

The influence of sediment properties and experimental variables on the efficiency of electro dialytic removal of metals from sediment

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

*Corresponding author: e-mail kbo@akvaplan.niva.no; tel. +47 928 799 28

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

^b Akvaplan-niva AS, Fram Centre - High North Research Centre for Climate and the Environment, Hjalmar Johansens gate 14, 9007 Tromsø, Norway (present address)

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

Abstract

Chemometrics was used to determine the influence of sediment properties and experimental settings for the electro dialytic removal (EDR) of Cu, Pb and Zn from six harbour sediments from Greenland and Norway. A Projection onto latent structures (PLS) model revealed that the most important sediment properties for achieving acidification (lag-phase, pH>4), necessary for desorbing and mobilising metals in the polluted sediments, were buffer capacity and grain size distribution. Higher stirring rate reduced the acidification time, stressing the importance of thorough mixing of the sediment suspension to achieve a fast and uniform acidification.

PLS models were calculated to determine the influence of sediment properties on the removal of metals during EDR, which was observed to vary depending on the targeted metal and the stage of the remediation. In general, buffer capacity, grain size distribution, element composition and metal partitioning were important for remediation efficiency and are important parameters for determining optimal experimental settings. In the fast removal phase (final pH 2-4), organic matter as well as stirring rate had increasing importance indicating oxidation and release of metals at this stage. Understanding the influence of sediment properties is important for determining experimental settings in accordance with the phase of EDR.

Keywords: Chemometrics, PLS, EDR, EKR, heavy metals, sediments

1 Introduction

The need for remediating harbour sediments arises either through development of harbours in which contact with, or removal of polluted sediments is inevitable, e.g. when increasing navigational depths, or due to governmental acts to decrease the adverse effects on the marine environment and human

health. The choice of remediation technology in a given situation depends on sediment properties, pollutant composition and quantity, as well as cost-effectiveness and site specific conditions. Understanding the influence of sediment properties on the efficiency of the remediation is vital for ensuring optimal settings and adjustments during the different stages of a remediation.

Multivariate analysis provides tools for analysing large sets of data, which is done by reducing the dimensions making it easier to visualise and retrieve trends. One such tool is projections onto latent structures (PLS) in which optimum settings for independent as well as correlated variables are determined and can for instance be used to evaluate the comparative importance of sediment properties on remediation processes. In remediation, sediment properties and experimental variables cannot necessarily be assumed to be independent; unlike some of the more traditional statistical analyses such as multiple regression PLS copes with collinearity between variables [1]. Other advantages of PLS is that it provides plots of the data compressed to fewer dimensions than the original dataset, easing the interpretation, it copes with noise in both the X and Y matrices and moderate amounts of missing data [2-4].

PLS and other multivariate methods, such as fractional factorial designs and principal component analysis, have been extensively used for optimisation in organic synthesis, the method has found limited use in pollution studies. It has however been employed for identifying important factors for formation of toxic PCB during waste combustion [5] and to assess the influence of soil properties on the chemical oxidation of PAH in soil [6]. In addition, our group has previously demonstrated the use of PLS models for evaluating the experimental variables for sediment-specific electrodialectic remediation (EDR) [7-10], as well as a tool for predicting experimental settings in new sediment [11].

EDR is a method originally developed for removing heavy metals from soil in the 1990s [12]. The method has since been developed for efficiently removing heavy metals from other polluted materials such as wood, fly ash, sewage sludge and harbour sediments [13-16]. EDR is based on the principles of electrokinetic remediation (EKR) in which an electric field of low current density is applied to the polluted material, initiating acidification processes and subsequent desorption of heavy metals. Transport processes are dominated by electromigration, i.e. the transport of ions and ionic complexes in the pore fluid of the polluted material [17-19].

The removal of metals in soils during EDR can roughly be divided into three phases [20];

1. Lag phase (acidification) in which pH decreases to the threshold value of initiating desorption of the specific metal. During this phase the metal removal is limited.
2. Fast removal phase in which rapid dissolution/desorption of the specific metal in the available fractions of the sediment occurs.
3. Slow removal phase in which a continuous dissolution/desorption of the specific metal in the lesser available fractions of the sediment occurs.

The duration of each phase and the metal removal rate depends on the sediment properties and also reflects how the metal is bound in the sediment [17, 19, 21-23]. The removal rate of Ca was for instance found to be much faster than the other investigated metals (Al, Fe, K, Mg, Mn and Pb) [20]. Sediment properties reported to prolong acidification in both EDR and EKR include high contents of carbonate, organic matter and salts [17, 19, 21, 22, 24] contributing to the buffer capacity of the soil/sediment. Other sediment properties reported to affect the efficiency of EDR are grain size and

concentration/composition of metals. Removal of metal is faster from soil fines (<63µm) [25, 26] due to the electric field being more being a more effective driving force for transport of fluid in fine-grained soils of low hydraulic conductivity than a hydraulic gradient. Studies summarised in [27] found that the composition and concentration of elements in the soil resulted in lower removal rates of each individual metal. This is related to transport under the influence of an electric field, when the concentration of a given metal decreases, relative to other metals present, the ion migration of the specific metal will be less efficient [17].

Current density and time have been shown to be the most important experimental variables influencing EDR [16, 25, 28-30]. High current densities may however impede the removal and increase the energy consumption significantly. The limiting current densities have been reported to depend on the soil/sediment properties. Stirring significantly improves removal efficiencies [14, 29, 31] and a high stirring rate could increase the removal of metals, for instance metals found in the organic fraction of the soil/sediments can be mobilised by oxidation of the sediment [29]. The liquid-solid (L/S) ratio of the sediment suspension may to a lesser extent influence removal efficiencies in EDR [25, 26, 32].

Sediment properties have been shown to affect the efficiency of EDR, however assessing the relative influence and scrutinising the influence in the different phases of EDR has yet to be undertaken. The focus of this study is to assess the comparative influence of sediment properties and experimental variables in the three phases of EDR. This is done through multivariate analysis of previously reported results, supplemented with additional experiments of six different sediments. The influence of sediment properties on the EDR process parameters acidification time and energy consumption has also been evaluated.

2 Methods and materials

2.1 Experimental sediments

Sediments from Sisimiut, Greenland and Hammerfest, Norway 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

The six sediments were analysed for pH, electric conductivity, cation exchange capacity (CEC), grain size analysis and content of elements (Al, Ca, Fe, K, Mg, Mn, Na, Cr, Cu, Ni, Pb, Zn), chloride, total carbon, sulphur, nitrogen, phosphorous, carbonate and organic matter. The results of these are summarised in table 1 and the description of methods and materials for these analysis are described in detail in [33]. In this study, the sediment characteristics were supplemented with metal desorption experiments to evaluate the availability of metals in the sediment.

Table 1: Sediment characteristics (6 sediments) from Hammerfest (H1, H3, H4 and H5) and Sisimiut (S1 and S2). A summary of the results were previously reported in [33] and the original sediment id have been kept.

Characteristic	Units	H1	H3	H4	H5	S1	S2
Carbonate	%	45	8.8	0.7	0.7	0.7	1.7
Organic matter	%	5.4	4.8	14.7	5.3	8.5	6.4
Total carbon	%	7.3	3.3	10.1	3.1	5.3	3.2
Sulphur	%	0.3	0.2	1.2	0.3	0.8	0.7
Nitrogen	%	0.5	0.1	0.1	0.01	0.5	0.3

pH		8.1	8.2	7.0	7.5	7.0	7.5
Conductivity	mS/cm	8.7	9.1	20.0	12.3	7.5	8.8
Grain size							
Clay (<2 μ m)	%	6.3	5.7	8.9	4.3	8.8	1.6
Silt (2-63 μ m)		22	38	32	18	52	20
Sand (63-200 μ m)		68	56	54	77	38	76
Gravel (>200 μ m)		3.7	0.3	5.1	0.7	1.2	2.4
CEC	meq/100 g	8.0	2.5	12.8	2.4	4.3	1.8
Chloride	mg/kg	7990	7780	14100	9200	6240	7950
P		645	1450	3100	800	1800	1870
Al		3700	8650	8050	6700	6650	4250
Ba		1350	137	370	121	159	100
Ca		1456000	28100	8800	4500	7100	6000
Fe		6400	15200	18700	11200	14500	10100
K		1700	4440	3500	2800	2300	1450
Mg		7560	5500	6750	4650	6000	3450
Mn		97	132	123	118	112	69
Na		6850	3750	15500	4500	7200	4600
V		25	50	77	44	69	35
Cd		0.1	0.3	1.1	0.1	0.5	0.4
Cr		15	23	47	24	37	25
Cu		116	54	167	47	216	184
Ni		10	15	23	15	18	18
Pb		49	46	152	42	73	57
Zn		83	140	540	94	340	960

Sequential extraction was made in four steps based on the extension of the three-step method described by Standards, Measurements and Testing Program of the European Union [34]. Air-dried sediment (0.5 g) was first extracted with acetic acid (0.11 M, 20 mL, pH3) for 16 hours; secondly with hydroxylammonium chloride (0.1 M, 20 mL; pH2) for 16 hours; thirdly with hydrogen peroxide (8.8 M, 5 mL) for 1 hour, followed by extraction at 85 °C for 1 hour, evaporation of liquid at 85 °C, and subsequent extraction of the cooled solid fraction with ammonium acetate (1 M, 25 mL, pH2) for 16 h; and fourthly the remaining solid particles were analysed for metal content after digestion. The solids 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 μ m filter and the liquid was diluted to 100mL. Metal concentrations in the liquid were measured by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) on a Varian 720-ES in the Arctic Technology Centre at The Technical University of Denmark.

Desorption of metals as function of pH were made by agitating 10 samples of dried sediment (5 g) with HNO₃ (25 mL) in varying concentrations (0.01, 0.05, 0.1, 0.5 and 1.0 M). Two extractions in distilled water were made as reference. The suspensions were agitated for a week on a horizontal shaker. Subsequently samples settled for 15 min and the pH was measured using a radiometric analytical electrode and the measuring instrument SenION+ MM374. The sediment suspensions were vacuum filtered through a 45 μ m filter. Metal concentrations in the liquid and solid particle fractions (after digestion) were measured by ICP-OES to determine the percentage of metals desorbed (liquid fraction).

2.3 EDR experiments

2.3.1 Materials

In all of the experiments a 3-compartment electro dialytic cell design was used and an illustration of the set-up can be found elsewhere [30]. The experimental set-up consisted of a centre compartment containing the sediment suspensions and electrolyte liquids were circulated in two adjoining compartments. The set-up was designed in a way that exploited water splitting at the anion exchange membrane to ensure acidifying conditions in the sediment suspension. Application of ion exchange membranes controlled the transport of ions between the electrolyte compartments and the sediment suspension compartment, thus preventing protons and hydroxyl ions from electrolysis reactions at the electrodes, from entering the sediment suspension compartment.

The electro dialytic cell was manufactured from Plexiglas. The length of the centre compartment was 10 cm, the length of each electrolyte compartment was 3.5 cm and all three compartments had an inner diameter of 8 cm. The choice of membranes in this study was based on functionality in the pH range 1-8. For further reference to the influence of membranes on the performance during electro dialytic treatment, the reader is referred to [35]. Ion exchange membranes from Ionics (anion exchange membrane 204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B) separated the electrolyte compartments from the polluted sediment compartment. NaNO₃ (0.01 M) was used as electrolyte liquids and was continuously adjusted to pH 2 by HNO₃ (5 M). The electrolytes (300 ml) were circulated via an Ismatec reglo pump with a flow rate of 10 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 a CAT R14 motor with a stirrer consisting of plastic flaps (4 cm x 0.5 cm) fastened to a glass rod.

After the EDR experiments sediments were filtered through a Whatman CAT 1113-320 filter (32.0 cm) and the metal concentrations in both the suspension liquid and solids were measured. The stirrer, membranes and electrodes were soaked in HNO₃ (5 M) overnight and the heavy metal concentrations in the soaking liquids as well as the electrolyte liquids were measured by ICP-OES.

2.3.2 Experimental design

A total of 47 experiments were used in this study, of which 43 were conducted in connection with other studies with different study objectives and were all based on fractional factorial designs. The experiments do not cover a perfect multivariate design, none the less, as is apparent from table 2, similar experimental domains were applied. The current density refers to current across the membrane, i.e the current per membrane area covering the inner circumference of the electro dialytic cell:

$$\text{Current density} = \text{Current (mA)} / \text{Area of inner circumference of electro dialytic cell (cm}^2\text{)}$$

Table 2: The experimental settings of the experiments used in multivariate analysis for assessing influence of sediment properties.

Experiment	Sediment	Time (h)	Time after acidification (h)	Current density (mA/cm ²)	L/S (ml/g)	Stirring rate (rpm)	Suspension liquid	Light/no light
1	H1	332	0	0.2	2	1300	Distilled water	Light
2	H1	163	0	0.2	2	1300	Distilled water	Light
3 [†]	H3	672	0	0.04	12	1	Distilled water	Light
4 [†]	H3	672	296	0.8	2	1	Tap water	Light
5 [†]	H3	192	0	0.04	2	1300	Tap water	Light
6 [†]	H3	672	0	0.04	2	1	Tap water	No light

7 ¹	H3	192	0	0.8	2	1	Distilled water	Light
8 ¹	H3	714	490	0.8	2	1300	Distilled water	No light
9 ¹	H3	192	0	0.04	12	1300	Distilled water	No light
10 ¹	H3	192	50	0.36	12	1	Distilled water	No light
11 ¹	H3	672	572	0.36	12	1300	Tap water	Light
12 ¹	H3	432	295	0.42	7	650	Distilled water	Light
13 ¹	H3	312	175	0.36	7	650	Distilled water	Light
14 ¹	H3	312	175	0.36	7	650	Distilled water	No light
15 ¹	H3	520	383	0.36	7	650	Distilled water	No light
16 ¹	H3	307	85	0.8	2	1300	Distilled water	Light
17 ¹	H3	308	85	0.68	2	1300	Distilled water	Light
18	H4	332	192	0.2	3	1300	Distilled water	Light
19	H4	163	0	0.2	3	1300	Distilled water	Light
20 ²	H4	484,5	444	0.2	4	1300	Distilled water	No light
21 ²	H4	517,5	444	0.52	2	1300	Distilled water	Light
22 ²	H4	236,5	48	0.2	2	100	Distilled water	Light
23 ²	H4	88,5	48	0.52	4	100	Distilled water	No light
24 ³	H5	474	444	0.2	6	1300	Distilled water	Light
25 ³	H5	163	133	0.2	6	1300	Distilled water	Light
26 ³	H5	307,5	278	0.2	6	1300	Distilled water	Light
27 ⁴	H5	25	0	0.2	6	1300	Distilled water	Light
28 ⁴	H5	81	48	0.04	6	1300	Distilled water	Light
29 ⁴	H5	51	24	0.12	6	1300	Distilled water	Light
30 ⁵	H5	307	278	0.36	6	1300	Distilled water	Light
31 ⁵	H5	190	163	0.28	6	1300	Distilled water	Light
32 ⁵	H5	75	48	0.52	6	1300	Distilled water	Light
33 ⁵	H5	190	163	0.28	6	1300	Distilled water	Light
34 ⁴	H5	184,5	163	0.12	6	1300	Distilled water	Light
35 ⁴	H5	478	446	0.52	6	1300	Distilled water	Light
36 ³	S1	95,5	48	50	4	100	Distilled water	No light
37 ³	S1	548	444	50	2	1300	Distilled water	Light
38 ⁶	S2	138,5	48	0.04	2	1300	Tap water	Light
39 ⁶	S2	465,5	444	0.04	12	100	Distilled water	Light
40 ⁶	S2	67,5	48	1	12	1300	Distilled water	No light
41 ⁶	S2	503,5	444	1	2	100	Tap water	No light
42 ⁶	S2	257,5	246	0.52	7	700	Distilled water	Light
43 ⁶	S2	261,5	246	0.52	7	700	Distilled water	Light
44 ⁶	S2	287	278	0.04	6	1300	Distilled water	Light
45 ⁶	S2	71	48	0.2	6	1300	Distilled water	Light
46 ⁶	S2	191,5	165	0.12	6	1300	Distilled water	Light
47 ⁶	S2	189,5	163,5	0.12	6	1300	Distilled water	Light

¹ Experiments previously reported in [30]

² Experiments previously reported in [8]

³ Experiments previously reported in [11]

⁴ Experiments previously reported in [10]

⁵ Experiments previously reported in [9]

⁶ Experiments previously reported in [7]

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 PLS modelling

In PLS, quantitative relations between a descriptor matrix, X, and a response matrix, Y, are calculated based on projections. Object points in each of the X and Y matrices are projected down to a PLS component representing the maximum correlation between the PLS scores of the Y- and X-matrix. New PLS components are iteratively introduced until the systematic variation in the Y-matrix has been exhausted.

Tools for evaluating the PLS models include correlation factors (R²Y), predictive powers (Q²), variable importance in the projection (VIP) plots, coefficient plots and weight vectors. The amount of the variance of the Y-matrix described by the model is R²Y, which accordingly should be high (approaching 1). Q² is the predictive power, an estimate of the reliability/stability of the model calculated by cross-validation. In order to obtain a high predictive power, R²Y should be high. A value of Q²>0.9 is excellent, while a value above 0.5 is good. With non-significant components, Q² can even be negative. The difference between R²Y and Q² should be as low as possible and a difference larger than 0.2-0.3 may indicate outliers or the presence of irrelevant variables in the X block. VIP plots present the importance of each parameter in the model with respect to its correlation to all the responses (Y) and to the projection (X), reflecting relative importance of the model parameters to each other (in absolute values). Parameters with high VIP values (>1) are considered most relevant for explaining the responses. Coefficient plots illustrate contribution of the variables in the X-matrix to each individual response in the Y-matrix and can for instance reflect how experimental variables and sediment properties affect remediation. Weight vectors, w*(X-matrix) and c (Y-matrix), are introduced to show the contribution of each variable in X to the description of the systematic variation in the Y matrix [5].

In this study SimcaP11 software was used for PLS modelling based on the 47 experiments listed in table 2. The X-matrix consisted of the 6 experimental variables (time, time after acidification, current density, stirring rate, L/S ratio, suspension liquid and light/no light) (table 2) and sediment properties (element concentrations, chloride, TC, S, N, P, carbonate, organic matter, CEC, grain size distribution, pH, conductivity) (table 1). The Y-matrix consisted of the final concentrations of the elements Al, Ca, Fe, K, Mg, Mn, Na, Cr, Cu, Ni, Pb and Zn.

3 Results and discussion

3.1 Metal availability in the sediments

It was previously found that of the seven analysed environmental priority metals (As, Cd, Cr, Cu, Ni, Pb and Zn), it was only Cu, Pb and Zn that exceeded the environmental quality criteria from Arctic countries to an extent at which potential effects on the marine environment could occur [33]. For this reason, they remain the focus for the remediation in this study.

Metal partitioning, determined by sequential extraction, is an indication of how available the metals are in the sediment and to what extent a metal will be mobilised by ion-exchange, dissolution of carbonates, reducing or oxidising conditions, or acidic (pH<2) conditions. It can be a useful tool for assessing the potential for removing metals from sediments by electrodialysis and higher removal rates have for instance been observed for the more available metals (exchangeable/reducible) in the sediment [7, 30].

Metal partitioning of Cu, Pb and Zn (figure 1) revealed that Cu is mostly found in the exchangeable and oxidisable fractions (>80%), while Pb is mostly found in the exchangeable fraction, apart from the H1

sediment, in which a large fraction is bound to organic matter. Zn is mostly bound in the exchangeable fraction. Metals found in the residual fraction, the most difficult to mobilise are, apart from Pb in sediment S2, below 25% indicating that there is potential for high removal rates by EDR in the sediments. Metals in the stable minerals may however also dissociate during EDR as previous studies showed acceleration in the weathering of the soil and changes in the availability of residual metal [36, 37].

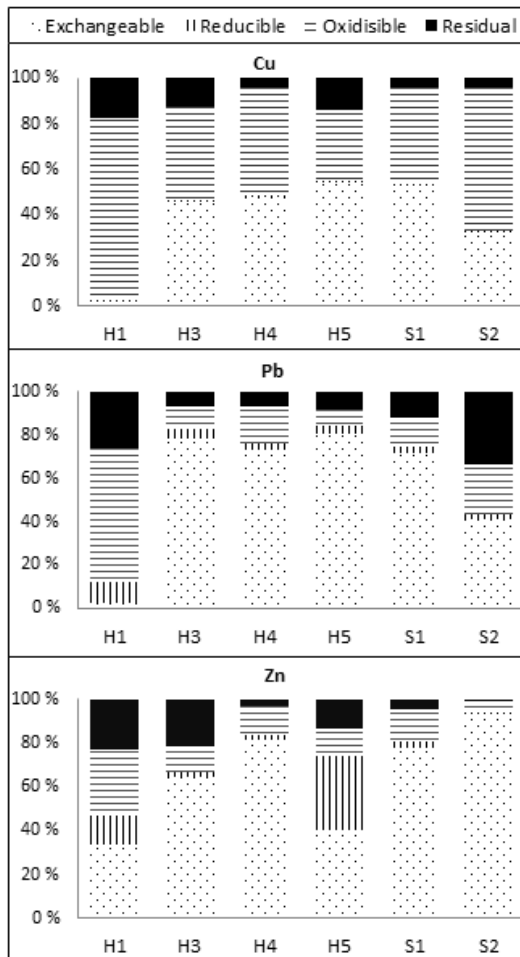


Figure 1: Metal partitioning of Cu, Pb and Zn in the six harbour sediments. Exchangeable – metals mobilised by ion-exchange or by dissolution of carbonates; reducible – metals bound in Fe/Mn oxides, desorbing under anoxic conditions; oxidisable – metals bound in organic matter, desorbing during oxidation of organic matter; residual – remaining metals in the sediment.

Desorption of metals with nitric acid in different concentrations were performed to determine metal desorption as function of time to complement the metal partitioning findings. For Cu and Pb, the desorption as function of pH were similar for the six sediments (figure 2) for pH values above 2. At pH<2, there were some deviations in the desorption, an indication that the sediment properties affected the binding/re-precipitation of desorbed Cu and Pb at acidic conditions. For Zn, it was revealed that there were deviations in desorption patterns for pH<4 suggesting that sediment properties, other than the buffer capacity was affecting the desorption/re-precipitation and binding of Zn in the sediment.

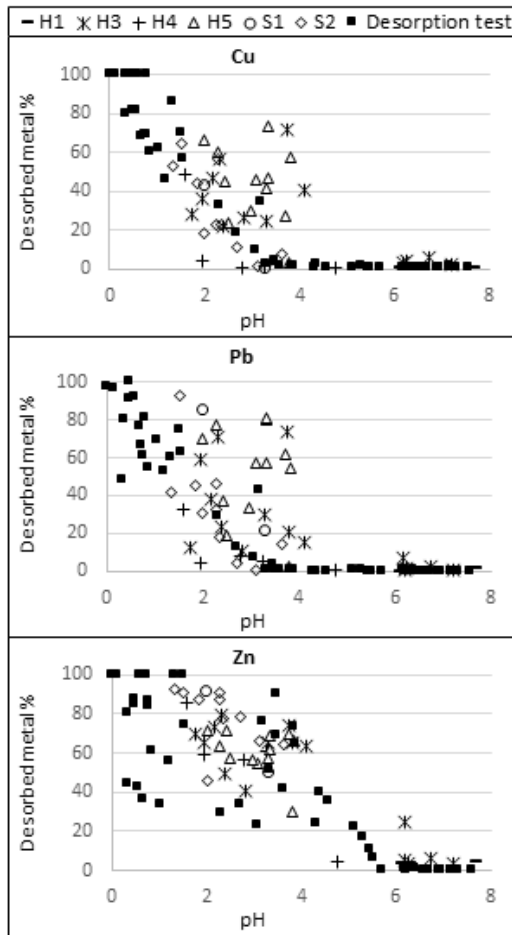


Figure 2: Desorption of Cu, Pb and Zn from the six sediments as function of pH (■), by acid treatment. Desorption of Cu, Pb and Zn at the end of the electrodynamic experiments as function of final pH for the six sediments (H1, H3, H4, H5, S1 and S2).

At the end of the EDR experiments, higher desorption of Cu and Pb were observed at final pH values from 2-4, indicating a higher removal potential than for the nitric acid desorption tests (figure 2). A similar trend is observed for Zn, although not as distinct. Comparison of the desorption tests with the percentage of metal desorbed at the end of the EDR experiments shows that higher desorption of Cu and Pb was observed in the pH range 2-4 indicating a higher removal potential than was expected from the desorption tests. The same trend is observed for Zn although not as distinct. None of the sediments appears to be correlated which indicate that other parameters (e.g. experimental variables) influence the mobilisation during EDR. In contrast to the findings of the nitric acid desorption experiments, it is apparent that higher desorption of metals during EDR was not dependent on continuously acidifying the sediment. By applying optimal experimental settings according to the sediment, it was possible to achieve high desorption of metals in the pH range 2-4.

3.2 Variable importance for the acidification time during EDR

In order to achieve more than 50% desorption of Cu, Pb and Zn it is apparent from figure 2 that final pH should be below 4. With the aim of evaluating the influence of sediment properties and how to optimise the experimental settings for ensuring efficient acidification, a PLS model was calculated. The acidification time of the EDR experiments was computed as a single parameter in the Y-matrix and the model included experiments with final pH around 4 (n=14). The PLS model had a correlation factor,

R²Y of 0.87 and a predictive power Q² of 0.64 indicating a good and stable model. The parameters with highest influence on the model (VIP values > 1) were sediment properties related to buffer capacity and grain size. The negative/positive correlations between variables and acidification time are revealed by coefficient values (figure 3). Sediments with high buffer capacity (high carbonate, pH) prolongs the acidification time. Ca and Mg were found as carbonates in the sediments and this is the main reason for the positive correlation with acidification time. Sediments with higher contents of the fine grained fractions (clay, silt) resulted in longer acidification times and is due to the higher buffer capacity of clay/silt compared to sand [38].

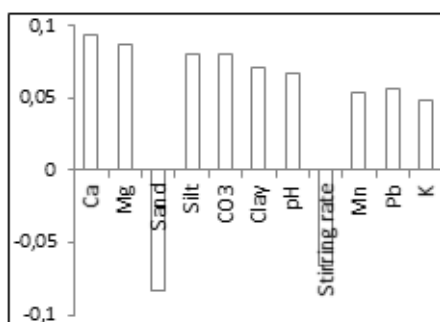


Figure 3: Coefficient plot of the PLS model on acidification time (final pH 4). The plot only shows the coefficients of the most important parameters (VIP values > 1), as determined by the model. Parameters with coefficient values < 1 have opposite correlation with acidification time, while parameters coefficient values > 1 are positively correlated with acidification time.

The only experimental variable with a high influence on the model (VIP value > 1) was stirring rate and the coefficient plot (figure 3) revealed that a high stirring rate decreased the acidification time. By applying a high stirring rate (1300 rpm), the acidification times were in the range 19-163 h, while applying a low stirring rate (<100 rpm), the acidification times were in the range 142-672 h for the studied sediments. This accentuates the importance of achieving a fast, uniform acidification in the sediment suspension, achievable by increasing the stirring rate.

3.3 Variable importance for metal removal during EDR

A PLS model was calculated to evaluate the comparative influence of sediment properties and experimental settings on metal removal during EDR. The model, hereafter referred to as Model 1, was based on the 47 experiments listed in table 2 and included all measured elements as responses (Al, Ca, Fe, K, Mg, Mn, Na, Cr, Cu, Ni, Pb and Zn). The model correlation factor, R²Y, was 0.82 and the predictive power, Q², was 0.74; an indication of a good and stable model.

Table 3: Variable importance in Model 1 (R²Y 0.82; Q² 0.74). Parameters with VIP values > 1 had the highest influence on the model, parameters with VIP values 0.5-1 had mediocre influence on the model and parameters with VIP values < 0.5 had low influence on the model.

VIP value	Experimental variables	Sediment properties	Trace elements	Priority metals
> 1		Grain size S	Al, Ca, Fe, K, Mg, Mn	Cr, Cu, Ni, Pb
0.5-1.0	Time after pH 4 Stirring rate	Carbonate CEC Organic matter TC		

		N		
< 0.5	Total treatment time Current density L/S ratio Suspension liquid Light	P Cl Conductivity	Na	Zn

A summary of the calculated VIP values in the model is given in table 3 and it is apparent that sediment properties were in general more important for EDR efficiency than the experimental settings, in line with previous investigations [10]. The grain size distribution as well as the initial content of metals had the highest influence on the model, indicating that the quantity and composition of elements in the sediment significantly influences EDR. A weight plot of the X (w^*) and Y (c) matrix of the first and second components (figure 4) reveals that the initial concentrations of some elements (Al, Fe, K, Mg, Mn, Cr, Ni) are plotted adjacent to the removal efficiencies of the same elements indicating that a high initial metal concentration results in lower removal.

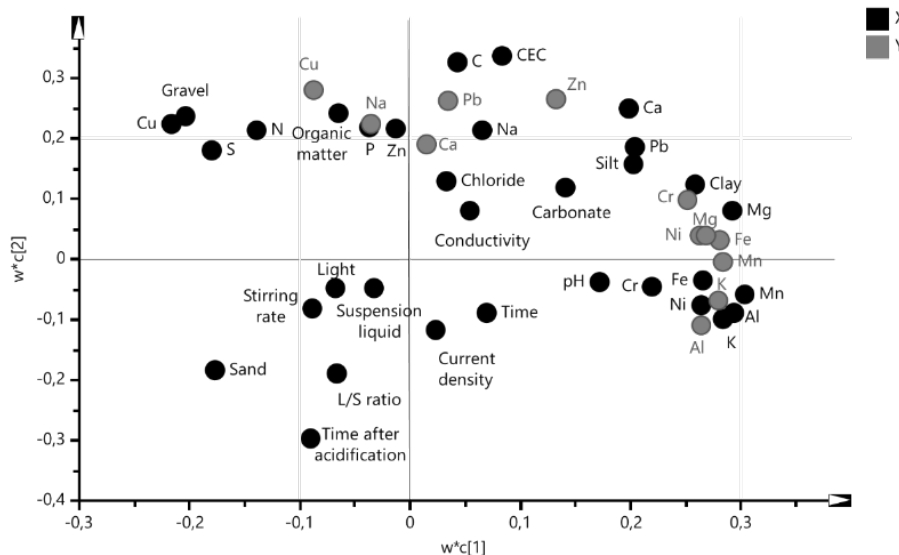


Figure 4: X (w^*) and Y (c) weights for the first and second component. Directly correlated X and Y variables are located adjacent to one another.

Model 1 was used to obtain a good overview of general trends and correlated variables and responses in the metal removal during EDR (figure 4). In order to assess possible differences in trends of the targeted metals, separate models were calculated for Cu, Pb and Zn and included metal partitioning data for the three metals. In addition, a model was calculated for each phase of EDR to evaluate the differences in variable importance during EDR. Based on the EDR desorption trends in figure 2, the limited experimental domains have been selected based on the final pH values:

Model 2a: pH > 4 (experiments that were stopped during the lag phase of Cu, Pb and Zn); n=14

Model 2b: pH 2-4 (experiments that were stopped during the fast removal phase of Cu, Pb and Zn); n=23

Model 2c: pH < 2 (experiments that continued until the slow removal phase; towards/entering the stationary phase); 10 experiments

The model correlation factors and predictive powers for all nine models were found to be good (figure 7) enabling evaluation of variable importance in the different phases of EDR. In general, sediment properties were found to be comparatively more significant than the experimental settings, in line with Model 1 findings. In the following, the variation in trends between the three metals and EDR phases will be assessed in the order *experimental settings*, *sediment properties* and *metal partitioning*.

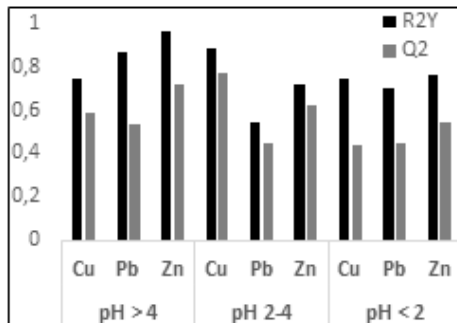


Figure 5: Correlation factors, R²Y and predictive powers, Q² for the models 2a (experiments with final pH>4), 2b (experiments with final pH 2-4) and 2c (experiments with final pH < 2).

3.3.1 Influence of experimental variables

For models 2a-c, the variables suspension liquid and light/no light consistently had VIP values below 0.5 with limited influence on EDR. The total remediation time also had low VIP values in line with a previous study in which it was revealed that better PLS models could be achieved by experimental designs based on time after acidification rather than the total remediation time. The assessment of experimental variables and their influence on the metal removal during EDR is henceforth focused on the remaining experimental variables – time after acidification, current density, L/S ratio and stirring rate. As illustrated in figure 6, similar trends for these variables were observed for Cu, Pb and Zn.

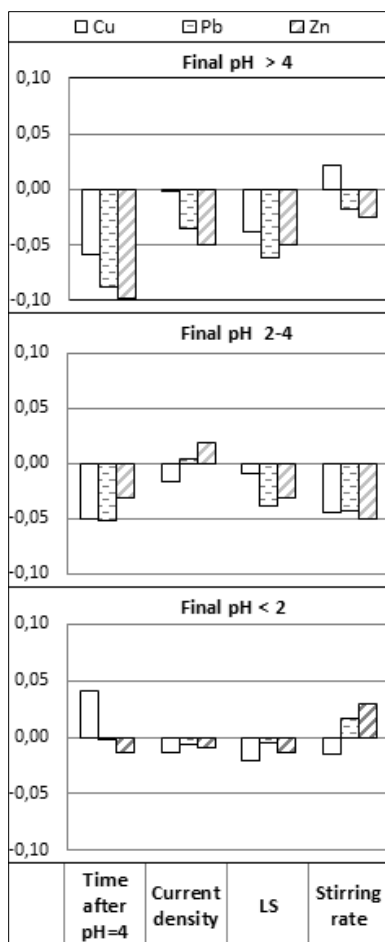


Figure 6: Coefficient plots of experimental variables for the separate PLS models of Cu, Pb and Zn: Model 2a (experiments with final pH > 4), Model 2b (experiments with final pH 2-4) and Model 3b (experiments with final pH < 2).

For the experiments covering most of the initial lag phase of the three targeted metals (model 2a), time after acidification and the L/S ratio were the most influential variables on the final concentrations of Cu, Pb and Zn. The coefficient plot in figure 6 reveals that low settings result in less efficient removal. The importance of the L/S ratio may imply that relatively more removal from the available fractions occurs in this phase of EDR. It is also worth noting that the experimental variables are comparatively less important to the removal of Cu. This may be related to a higher amount of Pb and Zn available for ion-exchange or dissolution in carbonates, in line with the results of the sequential extractions (figure 1).

For the experiments with final pH values 2-4 (Model 2b), the stirring rate is comparatively more important than in the initial stage of EDR, and is similar to the influence of time after acidification. This may be an indication of the oxidation of sediments, in which some of the metals bound to organic matter are released and may also be related to higher stirring rates ensuring better mixing of the sediment suspension. For Pb and Zn the importance of the L/S ratio is equivalent to time after acidification and stirring rate, indicating removal of Pb and Zn from the available fractions of the sediment, as was the case in the lag phase of EDR.

For the experiments with final pH below 2 (Model 2c) the comparative importance of the experimental variables on the removal of Cu, Pb and Zn from the sediment are lower (figure 6). This may be related

to the a lower difference in observed final concentrations of the metals than was the case for experiments with higher final pH and an indication of transition to the slow removal phase, in which removal may be relatively more dependent on sediment properties. This is due to lower availability caused by low concentration and tighter binding to the sediment.

3.3.2 Influence of sediment properties

In models 2a-c, all sediment properties had VIP values above 0.5 and are included in the discussion below. The sediment properties with highest influence on the removal of Cu, Pb and Zn differed in the three phases of EDR (figure 7). High CEC resulted in low removal of Cu, Pb and Zn and the influence of CEC is most distinct in the initial phase of EDR (figure 7). In Model 1 of all studied elements, other metals highly influenced by CEC (figure 4) included Ca, Na and to a lesser degree Mg. CEC had a higher influence on the removal of Na, Ca, Pb and Zn, which have higher relative amounts bound in the exchangeable fractions compared to Cu and Mg. These findings are in line with previous studies in which CEC of soil was shown to affect the efficiency of EKR [39, 40]. *Darmawan and Wada* for instance found that longer time was necessary to remove metals from soils with high CEC [21].

The influence of conductivity is limited in the initial phases of EDR and in the slow removal phase affects the metals differently. In this phase, it is limited for the removal of Cu, while it is significant for Pb and Zn (figure 7). Since an initial high conductivity in the sediment results in less removal of Pb and Zn in the later stage of EDR, this may imply that Pb and Zn are in the slow removal phase of EDR. This is further supported by amounts equivalent to exchangeable fractions being removed at this stage.

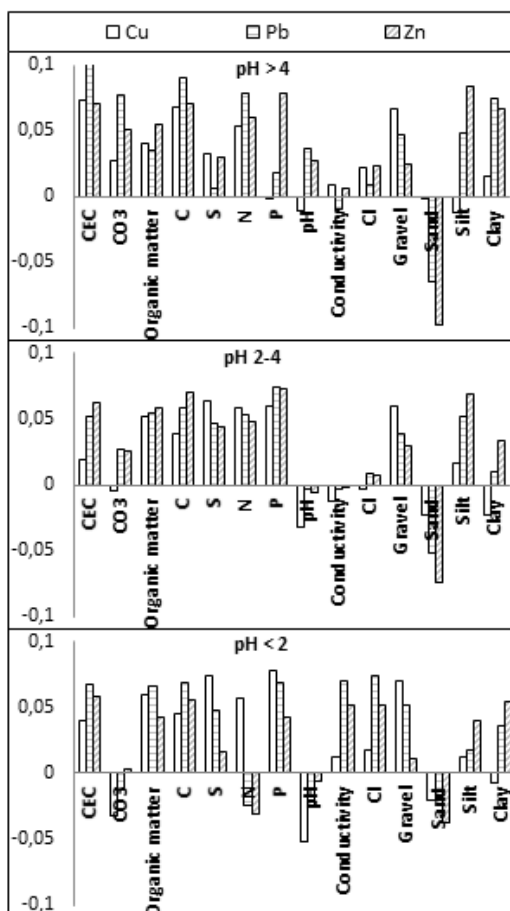


Figure 7: Coefficient plots of sediment properties for the separate PLS models of Cu, Pb and Zn: Model 2a (experiments with final pH > 4), Model 2b (experiments with final pH 2-4) and Model 3b (experiments with final pH < 2).

The influence of the initial pH of the sediments is generally low, but is however relatively higher for the experiments with a final pH below 2, especially for Cu. A low initial pH results in lower removal of Cu which is not necessarily related to the carbonaceous properties of the soil but to the release of Cu from the organic fraction (a low pH does not necessarily increase the release of Cu from the oxidisable fraction).

An initial high carbonate content results in low removal of Cu, Pb and Zn in the initial phase of EDR confirming the influence of buffer capacity as reported in literature [41, 42]. Carbonate appears to have the opposite influence in the slow removal phase of Cu and Pb (figure 7) which could be related to the low difference in final concentration range, so further removal of any residual carbonate would result in relatively higher removal. This would also indicate that Cu and Pb to a higher degree are bound to carbonates in the sediment (initially or via co-precipitation) than Zn.

Organic matter and components related to the organic matter; TC, S, N and P all highly influence the removal of Cu, Pb and Zn in all phases of EDR, in line with findings of organic matter influencing electrokinetic remediation of marine sediments [43]. In this study, some differences in influence depending on the given heavy metal and the EDR phase were observed. Oxidation of the sediment, e.g. caused by stirring, is expected to release some of the metals bound in the oxidisable fraction, high content of the organic matter however still result in a low electro-dialytic removal.

The initial content of chloride generally has a low influence on the removal of metals from the sediment. It is however noted that a high content of chloride appears to inhibit the removal of Pb and Zn in the experiments of final pH < 2. This may indicate complexation and co-precipitation with Cl; this trend has however not been found in previous studies and further investigations of the specific influence of Cl on the EDR phases are necessary to confirm these observations.

Grain size distribution highly influences the EDR of Cu, Pb and Zn. A high content of gravel, silt and clay generally results in lower removal in all phases of EDR. This may not necessarily be contradictory to previous findings of higher removal efficiencies in soil fines than for the original soil [26] and may be due to more metals bound in the silt and clay fractions of the sediment. It could also be related to faster acidification of sediments with higher sand fractions (figure 3).

Of the 12 elements included in the X matrix of models 2a-2c, VIP plots revealed that Al, K, Mn, Cu and Zn had the highest influence on the removal of Cu, while initial concentrations of Ca, Pb and Zn were most influential for the removal of Pb and Zn (table 4). Coefficient plots showed differences in correlations between the initial content of elements and final concentrations of the three targeted metals (not shown). For Cu, high concentrations of Al, K and Mn resulted in lower final concentrations of Cu, while high concentrations of Cu and Zn resulted in lower removal of Cu. For Pb and Zn, high initial concentrations of each element consistently resulted in relatively less removal. The high VIP values strongly indicate that the removal of Cu, Pb and Zn depends on the initial element concentrations and may be inhibited high levels of certain elements, different from metal to metal. In the studied experimental space, elements mainly bound in the exchangeable fractions (Ca, Pb, Zn and to a lesser degree Mg and Na) for instance had an inhibitory effect on the removal of Pb and Zn. These

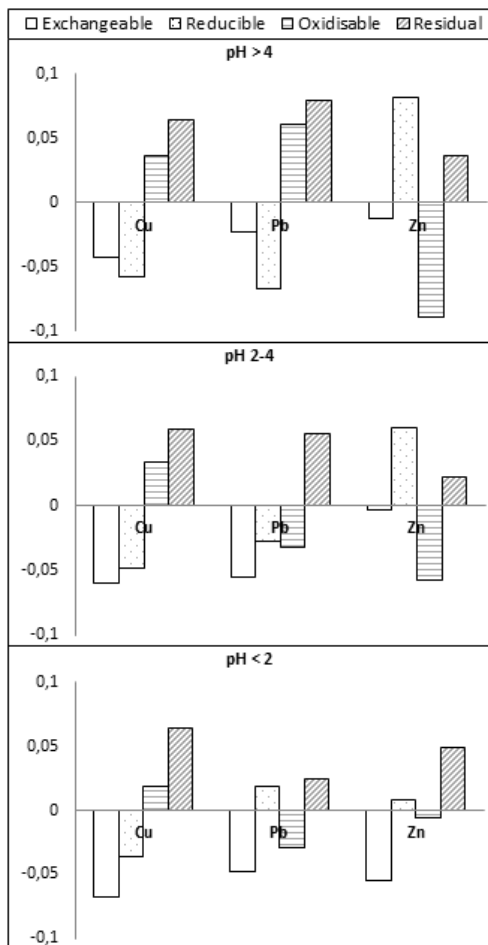
findings are in line with numerous reported studies on the inhibitory effect of elements and multiple metal contaminations on EDR/EKR efficiency summarised in [27].

Table 4: Summary of VIP values for elements (initial concentrations) in models 2a-c for the removal of Cu, Pb and Zn. Parameters with values > 1 had the highest influence on the model, parameters with VIP values 0.5-1 had mediocre influence on the model and parameters with VIP values < 0.5 had low influence on the model.

VIP value	Cu	Pb	Zn
> 1	Al, K, Mn Cu, Zn	Ca Cu, Pb, Zn	Ca Pb, Zn
0.5-1.0	Ca, Fe, Mg, Na Cr, Ni	Mg, Na	Fe, K, Mg, Na Cr, Cu, Ni
< 0.5	Pb	Al, Fe, K, Mn Cr, Ni	Al, Mn

3.3.3 Influence of metal partitioning

Metal partitioning of the targeted heavy metal in the individual models 2a-2c yield VIP values in the range 0.61-1.33, indicating that how the metals are chemically bound in the sediment highly influences the efficiency of EDR, building on previous findings of metal partitioning influencing the mobilisation of metals during electrokinetic remediation [44, 45]. Coefficient plots of Cu removal (figure 8) reveals similar correlations in metal partitioning during all phases of EDR. The influence of metal partitioning on the removal of Pb and Zn differs in the three phases of EDR (figure 8). Higher relative amounts of Pb bound in the exchangeable and reducible fractions in general increase the removal efficiencies of Pb with variations in importance between the three EDR phases. In the initial phases of EDR, the removal of Zn does not improve significantly with higher amounts bound in the available fractions. Increasing removal efficiencies appear to depend on differences in binding to the reducible and oxidisable fractions, suggesting that Zn bound in the oxidisable fraction is released at this stage.



Figure

8: Coefficient plots of sediment properties for the separate PLS models of Cu, Pb and Zn: Model 2a (experiments with final pH > 4), Model 2b (experiments with final pH 2-4) and Model 3b (experiments with final pH < 2).

The difference in trends of metal partitioning influence of Pb and Zn may indicate that removal occurs from all fractions of the sediment during EDR, as observed in previous studies [37, 46]. For Cu the influence of metal partitioning clearly indicates that removal is easier from the exchangeable and reducible fractions and may be removed from the exchangeable, reducible, oxidisable and residual fractions in that order to a higher degree than is the case for Pb and Zn.

4 Conclusion

Sediment properties were found important for deciding experimental settings for optimal removal of metals during EDR, i.e. removal of >75% Cu, >90% Pb and >90% Zn. Variable importance differed in the different EDR phase for the targeted metals, Cu, Pb and Zn. In all phases of EDR important parameters, with VIP values > 1, for the removal of Cu, Pb and Zn included initial element concentration, grain size distribution and metal partitioning. The influence of elements depended on the targeted heavy metal, e.g. high concentrations of Al (8,000-8,650 mg/kg) was found to increase Cu removal, while high concentrations of Ca (1400 g/kg) were found to inhibit the removal of Pb and Zn.

In addition to the aforementioned parameters, other important sediment properties, with VIP values >1, in the lag phase of EDR (final pH>4) included CEC and carbonate content, both related to the buffer capacity of the sediments with high contents inhibiting removal of metals. In the fast removal phase

of EDR (final pH 2-4), organic matter was important along with stirring rate reflecting that oxidation of the sediment was important in order to mobilise metals bound in organic matter. In the slow removal phase of EDR, important sediment properties included organic matter (contents higher than 10% inhibiting the removal) and conductivity. High contents of chloride (>9000 mg/kg) appears to have significant inhibiting effect on the removal of Pb and Zn suggesting that complexation occurs. The experimental variables had VIP values less than 1, much lower than the important sediment properties, indicating that EDR had entered in the slow removal phase in which chemical/physical properties are significantly more important for further removal of heavy metals from the sediment.

Variables related to the buffer capacity of the sediments and grain size distributions were found to highly influence the time for the sediments to reach pH 4. High contents of sand (70%) and low content of carbonate (<2%) reduced the acidification time. Stirring rate also had a significant influence on the acidification time stressing the importance of thorough mixing (>700 rpm) of the sediment suspension to achieve a fast and uniform acidification.

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