC). The latter is based on statistical calculations in which there is a 90% probability that the observed mean concentration will be below the BAC when the true mean concentration is equivalent to BC [31]. The national sediment quality guidelines of the countries included in table 3 are based on similar calculations, but different assessments of concentrations that pose low-high risks of adverse biological effects, giving rise to variation in sediment quality criteria. In table 3, the listed

threshold values are rarely associated with adverse biological effects and despite variations between the countries; do not excessively exceed the OSPAR BAC levels.

Table 3: Heavy metal concentrations in the sediment compared to selected sediment quality guidelines.

	Cr	Cu	Ni	Pb	Zn
	mg/kg dry matter				
<i>Initial concentrations</i>	22.1±3.3	171±54	12.7±1.7	55±15	249±45
OSPAR BC [31]	10	5	5	25	50
OSPAR BAC [31]	81	27	36	38	122
Danish EPA Class A [32]	50	20	30	40	130
Norwegian EA Class 1 [33]	70	35	30	30	150
Canadian CCME ISCQ [34]	52.3	18.7		30.2	124
US EPA TEL (Reg.3) [35]	52.3	18.7	15.9	30.2	124

BC – Background concentration

BAC – Background assessment concentrations

ISCQ – Interim sediment quality guideline

TEL – Threshold Effect Level

The concentrations of Cr and Ni are below national threshold values and within the statistical background values of OSPAR. Cu, Pb and Zn exceed all the sediment quality guidelines and were hence selected for remediation in this study.

The pH dependent desorption showed that heavy metals in the sediment were desorbed in the order Zn (pH 6) > Ni (pH 5) > Cr, Cu, Pb (pH 3). Another study of a carbonaceous sediment revealed a desorbing order of Zn (pH 6) > Pb (pH 2) > Cu (pH 1) [6], which shows that heavy metal desorption varies from sediment to sediment and is likely to be related to sediment characteristics. In this study, it appears to be essential to reach pH levels of 3 or lower in the electrodynamic experiments to desorb the targeted heavy metals Cu, Pb and Zn.

3.2 Differences in electrodialytic removal efficiency of cell designs

3.2.1 Electrolytic experiments

Table 4 summarises the results of the 12 electrolytic experiments of design 1 (table 1). The final pH in all of the 2-compartment cell experiments was lower than in similar experiments conducted in the 3-compartment cell, so potentially higher desorption of heavy metals from the sediment was expected in the 2-compartment cell. In both of the cell set-ups, the average final pH was well below 3, which, based on the results of the pH dependent desorption, suggests that desorption of the targeted heavy metals occurred over most of the experimental domain. pH was above 3 in one of the 2-compartment and two of the 3-compartment cell experiments.

As expected, there was a difference in the acidification time in the two cell set-ups [19] with an average difference of 9 hours (table 3). For the experiments with the longest total remediation time (>447 h), the difference in acidification time accounted for less than 2 % of the total time, while the difference was more significant for experiments conducted at the lowest time intervals, accounting for up to 20 % of the total remediation time. The sediment had a low buffer capacity and for sediments with higher contents of carbonate and organic matter, a more distinct difference in the acidification time between the two cells may be expected.

The energy consumption per mass of dry sediment (Wh/g) was lower in the 2-compartment cell both with regards to the acidification and the remediation time after acidification, which is also in line with our previous findings [19]. One of the experiments conducted in the 3-compartment cell had very high energy consumption (experiment 3); if this result was be excluded, the average energy consumption for the remaining experiments of the total remediation time, as well as time after acidification, would still be at levels equivalent to twice the average energy consumption in the 2-compartment cell.

Table 4: Results for the 2- and 3-compartment cells.

	2-compartment cell		3-compartment cell	
	Range	Average	Range	Average
Electrodialytic conditions				
<i>Final pH</i>	1.13-3.22	1.96	1.33-3.63	2.31
<i>Time for acidification/h</i>	3-168	42	12-186	51
Energy consumption/kWh/kg				
<i>Total</i>	0.005-0.83	0.34	0.003-11.6	2.46
<i>After acidification</i>	0.001-0.79	0.30	0.001-8.22	1.88
Removal efficiencies/%				
<i>Al</i>	0-54	33	0-36	22
<i>Fe</i>	5-65	39	6-48	34
<i>Mn</i>	2-62	37	21-47	36
<i>V</i>	0-67	45	2-55	37
<i>Ca</i>	23-91	70	37-79	63
<i>K</i>	26-57	40	26-57	35
<i>Mg</i>	17-69	48	29-52	45
<i>Na</i>	85-92	91	88-94	91
<i>Cr</i>	0-62	21	5-52	18
<i>Cu</i>	0-94	67	22-65	41
<i>Ni</i>	0-84	49	0-51	24
<i>Pb</i>	0-73	46	0-55	38
<i>Zn</i>	0-96	74	54-87	71

The removal efficiencies for Al, Fe, Mn, V, Ca, K, Mg and Na as well as the heavy metals Cr, Cu, Ni, Pb and Zn were higher in the 2-compartment cell. It is interesting to note that the least efficient removal of both heavy metals and trace elements are encountered in the 2-compartment cell (experiment 5). In this part of the experimental domain it appears that many of the heavy metals are still in the lag phase of the electro dialytic removal [36] in which there

is limited removal of the given metal. The same part of the experimental domain is not covered by the 3-compartment cell experiments and no direct comparison is possible.

3.2.2 Removal in relation to metal/heavy metal distribution in the sediment fractions

The distribution of metals/heavy metals in the different fractions of the sediment along with the highest observed removal percentages in the 2- and 3-compartment cell set-ups is illustrated in figure 2. For the trace elements Al and V the removal percentages in the 3-compartment cell are equivalent to the amounts found in the exchangeable and reducible fractions, while for Ca, Fe, Mg and Mn the quantity removed also included metals bound in the less available oxidisable fraction, which could be related to the oxidation of the sediment and subsequent mobilisation during the electro-dialytic removal. In the 2-compartment cell, removal of the trace elements from all of the sediment fractions occurred, indicating that there may be a risk of dissolving the stable minerals in the sediment than in the 3-compartment cell.

Figure 2: Distribution of the metals/heavy metals in the different sediment fractions based on sequential extraction; the highest removal efficiencies in the experimental domain of the 2- and 3-compartment cell set-ups are included.

The removal efficiencies of Cr, Ni, Cu and Pb in the 3-compartment cell are equivalent to amounts found in the exchangeable and reducible fractions, and in addition parts of the oxidisable fractions, indicating oxidation of the sediment during the electro-dialytic removal, subsequently releasing heavy metals bound to the organic matter in the sediment. The amount of Zn removed corresponded to removal only from the exchangeable fraction, which is most likely attributed to the fact that most of the Zn (>90 %) was found in this fraction. In the 2-compartment cell relatively higher amounts of Cu, Pb and Zn were removed from the oxidisable/residual fractions, which may indicate higher oxidation of organic matter in this set-up than the 3-compartment cell. Removal of Cr and Ni from the residual fractions in the 2-compartment cell may indicate dissolution of the more stable sediment minerals, since the initial concentrations were low implying naturally occurring levels (table 3).

3.2.3 Comparative variable influence

PLS modelling of all the metals/heavy metals was made to assess the comparative influence of the experimental variables in design 1 (table 1); yielding a model with a correlation factor R²_Y of 0.86 and a predictive power Q² of -0.076. The model was unstable, as reflected in the low predictive power, which could be related to the cell designs being too different to be treated in the same model. Modelling the two set-ups separately resulted in more stable models with predictive powers of 0.43 (3-compartment cell) and 0.89 (2-compartment cell). Even though the new models do not include identical settings it is possible to deduce indications of the variable importance.

The VIP plot of the 2-compartment cell (figure 3) reveals that the most significant variables are *time after acidification* and *stirring rate* (VIP values >1) and from coefficient plots it is found that both variables should be at high setting for best results. Analysing the 3-compartment cell in the same way identifies *current density* (high), *suspension liquid* (distilled water) and *L/S* (high) as the most important variables.

Figure 3: VIP values for the two cell set-ups, calculated from two separate PLS models.

Variables with high VIP values have the highest influence on the electro dialytic removal.

3.3 Development of remediation strategy

Prior to proceeding with PLS modelling for assessing optimal remediation conditions, remediation objectives for the studied sediment had to be determined. Remediation criteria can vary depending on country and which sediment quality is desired, e.g. whether concentration levels should be associated with low biological effects or whether higher risk of adverse biological effects are acceptable. In this study, remediation objectives have been set according to the Danish criteria for Class A, since there are no quality guidelines for Greenland. For the sediment at hand, minimum removal efficiencies of 88 % for Cu, 27 % for

Pb and 48 % for Zn compared to initial concentrations were necessary to meet the criteria. It was also clear that the remediation objectives were only met when using the 2-compartment cell in the studied experimental domain (table 3), which confirms the results from our previous study [19].

3.3.2 PLS model for the 2-compartment cell

In order to allow for an accurate model to be calculated an additional 4 experiments were performed, extending the experimental design of the 2-compartment cell (design 2 in table 1) to a 2^{6-3} design. The PLS model correlation factor R^2Y was 0.91 and the predictive power, Q^2 , was 0.24. The fairly low predictive indicated too large an experimental domain, in which several electrochemical removal phases [36] (different removal rates) were covered, or that the model included metals not behaving similarly. The model results can however be used for retrieving indicative and general trends.

The comparative variable importance for the electrochemical removal in the 2-compartment cell set-up was assessed by a VIP plot (figure 4), which revealed that *time after acidification* and *current density* were the most important variables. The *stirring rate* had a moderately high VIP value but could still significantly influence the removal of some metals/heavy metals in the 2-compartment cell. This is in line with the previous results, where the same three variables had the highest influence on the electrochemical removal in the 2-compartment cell (figure 3). It should be noted that the variables *current density* and *stirring rate* were in the reverse order in the previous calculations of the incomplete design.

Figure 4: VIP plot of the 2-compartment cell (design 2). Variables with high VIP values have the highest influence on the electrochemical removal.

Modelling the elements separately gives an overview of differences in variable importance for removal of the heavy metals. Since the targeted metals in this study were Cu, Pb and Zn, these have been modelled separately and the results of the VIP plots are summarised in figure 5.

For Cu the variables significantly influencing the removal from the sediment were *current density*, *stirring rate* and *time after acidification* in order of importance. The fact that *stirring rate* was more important than *remediation time* for the removal of Cu indicated that oxidation of the sediment and subsequent release of Cu from the sediment. More than 60 % of Cu was bound in the oxidisable fraction and substantial removal from this fraction was observed (figure 3) in parts of the experimental domain.

Figure 5: VIP values of Cu, Pb and Zn modelled separately. Variables with high VIP values have the highest influence.

The importance of the three experimental variables that significantly influenced Pb and Zn removal were in the order *time after acidification*>*current density*>*stirring rate* which was in line with the findings of the general model (figure 4). For Zn it appears that *L/S* also has a moderate influence on the removal, which could be due to more than 90 % of Zn in the sediment being bound to the exchangeable fraction. A higher *L/S* may lead to relatively higher solvation of Zn.

3.3.3 Optimal remediation conditions

VIP plots do not show whether high or low values of the experimental settings improve the removal efficiencies. Coefficient plots of the three target heavy metals show that high values of *current density*, *remediation time* and *stirring rate* provide the optimal conditions for removal of the heavy metals within the studied domain. Suspension liquid and light/no light does not significantly improve removal efficiencies of the three heavy metals.

Determining the optimal remediation conditions may be done for each heavy metal by contour plots, which plot the removal efficiencies as functions of relevant variables. As an example, in the contour plot of Cu (figure 6) the two most influential variables, current density and stirring rate are varied, while the other variables are fixed at: *time after acidification* (246 h); *L/S* (2 ml/g); *distilled water*; *light*. *L/S* was fixed at a low value since this would remediate a larger sediment quantity in relation to cell size.

Figure 6: Contour plot of Cu (removal efficiencies %) as a function of stirring rate and current density.

Based on the contour plot several remediation strategies for the removal of approximately 88 % of Cu from the sediment can be chosen. If for instance energy consumption is an issue, a high stirring rate and a low current density of 0.5 mA/cm^2 can be applied. Similar contour plots can be made with other variables, e.g. if the remediation time is a more crucial parameter.

Contour plots can be made for all of the target heavy metals subsequently developing remediation strategies for the three heavy metals. It is however possible to include the remediation objectives in one plot – a sweet spot plot, which illustrates in which parts of the experimental domain the remediation objectives are met as a function of two variables. Figure 8 is a sweet spot plot of the three remediation objectives; removal efficiencies for Cu (88 %), Pb (27 %) and Zn (48 %) as a function of time after acidification and current density. The other variables were fixed at stirring rate (1300 rpm); L/S (2 ml/g); distilled water; light.

Figure 7: Sweet spot plot of heavy metal removal to meet removal efficiencies for Cu (88 %), Pb (27 %) and Zn (48 %) equivalent to sediment quality class A of the Danish EPA.

The darkest shading in figure 7 illustrates the area in which all remediation objectives are met and a remediation strategy can be chosen according to whether energy consumption or time is essential for the remediation. If time is crucial, the remediation objectives could be met at a current density above 0.7 mA/cm^2 (figure 7) and if energy consumption is more important remediation could be achieved in a longer time frame at lower current densities (figure 8).

Figure 8: Contour plot of energy consumption (kWh/kg dry sediment) as a function of time after acidification and current density. The other variables are fixed at L/S 2 mL/g; stirring rate 1300 rpm; distilled water (suspension liquid) and light.

It is also possible to include objectives for energy consumption or removal of trace elements in the sweet spot plot. This would reduce the area in which the remediation objective are met,

but would however be a useful tool for developing remediation strategies with as low environmental impact as possible.

4. Discussion

In the 3-compartment cell the highest removal efficiencies were 65 % for Cu, 55 % for Pb and 87 % for Zn, which are comparable to previous electrodialytic remediation studies of harbour sediments [6, 15, 16, 19, 28, 37]. Within the studied experimental domain, the highest removal efficiencies reported in the literature are 82 % for Cu [37], 88 % for Pb [6] and 82 % for Zn [16]. The removal was significantly improved in the 2-compartment cell: Cu (94 %), Pb (73 %) and Zn (96 %). The relatively lower removal of Pb in both the 2- and 3-compartment cell may be related to the heavy metal partitioning in the sediment. More than 90 % of Cu and Zn are bound in the exchangeable, reducible and oxidisable fractions, while only approximately 70 % of Pb is related to these fractions. The removal of excess Pb may hence occur at a lower rate than those of Cu and Zn.

PLS models revealed differences in variable importance between the two set-ups. The relatively higher importance of *L/S* and *suspension liquid* (distilled water) in the 3-compartment cell are related to the dissolvable fractions, which could reflect that the removal of metals in this set-up is highly related to amounts found in the exchangeable fractions (figure 3). The need for higher current density in the 3-compartment cell may be due to the slower acidification process. The difference in importance of *time after acidification* may be related to acidification of the sediment suspension. In the 2-compartment cell, the continuous acidification may result in a faster and more substantial dissolution/desorption of metals, while the metal removal in the 3-compartment cell may have moved into the slow metal removal phase. The influence of the *stirring rate* is in line with the results of the removal efficiencies compared to the distribution of metals/heavy metals in the sediment. More

oxidation of the sediment occurs in the 2-compartment cell and this is directly linked to the stirring of the sediment suspension and may also be related to the oxidation at the anode. Since the 2-compartment cell was confirmed to be more efficient, both with regards to acidification time, removal efficacies and energy consumption, a new PLS model was calculated and included 4 new experiments to complete the fractional design. The most significant variables were *time after acidification*, *current density* and to a lesser degree, *stirring rate*; variable importance was however shown to vary depending on heavy metal. The *stirring rate* had a higher impact on Cu than Pb and Zn, which can be attributed to the relative lower proportions of Pb and Zn bound to the oxidisable fraction of the sediment.

The predictive power of the PLS model for the 2-compartment cell will steadily improve by adding more data, and/or limiting the experimental domains. The model reliability and stability was however sufficient for evaluating which part(s) of the experimental domains meet remediation objectives. The remediation objectives were set according to the Danish criteria for Class A, however the remediation strategy is easily adjustable and applying different remediation objectives would entail minor resources.

A previous study revealed that the removal of metals from all sediment fractions occur during electro-dialytic remediation; however within applied remediation times (<28 days) the majority of the removal was from the exchangeable, reducible and oxidisable fractions [28]. The difference in the impact of the electro-dialytic removal in the two cell set-ups used in this study can hence be used as indications of impact on the sediment by comparing removal efficacies of elements with the metal partitioning in the sediment. In the 3-compartment cell the highest amounts of metals removed during electro-dialytic remediation are equivalent to the amounts found in the exchangeable, reducible, and to a lesser degree the oxidisable fractions. In the 2-compartment cell the removal of metals exceeded the relative amounts found in the exchangeable, reducible and oxidisable fractions, indicating that part of the

removed metals were originally found in the residual fraction. In the 2-compartment cell relatively higher amounts of metals bound in the residual fraction are hence made available, indicating a larger impact on the sediment matrix than in the 3-compartment cell.

5. Conclusion

The 2-compartment cell was shown to be more efficient than the 3-compartment cell with regards to acidification times, clean-up levels as well as energy consumption. Stirring rate had a higher impact on the removal of metals/heavy metals from the 2-compartment cell than the 3-compartment cell, which was attributed to the more oxidation of the sediment resulting in removal of a larger fraction of the oxidisable fraction. The 2-compartment cell appeared to have a higher impact on the sediment mineralogy during treatment, since higher amounts of naturally occurring major elements and heavy metals were removed. If these results are confirmed in other studies, it would be of importance when developing remediation strategies. Removal efficiencies of the targeted heavy metals in the 2-compartment cell were up to 94 % (Cu), Pb (73 %) and Zn (96 %), well above the remediation objectives. The PLS model showed that remediation objectives could be met over a large region of varying *time* and *current density* while fixing *stirring rate* (1,300 rpm) and *L/S* (2 ml/g). If energy consumption proves to be crucial remediation could be run at a low *current density* of 0.2 mA/cm² and a *remediation time after acidification* of 440 hours. If time proves crucial the remediation could be run in 50 hours after acidification at 0.7 mA/cm².

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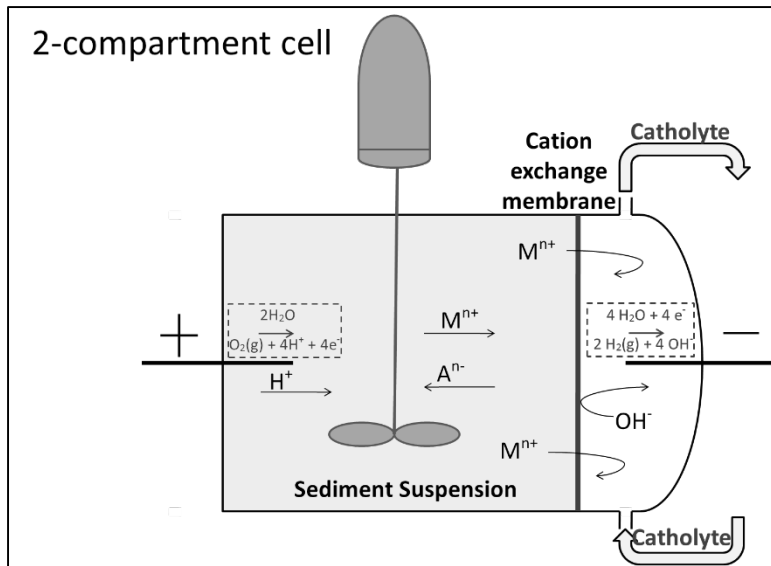


Figure 2: The 2-compartment electrochemical remediation cell.

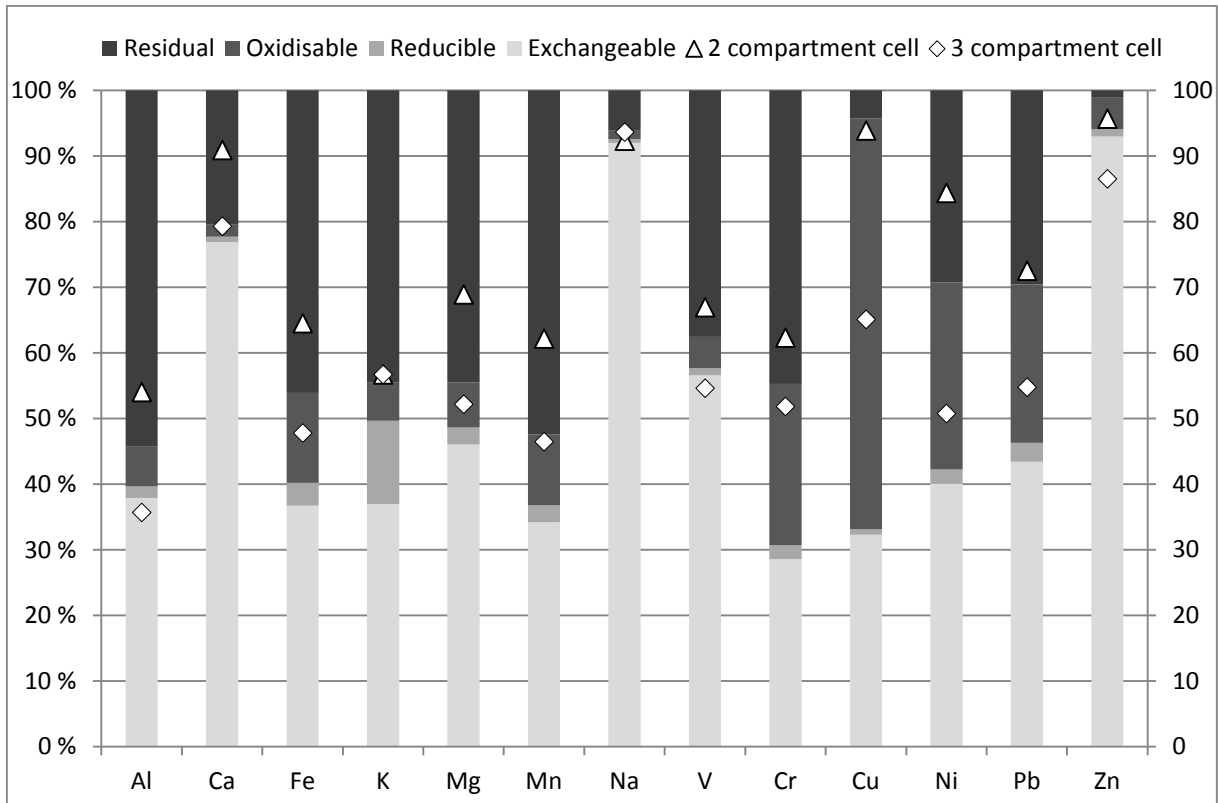


Figure 2: Distribution of the metals/heavy metals in the different sediment fractions based on sequential extraction; the highest removal efficiencies in the experimental domain of the 2- and 3-compartment cell set-ups are included.

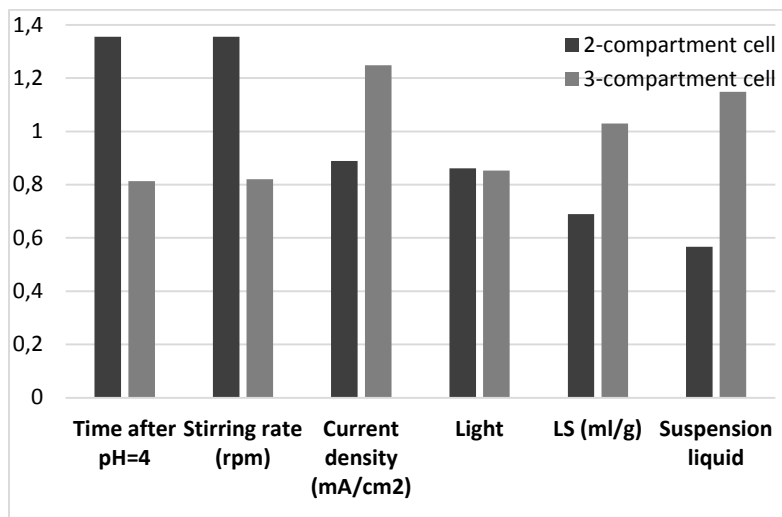


Figure 3: VIP values for the two cell set-ups, calculated from two separate PLS models. Variables with high VIP values have the highest influence on EDR.

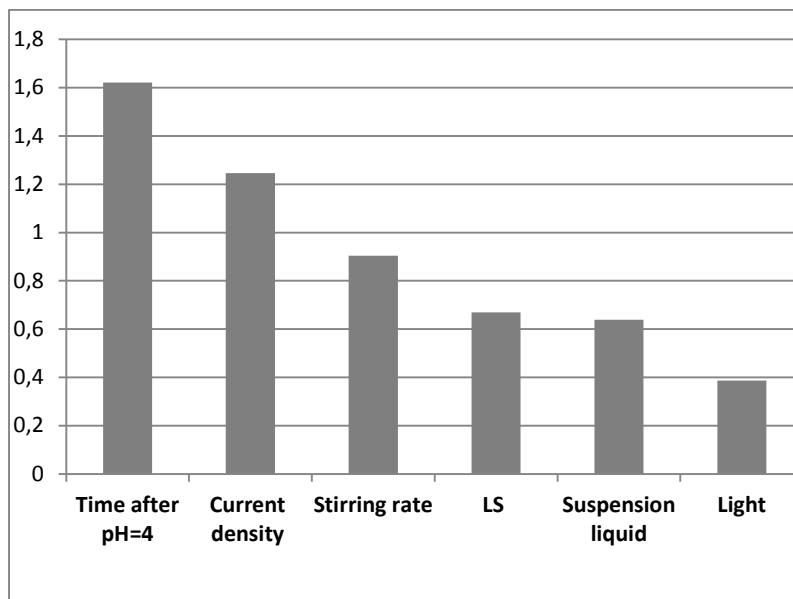


Figure 4: VIP plot of the 2-compartment cell (design 2). Variables with high VIP values have the highest influence on EDR.

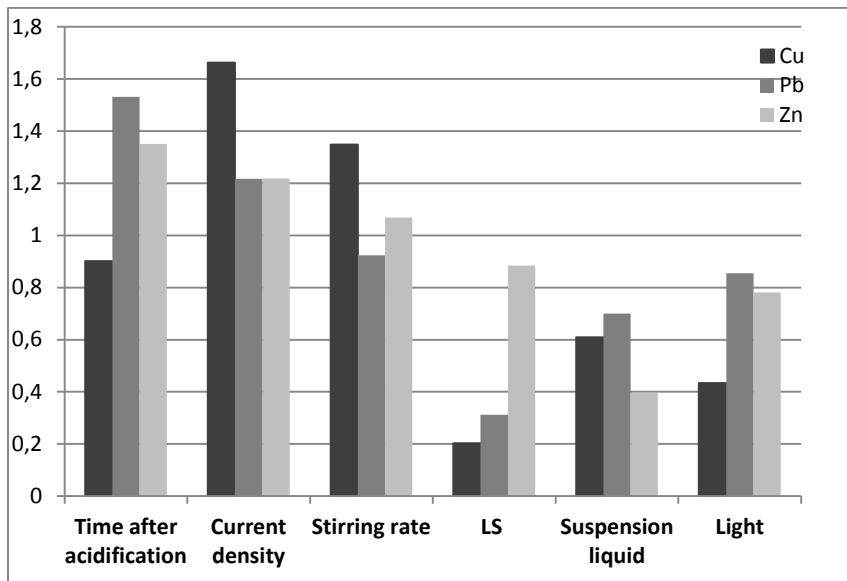


Figure 5: VIP values of Cu, Pb and Zn modelled separately. Variables with high VIP values have the highest influence.

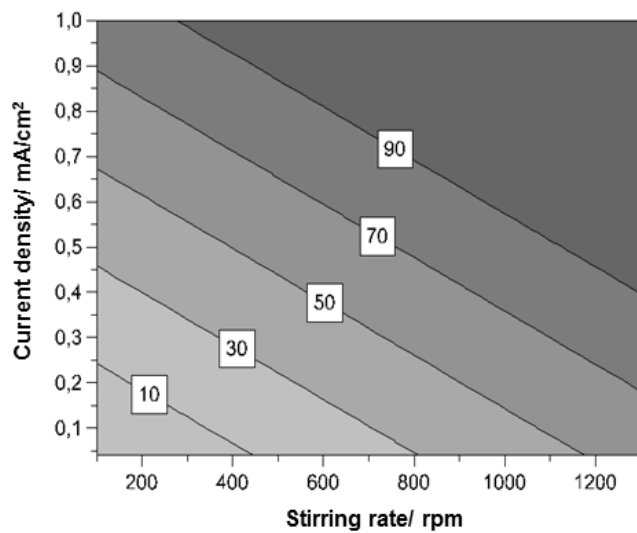


Figure 6: Contour plot of Cu (removal efficiencies %) as a function of stirring rate and current density.

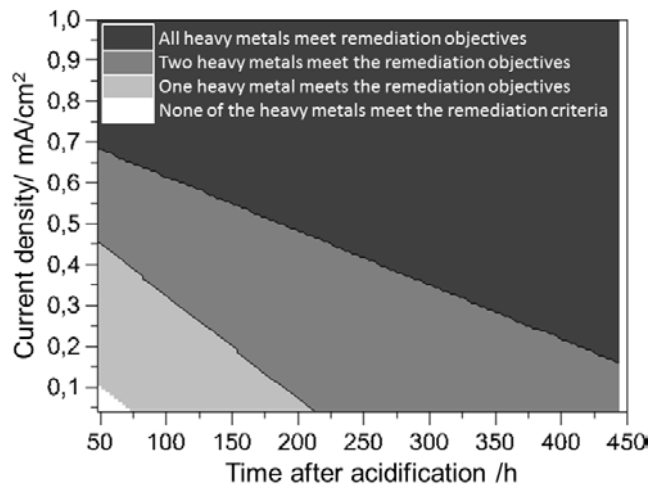


Figure 7: Sweet spot plot of heavy metal removal to meet removal efficiencies for Cu (88%), Pb (27%) and Zn (48%) equivalent to sediment quality class A of the Danish EPA.

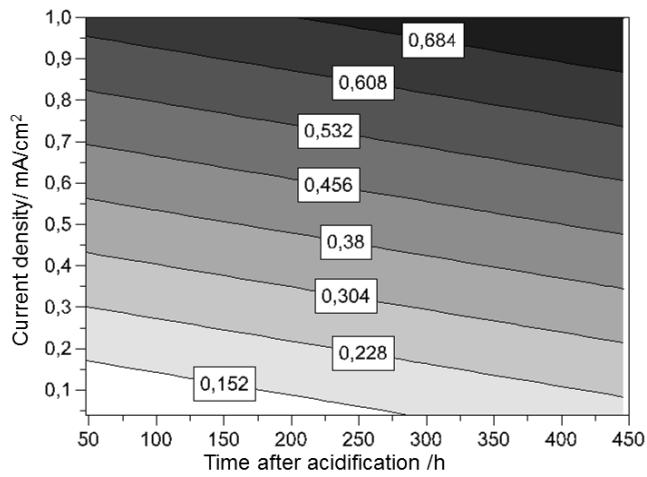


Figure 8: Contour plot of energy consumption (kWh/kg dry sediment) as a function of time after acidification and current density. The other variables are fixed at L/S 2mL/g; stirring rate 1300 rpm; distilled water (suspension liquid) and light.

Highlights

Multivariate design and analysis was used to compare 2 electro dialytic cell designs

Multivariate modelling revealed that the 2 cell designs were different

The highest efficiency was found in the 2-compartment cell

Apart from cell design the most important variables were current density and time

Stirring rate was also a significant parameter in the 2-compartment cell

The experimental domain in which remediation objectives were met, was determined