

Electrodialytic removal of cadmium from wastewater sludge

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Abstract

This paper presents for the first time laboratory results demonstrating electrodialytic removal of Cd from wastewater sludge, which is a method originally developed for soil remediation. During the remediation a stirred suspension of wastewater sludge was exposed to an electric dc field. The liquid/solid (ml/g fresh sludge) ratio was between 1.4 and 2. Three experiments were performed where the sludge was suspended in distilled water, citric acid or HNO₃. The experimental conditions were otherwise identical. The Cd removal in the three experiments was 69, 70 and 67%, respectively, thus the removal was approximately the same. Chemical extraction experiments with acidic solutions showed that 5–10 times more Cd could be extracted from decomposed sludge than from fresh sludge. It is likely that the mobilization of Cd during decomposition of the sludge contributes to the efficient removal of Cd by the electrodialytic method. Extraction experiments and electrodialytic remediation using distilled water as enhancement agent showed that 0.3% Cd could be extracted from decomposed sludge during 1 week in closed flasks, whereas 69% was removed during 2 weeks of electrodialytic remediation in a stirred solution in contact with atmospheric air. A combination of aerobic decomposition and electrodialytic treatment could be a promising method for Cd removal from wastewater sludge, and thus Cd could be removed without the addition of chemicals to the sludge.

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1. Introduction

Cadmium and Cd compounds are, compared to other heavy metals, relatively water-soluble and are therefore more mobile in soil and generally more bio-available. This results in bio-accumulation of an element which is toxic to plant and animal life. The major route of exposure to cadmium for the non-smoking general population is via food and the human exposure from agricultural crops is susceptible to increases in soil Cd. Increases in soil Cd contents, e.g. due to Cd in soil amendment products, result in an increased uptake by plants. In view of the danger of the chronic accumulation of Cd in the human body it is important to limit the daily intake through the diet, since even slightly elevated Cd concentrations in food can have significant effects in the long term [1]. Accumulation of Cd in agricultural land is a European problem, which has been a major focus area for the CSTEE, Scientific Committee for Toxicity, Ecotoxicity and the Environment.

Wastewater sludge has traditionally been applied as a fertilizer to agricultural land in Denmark. The relatively high Cd concentration in the wastewater sludge has caused concern and resulted in a lowered limit for Cd in wastewater sludge used for this purpose [2]. Legislation that forbids any import, use or sale of products containing Cd in Denmark [3] resulted in a decrease in Cd concentration in the wastewater sludge but average concentrations have now stabilized at a level that generally exceeds the limit value. The obvious Cd sources, such as e.g. Ni–Cd batteries have now been eliminated, and further reduction in the Cd concentrations of the sludge are difficult to obtain because the remaining sources are diffuse and therefore difficult to identify.

The upper limit of Cd in wastewater sludge for application to agricultural land varies between different countries being e.g. 0.8 mg Cd/kg DM in Denmark and 2 mg Cd/kg DM in Sweden [4]. Only a small proportion of the Danish and Swedish wastewater treatment plants fulfil the actual limit values, and it is necessary to develop methods to remove Cd from wastewater sludge to avoid large deposit sites [4]. Formerly tested methods use ferric sulfate and natural zeolite as ion exchangers [5,6] and EDTA has been used as a complex binder [7].

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The present paper reports a laboratory investigation on the use of an electrochemical method for the removal of Cd from wastewater sludge. The method tested is the electrodi-alytic remediation method, which was originally developed for remediation of heavy metal-polluted soil [8,9]. In addition to being used for soil remediation, the method has also shown a potential for treatment of other hazardous porous materials [10] such as for the removal of Cu, Cr and As from impregnated wood waste [11] and for removal of Cd from different bio ashes such as straw ash [12] and wood ash [13].

2. The principle of electrodi-alytic remediation

The development of electrodi-alytic remediation of solid waste products was initiated in 1992 and was patented in 1995 (PCT/DK95/00209). The method was first developed for remediation of heavy metal polluted soil and is based on application of an electric dc field to the soil. The basic cell composition for electrodi-alytic soil remediation is shown in Fig. 1. The electrodes are placed in separate compartments where electrolyte solutions are circulated and where the heavy metals are concentrated at the end of the remediation. The electrolyte solutions also ensure that a good contact between the electrode surface and the surroundings is maintained, and that the gases that are produced from the electrode reactions will be transported away from the electrodes. Bar electrodes are used and the current density in the electrolyte solution is equalized over the cross-sectional area of the soil next to the electrode compartments. In electrodi-alytic remediation, ion exchange membranes are separating the soil from the electrolyte solutions. An anion exchange membrane that allows only passage of anions is placed between the soil and the electrolyte solution at the anode end, and between the soil and the electrolyte solution at the cathode end a cation exchange membrane, that allows only passage of cations, is placed. The ion exchange membranes prevent the waste of current in transporting ions from one electrode compartment through the soil into the second electrode compartment. Furthermore, the ion exchange membranes make the conditions in the soil less dependent on the choice of electrolyte solution than if chemically passive membranes were used. This is beneficial especially when further concentration of the removed heavy metals for reuse is planned.

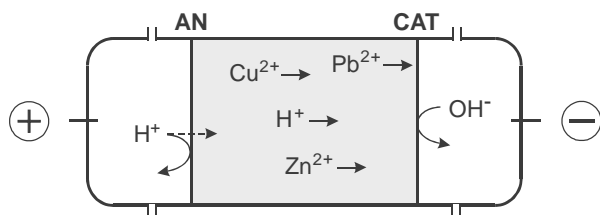


Fig. 1. Basic principle of electrodi-alytic soil remediation (AN: anion exchange membrane, CAT: cation exchange membrane).

For some soils or some combination of heavy metals it is necessary to add an enhancement solution to the soil prior to application of the electric field to aid desorption of the heavy metals, e.g. ammonia was used as an enhancement solution to mobilize Cu and As at the same time [14]. The method has been tested for removal of heavy metals from different fly ashes, too [15], and it was shown that the method was more efficient if the fly ash was remediated as stirred slurry. It was, therefore, decided to use the electrodi-alytic setup with a stirrer for the treatment of wastewater sludge.

3. Experimental procedure

3.1. Experimental wastewater sludge

The wastewater sludge used for the experiments was sampled on 8th October 2002 from the hydro extractor C at treatment plant Lynetten, Lynettefællesskabet I/S in Copenhagen, Denmark. Lynetten treats wastewater from more than 500,000 people each day. During the experimental period, the sludge was stored at of -18°C to preserve it freshness.

3.2. Experiments for characterizing the sludge

The content of Cd in dry sludge was measured after pre-treatment of the sludge as described in Danish Standard (DS259). A mixture of 0.5 g of dry sludge and 10 ml 7 M HNO_3 was heated at 200 kPa (120°C) in 30 min. The oxidized samples were filtered through a $45\ \mu\text{m}$ filter and the content of Cd was measured using a Perkin-Elmer atomic absorption spectrophotometry (AAS) equipped with a graphite oven. All Cd concentrations are given on the basis of sludge dry weight.

Samples from electrolyte, cathode, anode and membranes were heated at 200 kPa (120°C) in 30 min. The Cd content was measured using AAS.

Wastewater sludge pH was measured in 1 M KCl with a liquid-to-solid ratio of 2.5. The contact time was 1 h before pH was measured with a Radiometer combined pH-electrode.

The content of organic matter was found as a loss of ignition after 30 min in an oven set at 550°C .

The carbonate content was determined by the volumetric calcimeter method described in [16].

Water content of the sludge was measured as weight loss after 24 h in an oven at 80°C .

The pH-dependence of Cd desorption was examined. The following solutions were used for the experiment: 1.0, 0.5, 0.1, 0.05, 0.01 M of HNO_3 , 0.01, 0.05, 0.1, 0.5, 1.0 M of NaOH and distilled water. Five grams of dry sludge, which had been dried in an oven at 80°C , was added to 25 ml of each solution and the mixtures were left in closed flasks for 1 week on a horizontal shaker. After sedimentation of the solutions pH was measured using a Radiometer combined pH-electrode. Each sample was filtered through

a 45 μm filter and alkaline samples were preserved using 65% HNO_3 in a solution-to-acid ratio of 3. The Cd-content was determined by AAS.

The binding of Cd to the sludge particles was determined using a four step method of sequential extraction [17]. Firstly, 20 ml of 0.11 M CH_3COOH , pH 3 was added to 0.5 g of dry sludge. This solution is a weak acid, which releases the Cd-ions by replacing the positive Cd-ions with H^+ -ions. Secondly, 20 ml of 0.1 M $\text{NH}_2\text{OH-HCl}$, pH 2 was added to obtain weak reducing conditions. Thirdly, the sludge was washed with 8.8 M H_2O_2 and 25 ml of 1 M $\text{NH}_4\text{OOCCH}_3$, pH 2 was added to obtain an oxidizing phase. Finally, the remaining Cd content was determined by AAS.

3.3. Extraction experiments

The extraction experiments were carried out in order to determine the influence of different enhancement solutions on the removal of Cd from wastewater sludge. Solutions of 0.2 M HNO_3 , 0.25 M citric acid and distilled water were tested. Suspensions of 1.5 g dry sludge and 15 ml solution were in contact for 1 week in closed flasks.

The samples were filtered through a 45 μm filter and the alkaline samples were preserved by adding 3 ml of sample and 1 ml of 65% HNO_3 to a plastic vial before Cd measurement. The Cd-content was measured using AAS. Two replicate experiments were carried out.

Similar extraction experiments were carried out for decomposed sludge, which had been left to decompose at room temperature in a closed plastic container for 1 month, to compare the desorption efficiency and to investigate if this could have any effect on the binding of Cd.

3.4. Electrodialytic wastewater sludge remediation

Three electro-dialytic remediation experiments were carried out. Two different enhancement solutions, 0.2 M HNO_3 and 0.25 M citric acid were tested and distilled water was included as a reference. The experiments were made in plexiglas cells as shown in Fig. 2. The suspension of fresh hu-

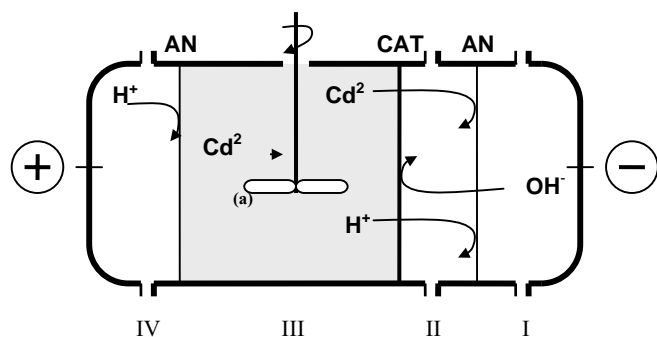


Fig. 2. Illustration of electro-dialytic remediation of cadmium from wastewater sludge (AN: anion exchange membrane, CAT: cation exchange membrane, (a) stirrer).

mid sludge and enhancement solution was added to compartment III before starting the experiment. The cells had an internal diameter of 8 cm. The length of the four compartments were I: 5; II: 1.5; III: 15; and IV: 5 cm. The compartments were separated with ion exchange membranes from IONICS (anion exchange membrane 204 SZRA B02249C and cation exchange membrane CR67HUYN12116B). The liquid/solid ratio between enhancement solution and fresh humid wastewater sludge was between 1.4 and 2 ml/g. The stirrer in compartment III had a constant speed with a rotation velocity of 1300 rpm.

The electrolyte in compartments I, II and IV was NaNO_3 adjusted with HNO_3 to obtain pH < 2. The electrolyte was circulated between the compartment and a flask with pumps to enlarge the total volume. The circulation system also prevents the formation of concentration profiles in the close vicinity of the membranes and the electrodes. Such concentration profiles may affect the passage of current. Compartment II was inserted between the cathode compartment (I) and the sludge compartment (III) to function as concentration compartment for Cd.

The electrodes in each end of the cell, anode and cathode, held a constant current of 40 mA (corresponding to a current density of 0.8 mA/cm^2). The voltage was measured every day.

During the experimental period of 2 weeks pH was adjusted in the electrolyte compartment to maintain it below 2. Using AAS, the content of Cd was determined after each experiment in samples from compartments I, II and IV, membranes, electrodes, desorption agent and the treated sludge.

4. Results and discussion

4.1. Characteristics of the sludge

The characteristics of the wastewater sludge are shown in Table 1. The initial concentration of Cd was 2.37 mg/kg DM, which was three times higher than the Danish limit for sludge used as fertilizer. The content of organic matter was 2/3 of the total, which showed that decomposing processes will take place under conditions favorable for microorganisms.

The pH-dependence of Cd desorption is shown in Fig. 3. It shows that Cd was desorbed at pH values below 4. Since pH of the fresh sludge was 5.65, treatment through the addition of an enhancement solution, decomposition or application

Table 1
Characteristics of the wastewater sludge

Cd concentration	2.37 mg/kg DM
Sludge pH	5.65
Organic matter	67%
Carbonate content	0.6%
Dry matter	20%

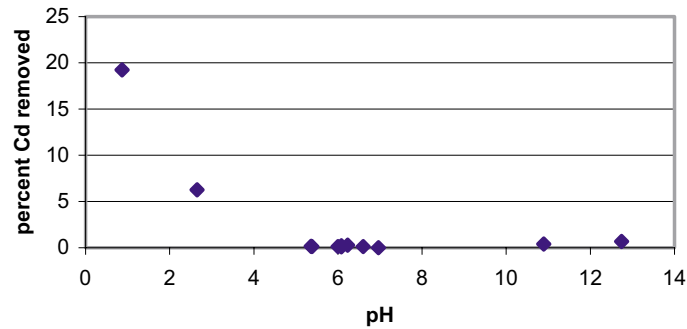


Fig. 3. pH-dependence of Cd desorption.

of current would be necessary to remove Cd from the fresh sludge.

The majority of the Cd was removed in Step 3, the oxidizing phase of the sequential extraction (Fig. 4). This showed that Cd was associated with the organic phase of the sludge, since it was the organic phase that was influenced strongly by the oxidation.

4.2. Extraction experiments

The efficiency of the extraction with distilled water was still low for both fresh and decomposed sludge, 0.7 and 0.3%, respectively.

Extraction experiments with the used acids and fresh sludge showed that only a small part of Cd was mobilized (Fig. 5). In 0.2 M HNO₃ and 0.25 M citric acid only about 3.9 and 6.1% was removed, respectively, which was quite low. However, the extraction experiments showed a clear difference between the batches of fresh decomposed wastewater sludge, and the extraction of Cd was remarkably higher for the decomposed sludge: 21.8 and 48.0% removal using 0.2 M HNO₃ and 0.25 M citric acid, respectively. The mobilization of Cd in decomposed sludge was, except for distilled water, 5–8 times the mobilization in fresh sludge,

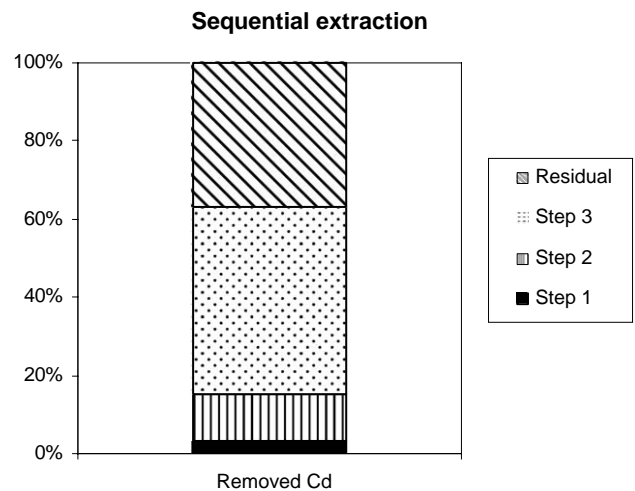


Fig. 4. Sequential extraction of cadmium from sewage sludge.

a difference which could be related to changes in sludge compounds during the decomposition process. Cadmium is primarily bound to the organic colloids. Changes in the structure of the organic compounds during decomposition could have affected the binding of Cd.

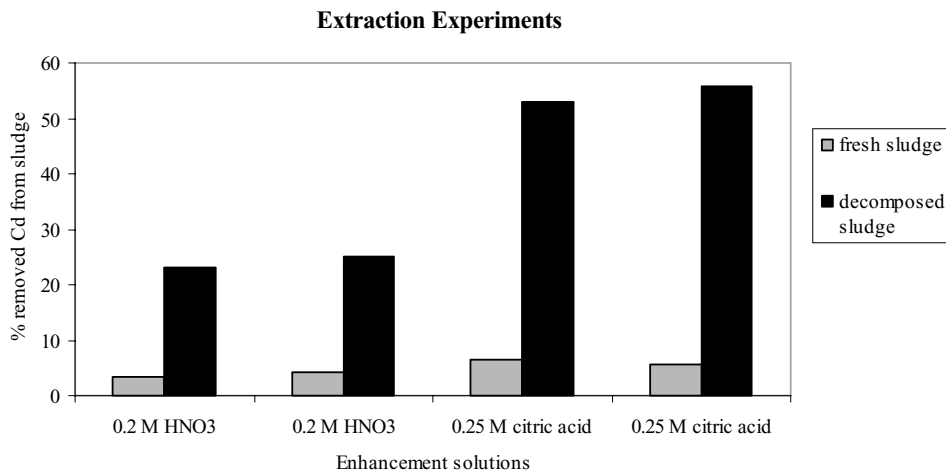


Fig. 5. Influence of different solutions on the removal of Cd from fresh or decomposed sludge.

Table 2

Proportions of Cd measured in the various compartments and components of the electrolysytic remediation cell

	Enhancement solution		
	0.2 M HNO ₃ , L/S = 1.4	0.25 M citric acid, L/S = 2	Distilled water, L/S = 2
Total removed (%)	67	70	69
NaNO ₃ , compartment II	44	43	46
NaNO ₃ , compartment I	8	15	8
NaNO ₃ , compartment IV	1	2	1
Filtered enhancement solution, compartment III	0	0	0
Cation exchange membrane	6	9	11
Anion exchange membrane, compartment I	0	0	3
Anion exchange membrane, compartment IV	1	0	0
Cathode	6	1	0
Anode	1	0	0
Residual Cd in sludge (%)	33	30	31

The membranes are soaked in 1 M HNO₃ and the electrodes are soaked in a solution of 5 M HNO₃ to release Cd (L/S: liquid/solid ratio).

4.3. Electrodialytic wastewater sludge remediation

Electrodialytic remediation experiments were carried out to reduce the high content of Cd in wastewater sludge. The solutions tested in the extraction experiment were used as enhancement solutions: 0.2 M HNO₃, 0.25 M citric acid and distilled water. Distilled water was tested to investigate the importance of the enhancement solution for the remediation.

The highest removal efficiency of 70% was obtained in the experiment with 0.25 M citric acid as enhancement agent (Table 2). Removal efficiencies with 0.2 M HNO₃ and distilled water were 67 and 69%, respectively. Similar removal efficiencies in the three experiments indicated that the enhancement solution was not of significant importance. The remarkable high removal-efficiency with distilled water could be related to two processes. Firstly, the 2 weeks experimental period under aerobic conditions with stirring would have promoted decomposition of the sludge and thereby extraction of Cd, and secondly, the sludge might have been slightly acidified during the remediation due to water dissociation at the anion exchange membrane as described in [18]. The result of the remediation being independent on the enhancement solution used could also be a combination of the two processes. The result shows, that it is not the addition of enhancement solution that is the main factor in mobilizing Cd from the sludge. Supported by the extraction experiments it is the decomposition that is of major importance.

Removal efficiencies might increase with a longer treatment, but this was not investigated in the present work.

The distribution of Cd in the cell at the end of the three experiments (Table 2) showed that almost the same percentage of Cd was concentrated in compartment II (between 43 and 46%). Concentrating the Cd in this compartment was the purpose of the way the ion exchange membranes were used in the setup of the cell. The distribution of Cd between the various compartments differed between the three experiments. In the experiment with 0.2 M HNO₃ Cd was measured on the cathode (6%), in the cation exchange

membrane, in compartment II (6%), and in compartment I (8%). In the experiment with 0.25 M citric acid the majority of the rest of the Cd was measured in compartment I (15%) and in the cation exchange membrane in compartment II (9%). In the experiment with distilled water 11% was found in the cation exchange membrane at compartment II, 8% was found in compartment I and 3% was found in the anion exchange membrane in compartment I.

The results showed that it was possible to remove Cd from wastewater sludge by electro dialysis with most enhancement solutions. It might be possible also to use this method to remove other heavy metals from wastewater sludge, in which case the choice of enhancement solution may be of significance.

5. Conclusions

Application of electro dialytic remediation to wastewater sludge showed promising results. As much as 70% of the Cd-content was removed from the sludge after 2 weeks of treatment and the final concentration of Cd was 0.7 mg Cd/kg DM. This is below the limit set by the Danish legislation. A longer remediation time than that used in the present experiments may lower the concentration further. It was found that the mobilization of Cd was connected with the aerobic decomposition of the wastewater sludge. It was also found that it was possible to remove Cd from the sludge using the electro dialytic method without any addition of chemicals.

References

- [1] European Commission, Heavy Metals in Waste, Final Report, DG ENV. E3, Project ENV.E.#/ETU/2000/0058, 2002.
- [2] Bekendtgørelse om tilsyn med spildevandsslam m.m. til jordbrugsformål, Bekendtgørelse nr. 56 af 24/01/2000, Danish law (in Danish).
- [3] Bekendtgørelse om forbud mod salg, import og fremstilling af cadmiumholdige produkter, Bekendtgørelse nr. 1199 af 23/12/1992, Danish law (in Danish).

- [4] A. Lindquist-Östblom, M. Eklund, Cadmium in Wastewater sludge in a Swedish Region, *Environ. Eng. Policy* 2 (2000) 145–154.
- [5] A. Ito, U. Teruyuki, J. Aizawa, T. Toshiyuki, K. Morinaga, Removal of heavy metals from anaerobically digested wastewater sludge by new chemical method using ferric sulfate, *Water Res.* 34, pp. 751–758.
- [6] A.A. Zorpas, M. Loizidou, Use of Inorganic Material such as Zeolite for the Uptake of Heavy Metals from the Composting Process, vol. 23, Technomic Publ. Co. Inc., 1999, pp. 611–620.
- [7] Miljøstyrelsen, Fjernelse af tungmetaller fra spildevandsslam (Removal of heavy metals from wastewater sludge), Report from Danish EPA no. 10, 1990 (in Danish).
- [8] L.M. Ottosen, H.K. Hansen, S. Laursen, A. Villumsen, Electrolytic remediation of soil polluted with copper from wood preservation industry, *Environ. Sci. Technol.* 31 (1997) 1711.
- [9] H.K. Hansen, L.M. Ottosen, B.K. Kliem, A. Villumsen, Electrokinetic remediation of soils polluted with Cu, Cr, Hg, Pb and Zn, *J. Chem. Technol. Biotechnol.* 70 (1997) 67.
- [10] L.M. Ottosen, I.V. Kristensen, A.J. Pedersen, H.K. Hansen, A. Villumsen, A.B. Ribeiro, Electrolytic removal of heavy metals from different solid waste products, *Sep. Sci. Technol.* 38 (6) (2003) 1269.
- [11] A.B. Ribeiro, E.P. Mateus, L.M. Ottosen, G. Bech-Nielsen, Electrolytic removal of Cu, Cr and As from CCA treated timber waste, *Environ. Sci. Technol.* 34 (2000) 784.
- [12] H.K. Hansen, L.M. Ottosen, A. Villumsen, S. Houmøller, Electrolytic removal of cadmium from straw ash, in: *Proceedings the Second Symposium on Heavy Metals in the Environment and Electromigration Applied to Soil Remediation*, Lyngby, Denmark, 7–9 July 1999, pp. 130–134.
- [13] A.J. Pedersen, Characterization and electrolytic treatment of wood combustion fly ash for the removal of cadmium, *Biomass Bioenergy* 25 (4) (2003) 447–458.
- [14] L.M. Ottosen, H.K. Hansen, G. Bech-Nielsen, A. Villumsen, Electrolytic remediation of an arsenic and copper polluted soil: continuous addition of ammonia during the process environmental technology 21 (2000) 1421.
- [15] A.J. Pedersen, L.M. Ottosen, A. Villumsen, Electrolytic removal of heavy metals from different fly ashes: influence of heavy metal speciation in the ashes, *J. Hazard. Mater.* 100 (1–3) (2003) 65–78.
- [16] R.H. Loeppert, D.L. Suarez, *Methods of Soil Analysis. Part 3. Chemical Methods*, SSSA Book Series No. 5, 1995, pp. 451–455.
- [17] Z. Mester, C. Cremisini, E. Ghiara, R. Morabito, Comparison of two sequential extraction procedures for metal fractionation in sediment samples, *Anal. Chim. Acta* 359 (1998) 133.
- [18] L.M. Ottosen, H.K. Hansen, C.B. Hansen, Water splitting at ion-exchange membranes and potential differences in soil during electrolytic soil remediation, *J. Appl. Electrochem.* 30 (2000) 1199.