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

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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 m1ultivariate 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.

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 electrodialytic 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 aniode 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

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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 electrodialytic 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].

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 (Fig. 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].

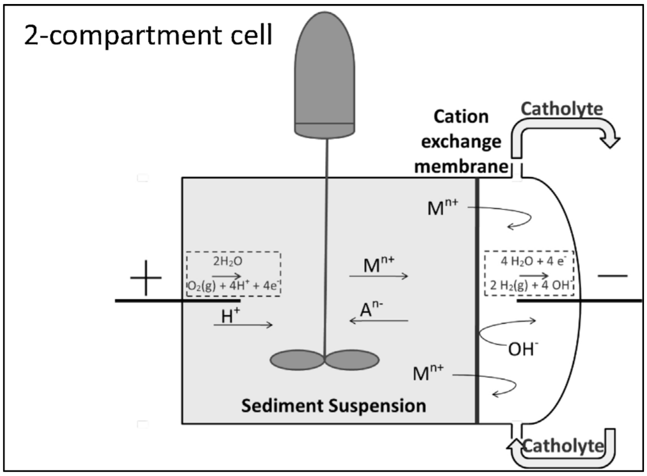

Fig. 1. The 2-compartment electrodialytic remediation cell.

Sequential extraction is a method widely used for investigating metal partitioning in soils and sediments. For harbour sediment studies in relation to EKR and electrodialytic 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 electrodialytic 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 electrodialytic remediation or EKR [26–28]. The removal of heavy metals from the oxidisable fraction was attributed to oxidisation of the sediment during electrodialytic 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 HNO_3 (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 CO_2 developed was measured volumetrically in a Scheibler apparatus, calibrated with $CaCO_3$.

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