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Organic acid enhanced electrodialytic extraction of lead from contaminated soil fines in suspension

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Abstract:

Implementation of the soil washing technology for the treatment of heavy metal contaminated soils is limited by the toxicity and unwieldiness of the remaining heavy metal contaminated sludge. In this work, we investigated the feasibility of combining electrodialytic remediation with heterotrophic leaching for decontamination of the sludge. The ability of 11 organic acids to extract Pb from the fine fraction of contaminated soil (grains $< 63\mu m$) was investigated, and application of the acids as enhancing reagents during electrodialytic remediation (EDR) of Pb-contaminated soil fines in suspension was tested. Five of the acids showed ability to extract Pb from the

soil fines in excess of the effect caused solely by pH-changes. Addition of the acids, however, severely impeded EDR, hence promotion of EDR by combination with heterotrophic leaching was rejected. In contrast, enhancement of EDR with nitric acid gave promising results.

INTRODUCTION

Electrodialytic soil remediation (EDR) is an electrokinetic remediation (EKR) method, in which ion-exchange membranes are applied as barriers between soil and electrolytes. In order to solve an essential waste-problem of the remaining sludge after soil-washing, EDR of soil fines in suspension has been suggested as a potential treatment method.[1] Prior to treatment, the sludge contains the bulk of the contaminants washed out of the coarser fractions. In addition, the sludge has a high water-content (commonly up to 95%), and due to its surface properties, it is not easily dewatered. Thus soil washing, although successfully and efficiently implemented, produces not only a considerable fraction of cleaned materials, but also a significant volume of relatively more toxic material which is difficult to handle and not easily disposed of. The aim of the present work was to investigate the enhancement of the EDR process, already documented,[1] for the improved treatment of Pb-contaminated sludge by addition of a suiting enhancing reagent.

Enhancing reagents

The efficiency of various reagents for extraction of Pb and other heavy metals from soil during soil wash has been extensively investigated. The strong chelating agent ethylenediaminetetraacetic acid (EDTA) has been repeatedly and successfully tested.[2-4] Its suitability has, however, been questioned because of its low biodegradability and potential hazard to the environment.[5,6] Similarly, enhancement of EKR with EDTA is well documented,[7-9] with the important note that although the extraction of Pb from soil by EDTA was shown to be pH-independent,[10] enhancement of EKR was obtained only at pH values above 5.[9] Chelating agents more susceptible to biodegradation such as [s,s]-ethylenediaminedisuccinic acid (EDDS) and nitrilotriacetic acid (NTA) extracted Pb less efficiently than EDTA due to a much stronger complexation of Pb by EDTA.[11]

Besides chelating agents, organic acids possess potential to extract heavy-metals due to their complexing behaviour. In contrast to EDTA, extraction of Pb from soil by organic acids and their ammonium-salts was shown to be highly pH-dependent,[10] but in the pH range 2-7 citrate (0.2M) and tartarate (0.5M) extracted Pb as efficiently as EDTA. In addition, the organic acids were shown to act more gentle towards the soil by removing 80% less macronutrients (Ca, Mg, Fe) compared to EDTA.[10] In accordance, a substantial improvement of EKR of Pb from a spiked silt loam was demonstrated after citric acid addition at pH values between 3.3 and 5.4,[12] while EDR of Pb from municipal solid waste incineration (MSWI) fly ash was enhanced by addition of sodium citrate[13] and ammonium citrate[14] at alkaline pH values. Although

acetate was shown to be a moderate extractant of Pb from soil,[10] several authors reported on the successful enhancement of EKR by acetic acid at low pH,[7,12,15,16] however, less efficiently than by citric acid.[12]

Altogether current knowledge supports the feasibility of enhancing EKR/EDR of soil by addition of either chelating agents or organic acids. The fact that biodegradable organic acids were shown to extract Pb as efficiently as the persistent EDTA, encourages the use of organic acids, such as citric acid and tartaric acid.

Heterotrophic leaching

Several authors suggested leaching by heterotrophic bacteria or fungi as an economical alternative method of extraction of valuable metals from non-sulfide, low-grade ores in the mining industry.[17-19] The technique is based upon the ability of selected microorganisms to produce organic acids during growth, and their potential growth on cheap organic waste-products. Heterotrophic leaching was later suggested for treatment of industrial wastes, sewage sludge and heavy metal contaminated soil.[20-22] Most research within the heterotrophic leaching of contaminated materials was conducted with fly ash. It was shown that *Aspergillus niger* grew and produced gluconate in the presence of 10% (w/v) fly ash, while citrate was produced in its absence. Chemical leaching with commercial citric acid was only slightly higher than microbiological leaching.[23] In another study *Penicillium simplicissimum* was shown to produce citric acid in the presence of Zn-contaminated filter dust while no acid production was seen in its absence,[24] and it was shown how extraction of Pb from

filter dust by yeasts isolated from seeping water, waste compost, and sewage was possible.[25] These studies suggest that growth and acid production would also take place in the presence of heavy-metal contaminated soil fines. The idea that microbial extraction of even very stabile Pb-compounds is possible, was suggested by Sayer *et al.*, who observed growth of *A. niger* with pyromorphite as sole phosphate source.[26] In addition, it was shown that application of direct current increased the metabolism of bacteria in soil slurries,[27] which supports the feasibility of heterotrophic leaching in combination with EDR/EKR.

In the present work, the feasibility of a new approach, in which combination of heterotrophic leaching and EDR of Pb contaminated soil fines in suspension, is studied. The aim of this technique is to induce production of organic ligands by heterotrophic organisms for complexation and mobilization of Pb prior to or simultaneously with removal of charged ligand-Pb complexes by EDR. Positive side effects such as mobilization of nutrients for increased heterotrophic leaching could be expected. The potential of the technology depends on the ability of organic acids to enhance EDR of Pb from soil fines. Our research comprises batch extraction experiments with 11 organic acids at neutral to slightly acidic pH, where acid producing fungi grow, and an experimental evaluation of the effect of addition of selected organic acids on EDR. The acids were all chose as naturally produced products of heterotrophic microorganisms.[21]

MATERIALS AND METHODS

Soil: An industrially contaminated Danish soil was used for the experiments. The soil fines were obtained by wet-sieving of the original soil with distilled water through a 0.063 mm sieve. Concentrated slurry of fines was obtained by centrifugation at 3000 rpm for 10 min and decantation of the supernatant. The soil fines were kept as a slurry and stored at 5ºC in access of oxygen. The metal content (Fe, Mn, Al, Pb) was determined by atomic absorption spectrophotometry (AAS). Prior to analysis of soil samples, 1.00 g soil fines were digested in an autoclave with 20.00 ml 1:1 HNO_3 for 30 min at 120ºC and 200 kPa according to the Danish standard method DS259,[28] and filtered through a 0.45 μm filter by vacuum. Liquid samples with pH > 4 were preserved by digestion with concentrated HNO_3 (1:4). Validation of AAS results for all metals was obtained by measurement against liquid reference samples. The carbonate content was determined volumetrically by the Scheibler-method after reacting 3 g of soil with 20 ml of 10% HCl. For calculations it was assumed that all carbonate was present as calcium-carbonate. Organic matter was determined by loss of ignition at 550ºC for one hour. The Cation Exchange Capacity (CEC) was analyzed by a method comparable to the acid-NaCl method described in EPA Standard Method 9080 including ion exchange of 10 g dry soil with NH_4^+, followed by exchange of NH_4^+ for Na^+. The ammonium concentration of the centrifugate was measured via flow-injection spectrophotometry. For pH-measurements 5.0 g dry soil was shaken with 12.5 ml 1 M KCl for one hour followed by settling for 10 min and measurement by a Radiometer Analytical ion selective electrode. Sequential extraction was

performed according to the method from the Standards, Measurements and Testing Program of the European Union:[29] 0.5 g of dry, crushed soil was treated in four steps as follows:

1) Extraction with 20.0 ml 0.11 M acetic acid pH 3 for 16 hours;

2) Extraction with 20.0 ml 0.1M $NH_2OH \cdot HCl$ pH2 for 16 hours;

3) Extraction with 5.0 ml 8.8M H_2O_2 for one hour and heating to 85ºC for one hour with lid followed by evaporation of the liquid phase at 85ºC until it had reduced to < 1ml by removal of the lid. The addition of 5.0 ml 8.8M H_2O_2 was repeated followed by heating to 85ºC for one hour and removal of the lid for evaporation until almost dry. After cooling, 25.0 ml 1M NH_4OOCCH_3 pH 2 was added, and extraction took place for 16 hours.

4) Finally digestion according to DS 259 was made for identification of the residual fraction. Between each step the sample was centrifuged at 3000 rpm for 15 min, and the supernatant was decanted and stored for AAS.

Before addition of the new reagent, the sample was washed with 10.0ml distilled water for 15 min, centrifuged at 3000 rpm for 15 min and the supernatant decanted. All extractions were performed at room temperature under shaking at 100rpm unless otherwise mentioned.

All analyses were made in triplicate except CEC and sequential extraction, which were duplicated.

Extraction experiments: Soil fines (5.00 g) were allowed to equilibrate with 25 ml reagent at room temperature for 7 days while shaken at 180 rpm. Metal content and pH were measured on the liquid phase. HNO_3 extractions were made at concentrations between 0.01 and 2 M. Organic acids (acetic acid, citric acid, DL-malic acid, formic acid, fumaric acid, gluconic acid, lactic acid, L-glutamic acid, oxalic acid, pyruvic acid, tartaric acid) were all used at 0.2 M concentration and adjusted to pH values of 2, 3, 4 and 5 with HNO_3/NaOH. Citric and DL-malic acids were chosen for further study, and prepared in concentrations between 0.2 M and 1 M at pH values of 5 and 6 prior to extraction in accordance with the described procedure. All extractions were made in duplicate.

Remediation experiments: Electrodialysis experiments were made in cylindrical Plexiglas-cells with three compartments (Figure 1). Compartment II, which contained the soil-slurry was 10 cm long and 8 cm inner diameter. The slurry was kept in suspension by constant stirring with plastic-flaps attached to a glass-stick and connected to an overhead stirrer (RW11 basic from IKA). The anolyte was separated from the soil specimen by an anion-exchange membrane, and the catholyte was separated from the soil specimen by a cation-exchange membrane. Both membranes were obtained from Ionics® (types AR204SZRA and CR67 HVY HMR427). Electrolytes were circulated by mechanical pumps (Totton Pumps Class E BS5000 Pt 11) between electrolyte compartments and glass bottles. Platinum coated rod electrodes (surface area approximately 3 cm³) from Permascand® were used as working electrodes, and the power supply was a Hewlett Packard® E3612A. The

inter-electrode gap was 14 cm. The electrolytes (compartment I and III) initially consisted of each 500 ml 0.01 M $NaNO_3$ adjusted to pH 2 with HNO_3. Conductivity in compartment II, pH in all compartments, and voltage between the working electrodes were observed approximately once every 24 hours. The electrolyte pH was adjusted and maintained between 1 and 2 by manual addition of HNO_3/NaOH. Experiments were made according to the experimental plan (Table 1). All experiments lasted 240 hours and were designed with a liquid-to-solid-ratio (L/S) of 10.5 (37g soil, 390 ml liquid). The pH of malic and citric acid solutions was adjusted with NaOH. In the last three experiments (MA40N, CA40N and KC40) the reagent was allowed to react with the soil fines for 24 hours prior to application of the current. In four of the experiments (MA20N, CA20N, MA40N, CA40N) compartment II was kept at pH 6 by manual addition of NaOH.

After each experiment, membranes were cleaned overnight in 1M HNO_3, and electrodes were cleaned overnight in 5M HNO_3. Volumes of the cleaning acids, the electrolytes, and the solution in the middle compartment were measured followed by analysis of the cation-concentrations by AAS. The remaining soil mass was determined and the Pb concentration in the soil measured by AAS after digestion according to DS259 as described above. The mass balance for Pb was calculated as the mass of Pb found in the whole system after remediation (in soil, soil solution, electrolytes, membranes, and at electrodes) as a percentage of the total amount found in the soil prior to remediation. The current efficiency is defined, and was calculated as the fraction of the current passing through an electrolytic cell that accomplishes a

specific chemical reaction (in this case transfer of Pb from the soil fines into the electrolyte). The current efficiency of the Pb removal was calculated as follows:

$$\varepsilon_{Pb} = \frac{Q_{Pb}}{Q_{tot}} = \frac{(M_{Pb} \cdot z_{Pb}/MW_{Pb})}{(I \cdot t/F)}$$

where Q_{Pb} is the amount of current (moles) transferred by Pb^{2+}, and Q_{tot} is the total amount of current passed through the cell during remediation. M_{Pb} is the mass of Pb transferred from the soil fines, z_{Pb} is the valence of the species Pb (i.e. 2+), MW_{Pb} is the molar weight of Pb. I is the current (in A) passed through the cell, t is the experimental time (in seconds), and F is the Faraday constant.

RESULTS

Soil characteristics: The characteristics of the soil fines are listed in Table 2. Pb was analyzed in triplicate for each batch of soil-fines. The soil is carbonaceous and has a significant content of organic matter. Three different batches were used in the present work containing between 670 and 1170 mg/kg Pb. Sequential extraction (Figure 2) shows how Fe and Al are more strongly bound in the soil than Pb and in particular Mn.

 Extraction experiments: The ability of 10 of the organic acids to extract Pb is illustrated in Figure 3. Extraction results with oxalic acid are not shown because the final pH of the slurry was above 7. The maximum extraction of Pb with oxalic acid

was 1% obtained at pH 9-10. Six of the acids showed similar or worse extraction results than HNO_3 in this slightly acidic to neutral pH interval (pH 3-7), while five of the acids (citric acid, DL-malic acid, gluconic acid, tartaric acid and fumaric acid) showed pronounced improvement at near neutral pH probably due to complexation between Pb and the organic ligands of the acids. The best extraction was obtained with citric and malic acids. Citric acid extracted 22% of the Pb at pH 7.2, while DL-malic acid extracted 11% of the Pb at pH 6.8-7.1 (initial pH of extractants 5.0).

Based on these results, the effect of increased extractant concentrations on the extractability of Pb, Fe, Mn and Al by citric and DL-malic acids was investigated (Figure 4). Increased extraction of Pb and the natural soil cations Fe, Mn and Al was obtained by increasing the concentration of both citric acid and DL-malic acid. However, at the highest concentration of citrate acid (1M) a significantly decrease in extraction of all investigated elements was observed. This could be due to precipitation of the complexes formed. The best extraction of Pb was obtained with 0.4 and 0.6M citrate and 1.0M malate, which extracted equivalent amounts of all metals including 35% of the Pb.

 Remediation experiments: Based on the results of the extraction experiments, it was decided to perform EDR experiments with citric and malic acids as reagents. Reference experiments were made with distilled water and nitric acid. The main results of the 10 EDR experiments are summarized in Table 3. Mass balances for Pb between 61 and 115% were obtained. Although the low mass balances in some of the experiments mean that interpretation of the data should be made with caution, the

results of the experiments were significant enough to draw conclusions. The Pb-concentrations in the soil-fines post treatment obtained were between 40 and 980 mg/kg. In some of the experiments a considerable amount of the released Pb remained in the solution in compartment II (up to 55%), while in other experiments all the released Pb was transported into the electrolytes. Between 0.05 and 2.31‰ of the current transferred Pb-ions out of compartment II (calculated as the ‰ of the total transferred charges carried by Pb^{2+} into the electrolytes).

The first four experiments (DW20, MA20, CA20, NA20) were run under identical conditions except for the reagent in which the soil fines were suspended. From Table 3 it can be seen that the lowest final Pb-concentration in the soil fines was obtained in the experiment with nitric acid (NA20), followed by the experiment with distilled water (DW20), while less successful remediation was obtained in the experiments with malic acid (MA20) and citric acid (CA20). The distribution of Pb in the remediation cell after experimental remediation is given for all experiments in Figure 5. Here it can be seen that the removed Pb was successfully transferred out of compartment II and into compartment III in the experiment with distilled water, while a large fraction of the Pb remained in the solution in compartment II in the experiments with nitric acid and malic acid. Almost all the Pb remained bound to the soil particles in the experiment with citric acid. The higher Pb-transport out of compartment II in the experiment with distilled water is reflected by a higher current efficiency (Table 3) in this experiment. The overall result of these four experiments is that distilled water is superior for EDR of Pb-contaminated soil-fines in suspension.

The pH-development in the middle compartment (II) during the first four electrodialytic remediation experiments (DW20, MA20, CA20, NA20) is illustrated in Figure 6. This figure shows how the pH decreased in the experiment with distilled water as expected.[1] The pH in the experiment with nitric acid was initially slightly lower than in the experiment with distilled water; however, it increased during the first 80 hours to reach values similar to the distilled-water experiment. The pH in the organic acid experiments decreased slowly throughout the experimental period to reach a final pH of approximately 4.5.

Because the extraction experiments showed that Pb was more efficiently extracted at near neutral pH with the organic acids, experiments were made to show if the pH-drop in experiments MA20 and CA20 was responsible for the reduced remediation when adding these acids. In the following two experiments (MA20N and CA20N) the pH was kept between 6 and 7 in compartment II throughout the experiment . The results in Table 4 show that keeping the pH neutral worsened the result of remediation with malic acid slightly, while citric acid was more efficient, although still less efficient than either distilled water or nitric acid. Hence the pH-drop was not solely responsible for the reduced remediation.

The conductivity of the soil solution in the first four experiments (Figure 7) was directly related to the concentration of added acid. The highest conductivity was seen in MA20, in which 1M malic acid was added. Compared to this, the conductivity was about half in CA20, in which 0.5M citric acid was added. The initial conductivity was only slightly elevated in NA20 with nitric acid (pH 1.4) compared to DW20, and by the end of the experiments, the conductivity had increased in DW20 beyond that of

NA20. The conductivity decreased constantly in the organic acid experiments, because organic ligands were transferred out of the soil solution. This transport was confirmed by visible inspection of CA20, in which the anolyte turned yellow after only 24 hours with a clear intensification of the colour during the experimental period.

The fact that the conductivity was substantially higher in MA20 and CA20 compared to DW20, suggested that the current density in these experiments could be increased beyond what is ideal for remediation with distilled water. It was shown in a previous study that 20mA is the optimal current density for EDR of soil fines in suspension at L/S 10.5 with distilled water as reagent.[1]

This hypothesis was tested by increasing current to 40mA in experiments with malic acid and citric acid (MA40N and CA40N). In addition, additional experiments with nitric acid (NA40), and potassium citrate (KC40) at increased current densities were made. Potassium citrate was chosen because it required a large amount of NaOH to adjust the organic acids to near neutral values, and addition of the salts of the acids seemed more practical. In NA40 the concentration of nitric acid was increased compared to the concentration in NA20 to exceed the buffer capacity of the soil and increase the conductivity sufficiently to enable application of the higher current without induction of water splitting at the cation-exchange membrane.[1] In addition, the reagents were allowed to react with the soil fines for 24 hours prior to application of the current to make sure that the lack of remediation success with the organic acids was not due to insufficient reaction time to form complexes between Pb and the organic ligands.

From the results in Table 3 it is seen that the increased current seems to have no or even adverse effects on the remediation with malic acid. In the experiment with citric acid, increased current density seemed to have a positive influence on extraction and transfer of Pb into the anolyte, however, by no means reaching the efficiency of EDR with distilled water. Addition of potassium citrate strongly impeded remediation compared to all other experiments even the ones with citric acid. Thus too low a current density or too little time to react could also not explain the low remediation with malic and citric acids as reagents. The best results were obtained with increased current ($0.8mA/cm^2$) and addition of 0.5M nitric acid (NA40). Here 90% of the Pb was removed from the soil, 81% of the Pb had been transferred to the cathode/catholyte, and the final Pb concentration was 40 mg/kg, which is exactly the limiting value set by the Danish authorities for clean soil.

DISCUSSION

Extraction experiments: The promising Pb-extracting properties of citrate, tartarate and malic acid are consistent with previous findings,[10,30] although the previous works reported substantially higher extraction than what was found in the present work. The discrepancy may be due to the 5 times higher liquid-to-solid ratio and the more coarse grained material used in the previous studies.[10] It may also be linked to the high carbonate content of the present soil, or possibly the presence of less soluble Pb-compounds. The fact that the pH of the soil increased after addition of oxalic acid at pH values 2-5, well below the initial soil pH, indicates a complex interaction between soil constituents and oxalate, which may include dissolution of iron oxides and

hydroxides resulting in the observed increase in pH. Concerning the mineral dissolution occurring during Pb-extraction, it was obvious that no extraction of Pb could be obtained with these acids without a significant simultaneous extraction of Mn. Fe and Al were dissolved to a smaller extent than Pb. The extraction of Mn, Fe and Al were all above that obtained during steps I-III of sequential extraction, while Pb was less affected by the organic acids than by the first three steps of sequential extraction.

Remediation experiments: It is well established that the pH decrease occurring during EDR of fine grained materials suspended in distilled water is a result of water splitting at the surface of the anion-exchange membrane.[1,31,32] Thus the pH decrease observed in DW20 (Figure 6) is consistent with previous findings. The phenomenon of water splitting appears because the soil-suspension contains an insufficient amount of mobile anions available for migration across the anion-exchange membrane to compensate for the more abundant mobile cations, which are transferred across the cation-exchange membrane. The slower pH-decrease seen in MA20 and CA20 is likely to result from reduced water-splitting because of the higher concentration of mobile anions (the organic ligands of the acids) in the suspension and the buffer effect of the organic acid itself. The slightly slower pH-decrease in NA20 compared to DW20 could likewise be a result of the nitrate added with the acids.

The less successful remediation obtained in the experiments with malic acid and citric acid could be explained by the observed pH decrease, which may result in changes in the speciation of Pb towards less mobile species. Such changes were confirmed by the

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results of the extraction experiments, which showed less mobility at lower pH when adding organic acids. We modeled the speciation of Pb in the presence of malate and citrate by use of the programs HYDRA/MEDUSA (Puigdomenech I (http://www.kemi.kth.se/inorg/medusa)) using equilibrium constants for malate from Smith and Martell.[33] The results are shown in Figures 8 and 9.

The impeded transport of Pb into electrolytes after addition of the organic acids in MA20 and CA20 could well be explained by the prevalence of uncharged complexes at pH values below 5. In particular neutral complexes dominate between malate and Pb, which may explain the observed extraction without subsequent transfer of Pb in MA20. The fact that remediation was not enhanced in MA20N, however, suggests that other mechanisms are dominating, or else the Pb-malate system may not be sufficiently well described. The Pb citrate system is indeed more detailed (Figure 9), and the results of CA20N show increased mobilization and transfer of Pb consistence with the model and the results of the extraction experiments. Still, however, the remediation was seriously impeded compared to the results obtained with distilled water and nitric acid, and the amount of Pb found in solution in the middle chamber, which may reflect the amount bound to the organic ligands in uncharged complexes, does not account for the difference. Thus the prevalence of neutral complexes cannot alone explain our results.

It was previously observed that EDR of sediments may be less efficient when acids are used as suspending fluid as compared to distilled water. This effect was suggested to arise from the competitive transfer of the ions from the acids in the current field.[34] An effect, which may also explain the results of the experiments with nitric acid (NA

20 and NA40) of this work, in which substantially better remediation was obtained at the elevated current density, and supported by the fact that the conductivity was higher when acid was added (Figure 7). When the organic acids were used, the same effect was, however, not observed; hence competitive transfer of the ions from the acids can also not explain the impeded remediation when these acids were used. Overall, the results may be due to a combined effect of size-exclusion, reduced transfer over the ion-exchange membranes of the large organic complexes, prevalence of uncharged complexes and competitive transfer of the ions of the acid; however none of these mechanisms explain the low desorption of Pb from the soil fines in the experiments with organic acids (Figure 5), and in particular in the experiments with citric acid and potassium citrate. The results of the extraction experiments with citrate (Figure 4a) suggested that adverse effects of the acid addition occur at a citrate concentration above 0.6 M. We suggest that precipitation of complexes between Pb (Fe, Al and Mn) and citrate could be the reason for this. It may be that the application of the direct current stimulates the formation of precipitates, which would explain our results.

The overall result of our work is to reject the feasibility of using organic acids as enhancing reagents during EDR in suspension. Thus combination of EDR and heterotrophic leaching does not seem to be a potential method of remediation for contaminated sludge from soil washing. Addition of nitric acid in combination with an increased current density is, in contrast, a qualified suggestion for promotion of EDR of Pb contaminated soil fines in cases where the removal rate is considered to be more important than the energy expenditure and the acid consumption.

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CONCLUSIONS

Citric acid, DL-malic acid, gluconic acid, tartaric acid and fumaric acid (0.2M) are able to extract Pb from contaminated soil fines in excess of the extraction obtained solely by pH-changes at neutral to slightly acidic conditions. The most efficient extraction was obtained with citric and malic acids, with which extraction results were improved when increasing concentrations to 0.5 and 1.0M respectively. A maximum of 35% Pb was extracted from the present soil. Mn was completely extracted by the organic acids while Fe and Al were extracted to a smaller extent than Pb. Electrodialytic remediation of soil-fines in suspension was strongly impeded by the addition of citric acid and malic acid (0.5M and 1.0M respectively) independently of pH control of the suspension in regions where the Pb-complexes of these acids ought to be charged. No improvement was obtained when the contact time between reagent and soil prior to application of current was increased or at increased current densities with the organic acids as reagents. The feasibility of combining EDR and heterotrophic leaching of soil fines in suspension is therefore rejected. In contrast, enhancement of EDR with nitric acid showed promising results at current densities increased beyond what is feasible with addition of only distilled water. Thus nitric acid addition is recommended as enhancing reagent in situations, for which a high removal rate is considered more important than energy expenditure and chemical consumption.

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Table 1. Experimental plan. The soil-fines were suspended in the reagent during

remediation.

Expt.	Reagent (pH of reagent)	J** [mA]	Adjustment of pH in II with NaOH
DW20	Distilled Water (pH 6.5)	20	-
MA20	1 M Malic acid (pH 5)	20	-
CA20	0.5M Citric acid (pH 5)	20	-
NA20	HNO_3 (pH 1.4)	20	-
MA20N*	1 M Malic acid (pH 7)	20	Kept at 6.0 (±1.0)
CA20N*	0.5M Citric acid (pH 7)	20	Kept at 6.0 (±1.0)
NA40	0.5 M HNO_3 (pH 0.0)	40	-
MA40N*	1 M Malic acid (pH 5)	40	Kept at 6.0 (±1.0)
CA40N*	0.5M Citric acid (pH 5)	40	Kept at 6.0 (±1.0)
KC40	0.5M Potassium citrate (pH 8.5)	40	-

*N = neutral conditions in compartment II. The pH-adjustment in II was maintained

throughout the experiment .

**20mA is equivalent to $0.4mA/cm^2$; 40mA is equivalent to $0.8mA/cm^2$.

Table 2. Characteristics of the soil fines.

Pb [mg/kg]	670-1170
pH	7.8 +/- 0.2
$CaCO_3$ [%]	17.3 +/- 0.1
Organic matter [%]	7.8 +/- 0.1
CEC [meq/100g]	14.1 +/- 0.3
Fe [g/kg]	27.3 +/- 0.3
Mn [mg/kg]	587 +/- 26
Al [g/kg]	9.9 +/- 0.2

Table 3. Experimental performance.

Exp. Name	Pb Mass balance [%]	Start Pb [mg/kg]	Final Pb [mg/kg]	Current efficiency [‰]
DW20	115	1170	220	2.31
MA20	86	1040	400	0.20
CA20	84	1040	980	0.11
NA20	84	670	48	0.34
MA20N	94	1040	540	0.11
CA20N	61	1040	560	0.16
	96	670	40	0.93
MA40N	89	670	355	0.09
CA40N	69	670	315	0.17
KC40	70	670	519	0.05
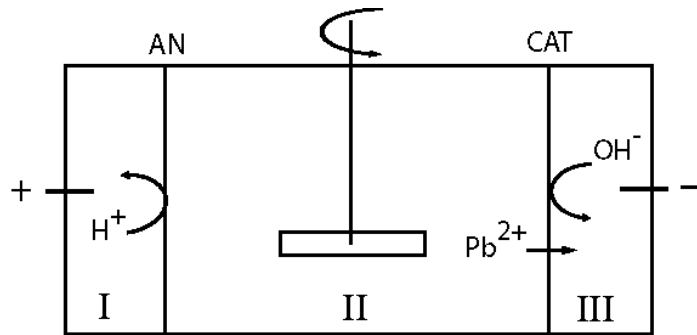
Figure 1. Schematic view of a cell used for experimental EDR of soil fines in suspension. AN = anion-exchange membrane, CAT = cation-exchange membrane.
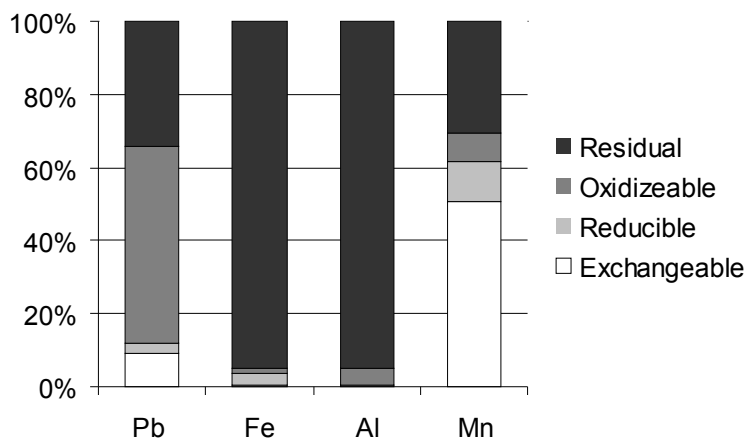
Figure 2. Sequential extraction of Pb, Fe, Al and Mn from the soil fines.
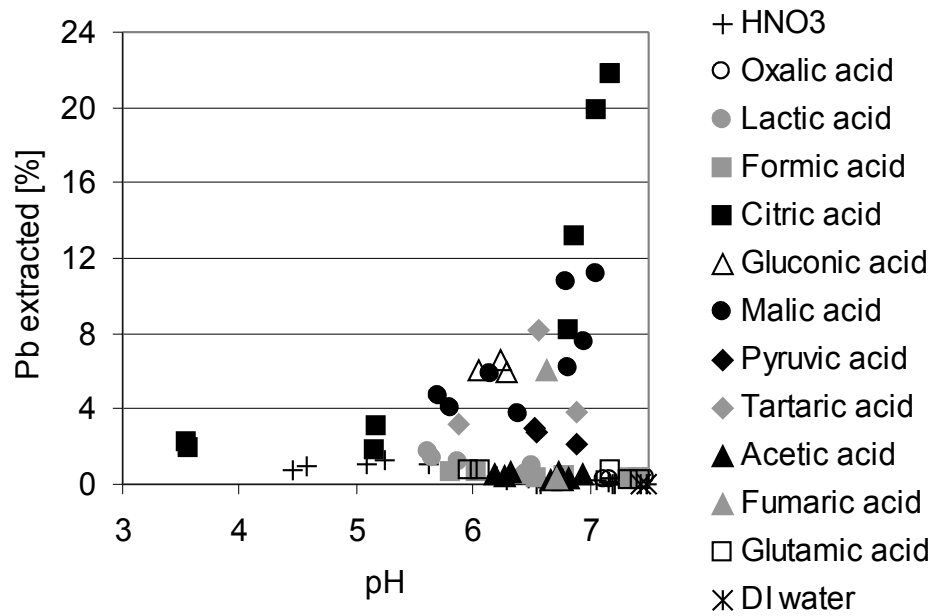
Figure 3. Extraction of Pb from soil fines with HNO_3 and organic acids (0.2M).
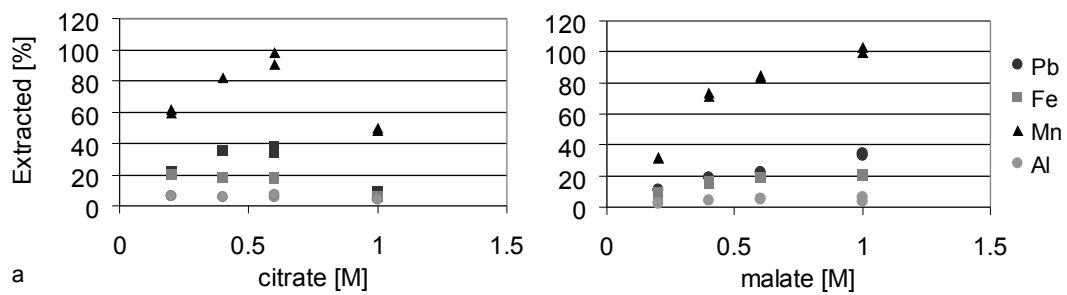
Figure 4. Extraction of Pb, Fe, Mn and Al from soil fines with a) citric acid (final pH between 7.1 and 7.7) and b) DL-malic acid (final pH between 6.8 and 7.2). Results of both duplicate experiments plotted.
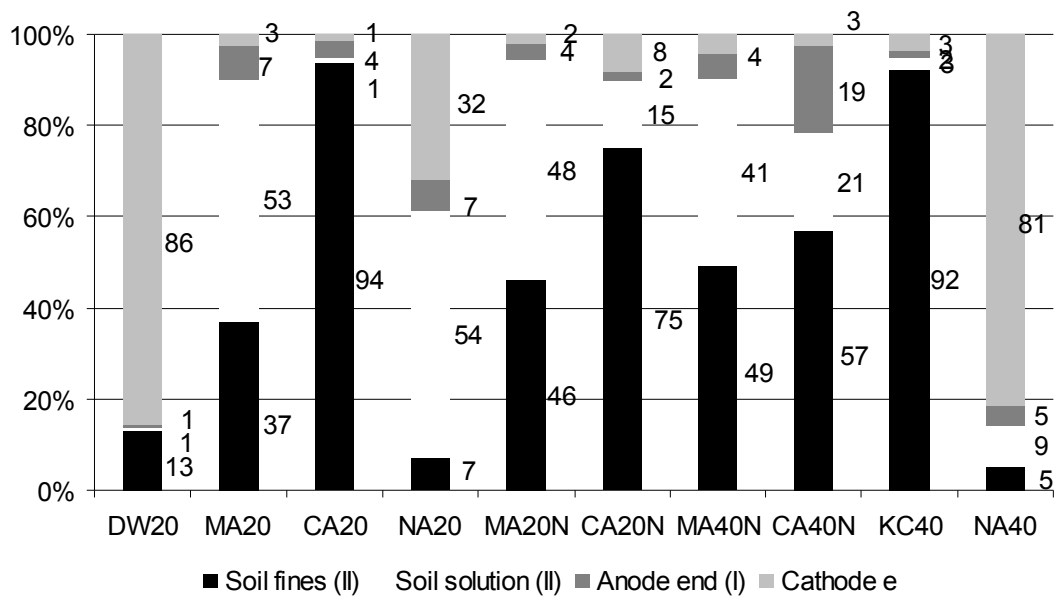
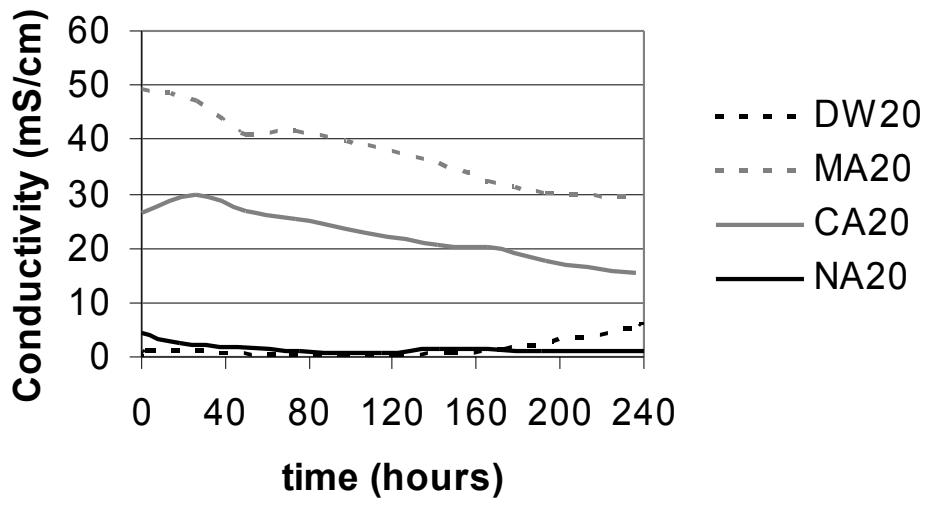**Figure 5.** Distribution of Pb in the compartments of the remediation cell after experimental remediation [%].
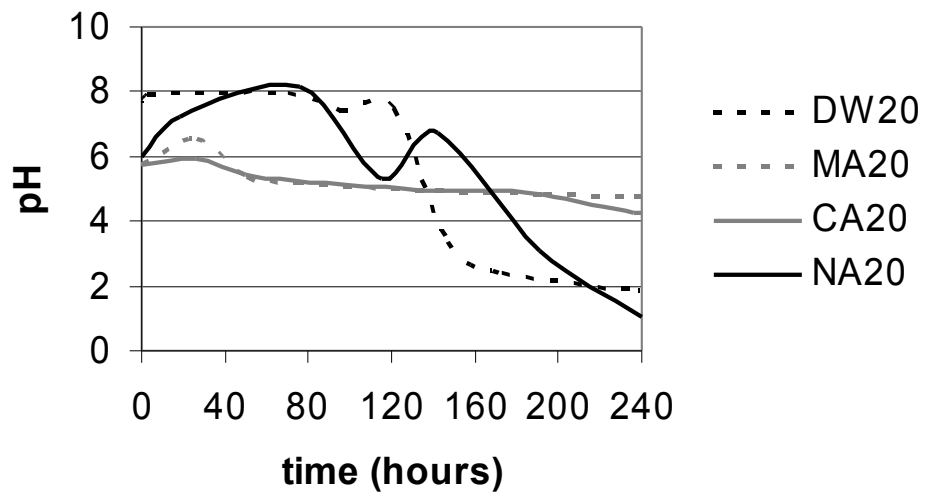
Figure 6. pH in the soil solution during experimental remediation with distilled water (DW), malic acid (MA), citric acid (CA) and nitric acid (NA) as reagents at 20mA (0.4mA/cm^2).
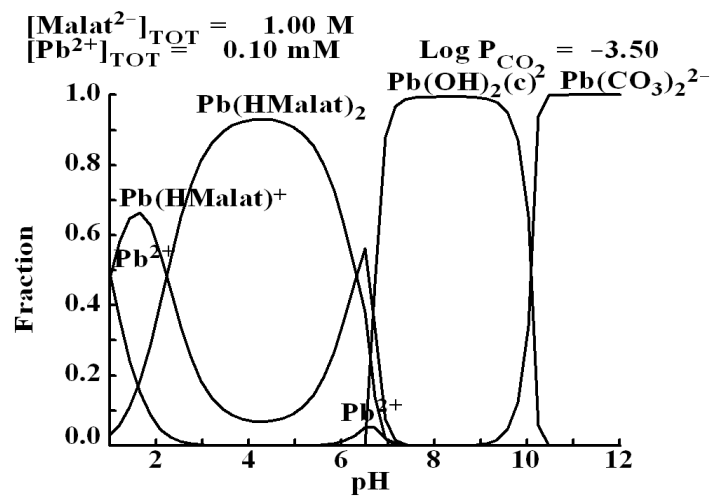
Figure 7. Conductivity in the soil solution during experimental remediation with distilled water (DW), malic acid (MA), citric acid (CA) and nitric acid (NA) as reagents at 20mA (0.4mA/cm^2).

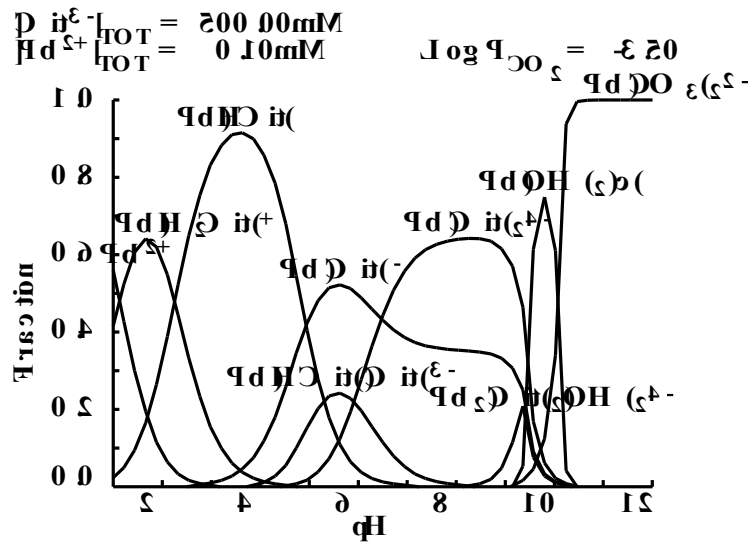**Figure 8.** Speciation of Pb in the presence of excess malate, and carbonate in equilibrium with the atmosphere, as a function of pH. Equilibrium constants for malate form.[33]