Migration of ions and organic matter during electro-dewatering of anaerobic sludge

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ABSTRACT

This paper reports the migration of ions and organic matter, initially present in anaerobically digested sludge taken from the effluent of an anaerobic digestion unit in Mikkeli Wastewater Treatment Plant (SE Finland) during electro-dewatering process, employing various experimental strategies such as freeze/thaw and polyelectrolyte conditioning and various sludge loading rates. It was found that a decrease in sludge loading rate (from 20 to $5\,kg\,DS\,m^{-2}$) resulted in an increase in the maximum current density (145–$467\,A\,m^{-2}$). The principle component analysis (PCA) showed a significant correlation between the dry solid (DS) content in the final sludge cake, sludge loading rate, freezing conditions, energy consumption and maximum current density during electro-dewatering process. The decrease in sludge loading rate resulted in the reduced time to achieve the highest concentrations of Na^+ and K^+ in the removed water at the cathode. Moreover, concentration of Na^+ and K^+ was reduced by 51 and 78% in the sludge cake, respectively, in comparison to blank experiments. Fe ions, Ca^{2+} and Mg^{2+} concentrations were found lower in the sludge cake at the anode and higher at the cathode. According to the statistical analysis, Fe and Ca ion concentrations at the anode and sludge loading rate had a negative correlation with the volatile solids/dry solids (VS/DS) ratio in sludge at the anode. High P concentration at the anode was only observed in experiments using freeze/thaw conditioned sludge samples and highly depended on the initial sludge freezing temperatures. Furthermore, at the end of experiments, concentration of problematic elements in the sludge cake such as Cr^{6+}, Zn^{2+} and Mn ions increased from 63 to 100% and decreased from 23 to 70% at the anode, respectively, in comparison to the blank experiment.

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1. Introduction

Generally, the increase in municipal and industrial wastewater purification activities, relates to the production of large amounts of waste sludge that must be dewatered as well as toxic contaminants must be removed prior waste sludge reuse as fertilizer, for composting or incineration and/or disposal to landfill. It is well documented that sludge dewatering is one of the most challenging technical tasks in the field of wastewater engineering [1,2]. Currently, conventional sludge dewatering methods are based on mechanical processes (centrifuge, diaphragm filter press, vacuum filter) combined with flocculation. However, mechanical methods cannot reach a sufficiently high potential to drive the interstitial water along with contaminants through the very narrow pore spaces, therefore dewatering using mechanical means is extremely limited and requires substantial further treatment [2].

The application of a low-level electric field onto the sludge segment results in electro-osmotic and electro-migration flow, which are able to induce the migration of ions, reduce the interstitial and some of the vicinal water, causing a dryer sludge cake [2–5]. Moreover, it has also been determined that electro-dewatering process may be a cost-effective method in comparison to other more conventional sludge treatment methods [6,7].

Therefore, over the last decade, there has been an increased interest in applying electricity that facilitates the removal of water along with charged and un-charged species from various matrices [8–10]. There have been numerous successful attempts for electrical treatment in contaminated soils [8,9,11–17], sludge [18–21], process waters [22–24] and fly ash [25,26]. However, there are still some limitations that impair the remediation process such as the solubility and desorption of heavy metals from matrices, low target ion and high non-target ion concentrations and the requirement of a conducting pore fluid to mobilize the contaminants [10].

In this study, a laboratory scale pressure-driven electro-dewatering experiments were set up to investigate the effect of various sludge loading rates, conditioning with different polyelectrolyte doses and freezing temperatures on the alteration of sludge

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Table 1
Main characteristics of sludge obtained from Mikkeli Wastewater Treatment Plant (South East Finland).

Parameters	Sludge after anaerobic digestion
Temperature (°C)	33.4–34.0
Electric conductivity – EC (μs cm^{-1})	7160–7500
pH	7.16–7.38
Alkalinity (mg kg^{-1} CaCO$_3$)	6862–10487
Total solid – TS (%)	3.17–2.87
Volatile solid – VS (%)	1.53–1.70
VS/DS (%)	55.1–53.4
Zeta potential (mV)	−15.9 to −14.0
Capillary suction time – CST (s)	307.7–345.8
Fe (g kg^{-1} DS)	165–170
Ca (g kg^{-1} DS)	18.2–20.3
Mg (g kg DS^{-1})	2.58–3.32
P (g kg^{-1} DS)	43.6–46.4
Cr (mg kg^{-1} DS)	62.3–74.6
Zn (mg kg^{-1} DS)	595–615
Mn (mg kg^{-1} DS)	273–294

properties that affect the migration of organic matter, macro and some trace elements from the sludge matrix.

2. Materials and methods

2.1. Sludge samples

Laboratory scale experiments were conducted with anaerobically digested sludge taken from the effluent of an anaerobic digestion unit in Mikkeli Wastewater Treatment Plant (SE Finland). The continuous anaerobic digester was used for primary and secondary sludge treatment with 17–20 days retention time at 35–38 °C. The main characteristics of sludge are shown in Table 1. The samples were pre-treated by settling to increase the sludge dry solid (DS) content from 3 to 5% and then stored in cold room (4 °C) prior experiments. Before the experiments, sludge was kept out of the cold room to reach the room temperature.

2.2. Sludge conditioning

A deep freezing room with a digital controller was used to freeze the sludge samples at −5, −10, −15, −20, and −25 (±1) °C. The preliminary experiments (at −5 °C) showed that sludge was completely frozen within 36 h, therefore the freezing time of 36 h was adopted throughout experiments. According to Ormeci and Vesilind [27], long term thawing results in altered sludge characteristics due to the activation of anaerobic micro-organisms present in sludge. Thus, after freezing, the sludge samples were thawed at a room temperature for 10 h.

Granular polyelectrolyte Praestol 855BS (Praestol, Ashland Water, Germany) was used for sludge conditioning. This granular polymer had a medium cationic charge, effective at the pH range from 1 to 10. Polymer solutions of 4 g l^{-1} (0.4%) were prepared at least 24 h before the use [28]. A conventional Jar Test was used to mix appropriate amount of sludge and the polymer solution. Sludge samples (500 ml) were placed in 1000 ml beakers, and then various polymer solutions equivalent to 5, 10, 15, 20 kg ton^{-1} of DS (kg polymer per ton of DS) were added. Sludge and polymer mixture was then intensively mixed at 300 rpm for 1 min, followed by 10 min of slow mixing at 50 rpm. After that sludge samples were fed into the reactors for the consequent dewatering tests.

2.3. Electro-dewatering tests

Laboratory scale electro-dewatering experiments were conducted in a pressure-driven reactor as described by Tuan et al. [29] (Fig. 1). The reactor made of polyvinyl chloride (9.8 cm in diameter and 30 cm in length) and operated at a room temperature (22 ± 1 °C). The stainless steel mesh (0.5 mm) and titanium plate electrode (2 mm) were used as the cathode and the anode, respectively [29]. The electrodes were connected to the direct current (DC) power supply (GW Instek, Taiwan) to provide a constant voltage (20 V). Multimeter (Fluke 110, The Netherlands) was used to monitor current fluctuations. The cloth filter (Z104256 PP, Sigma–Aldrich), with permeability factor of 7.62 (m^3 m^{-2} min^{-1}) was placed by the electrodes. To ensure the reliability of data, old pieces of the cloth filter were replaced by the new ones for every electro-dewatering experiments.

After the sludge sample was introduced into the reactor, it was subjected to the constant pressure (5.0 bars) and voltage (20 V). The ions and organic matter were collected from both, the anode and the cathode throughout the experiments. It was assumed that the electro-dewatering process was finished, when the water removal rate at the cathode decreased below 2 l m^{-2} h^{-1} (liters of removed water per square meter of filter per hour). Then, sludge was removed from the reactor and sampled at the anode, the cathode and the sludge cake for quantitative analysis.

2.4. Experimental design

The series of experiments are shown in Table 2. The sludge loading rate was 15 kg DS m^{-2} (kilogram DS per square meter of filter) for the experiments using sludge samples conditioned with various polyelectrolyte doses and freezing temperatures. To investigate the effect of sludge loading rate on the final sludge cake, experiments were conducted employing 5, 10, 15, and 20 kg DS m^{-2} sludge loading rates with sludge samples frozen at −20 °C and 15 kg ton^{-1} DS of added polymer. To assess the effect of electrical treatment, the blank experiments were performed without the applied electricity. Moreover, to avoid discrepancies and ensure the reliability of data, all the experiments were performed in duplicates.

2.5. Analyses

The amount of the removed water was measured by electrical balances. Temperature of sludge was measured by electronic thermometer (Fluke 53 II, USA). Characteristics of sludge, such as pH,
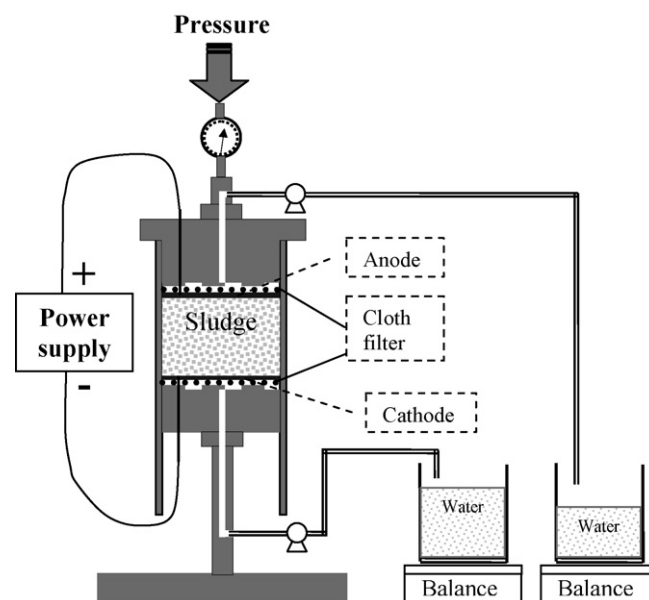

Fig. 1. Schematic representation of the laboratory scale pressure-driven electro-dewatering reactor.

Table 2
Series of experiments and experimental conditions.

Exp. number	Conditioning		
	Polymer dose (kg ton^{-1} DS)	Freeze/thaw temperature (°C)	Sludge loading (kg DS m^{-2})
Exp. 1	None	None	15.5
Exp. 2	5.3	None	15.9
Exp. 3	10.8	None	15.0
Exp. 4	15.9	None	15.6
Exp. 5	20.2	None	15.1
Exp. 6	14.7	None	5.3
Exp. 7	14.7	None	10.8
Exp. 8	15.7	None	15.9
Exp. 9	14.7	None	20.2
Exp. 10	None	−5.3	15.6
Exp. 11	None	−9.9	15.8
Exp. 12	None	−14.9	15.9
Exp. 13	None	−20.3	15.7
Exp. 14	None	−26.2	15.8
Exp. 15	None	−20.1	5.8
Exp. 16	None	−20.3	11.4
Exp. 17	None	−20.1	15.7
Exp. 18	None	−20.2	20.9

alkalinity, dry solids (DS), volatile solids (VS) and capillary suction time (CST) were determined using Standard Methods [30].

To determine the total amount of macro and some trace elements in anaerobically digested sludge, samples were subjected to aqua regia treatment and digested using a microwave digester (PerkinElmer, Anton Paar GmH, Austria) [31]. About 0.3 g total suspended solid (TSS) of sludge samples were treated with 5 ml aqua regia (HCl/HNO$_3$, 1:3) in closed pressurized-vessels. The digestion procedure was programmed in three steps (6 min increase in temperature to 200 °C, 30 min treatment at 200 °C and 30 min cooling down to a room temperature). ICP spectrometer (ICAP-6000, Thermo, England) was used to measure Na, K, Fe, Ca, Mg, P, Cr, Zn, and Mn concentrations in sludge and removed water applying following wavelengths of 588.995, 766.490, 259.940, 422.673, 285.213, 177.495, 267.716, 213.856, and 257.610 nm, respectively. Total organic carbon (TOC) and inorganic carbon (IC) were deter-

mined by TOC analyzer (TOC-VCPH, Shimadzu, Japan). Chloride (Cl$^-$) was measured by capillary electrophoresis system (Beckman Coulter, USA) and nitrogen ammonium (NH$_4^+$) was measured by Dr. Lange test kits (LCK 302, Germany).

2.6. Statistics

Principal component analysis (PCA) was used to correlate different parameters from all experiments and to get an overview of the total data set using the statistic software program (Unscrambler 9.8, CAMO AS Trondheim, Norway). Prior to PCA, all data were normalized and scaled to equal unit variance (mean value 0 and standard deviation 1). The components of the PCA were rotated by the Varimax rotation.

3. Results and discussion

3.1. Current density fluctuation during the electro-dewatering process

Fig. 2a and b show the current density fluctuation during the electro-dewatering process of polyelectrolyte and freeze/thaw conditioned anaerobic sludge. Current density did not change significantly throughout Exps. 1 and 2 when no freeze/thaw conditioning and no or polymer dosage of 5.3 kg ton^{-1} DS were used, respectively. However, experimental data from other experiments showed that during initial stages of the electro-dewatering tests, current density sharply increased to the highest value and then kept declining until the end of experiments. The highest current density was observed with the lowest sludge loading rates (Fig. 2c and d). Thus, the Ohm's law may be used to describe the process:

$$J = \sigma E \tag{1}$$

where J is the current density (A m^{-2}), E is the applied electrical field (V m^{-1}) and σ is conductivity (S m^{-1}).

Let us assume that during initial stages, the migration of ions and the amount of water in sludge did not have any effect on the conductivity. The polyelectrolyte and freeze/thaw conditioning
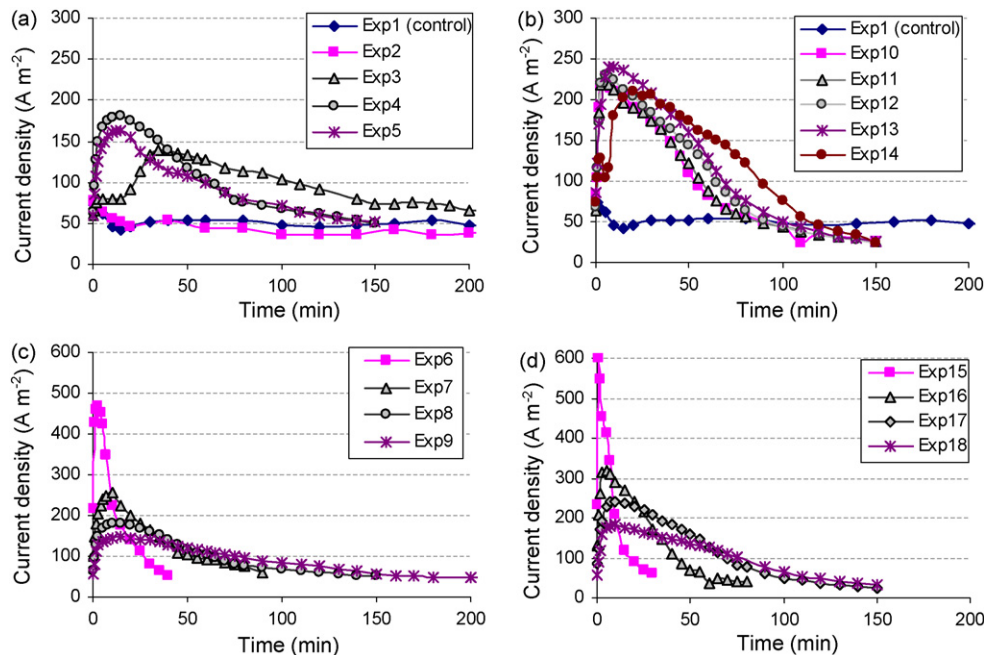

Fig. 2. Current density fluctuation during electro-dewatering process using sludge conditioned at (a) different polymer dosage, (b) freezing temperatures and (c) and (d) electro-dewatering with different sludge loading rates.

of sludge samples resulted in the increased dewatering at the beginning of the experiments, which simultaneously reduced the distance between the anode and the cathode from 30 to 12 cm after the initial 3 min of the Exp. 10. The decrease in distance may be associated with an increase in the electric field (E), which cause a significant growth in the current density (Eq. (1)).

A decrease in sludge freezing temperature resulted in the 15 min delay to achieve the highest current density in Exp. 14 (Fig. 2b). The same delay was also observed during Exp. 3 using 10.8 kg ton^{-1} DS polymer conditioning sludge samples. Furthermore, the drop in the current density (Fig. 2) may be associated with the decreased electrical resistance of sludge towards the end of the electro-dewatering process [32] and the loss of contact between the anode and dry sludge [33]. However, high filter sludge cake resistance occurred during Exp. 1 (control), limiting the amount of removed water from sludge. The electrical field remained unchanged and, thus, the increase in the current density was not well pronounced as in the other experiments. Moreover, higher sludge loading rates resulted in larger distances between the anode and the cathode, causing lower current density during electro-dewatering process with different sludge loading rates (Fig. 2c and d).

3.2. Multivariate analysis of data

Principal component analysis (PCA) was applied to the sludge samples to obtain an overview of the similarities and differences as well as variation patterns among the various experimental strategies and to investigate the relationships between the sludge dewaterability/migration of ions and sludge loading rates as well as polyelectrolyte and freeze/thaw conditioning of the sludge samples. According to Dytham [34], the variables in the first principal component (PC1) would explain the most variation, and their weightings help identify what contribute most to the differences between the individual cases [34]. The first two principal components (PC1 and PC2) accounted for more than 90% of the total variation in the dataset (PCA output matrix not shown). Statistical analysis of data based on PCA is presented in Fig. 3a and b. The scores plot for Group 1 from left to right corresponded to an increase in polymer dosage whereas in Groups 2 and 3 it corresponded to a decrease in the sludge loading rates (Fig. 3a).

Freeze/thaw conditioning of sludge showed a positive correlation with the DS in the final sludge cake, which was further demonstrated by Pearson's correlation ($r^2 = 0.98$, $p < 0.05$) analysis (Fig. 3b). Water was easier removed from sludge resulting in the high DS content in the final sludge cake, when freeze/thaw conditioning was applied. Indeed, it is well documented that the freeze/thaw conditioning increases sludge dewaterability, whereas a significant decrease in freezing temperature without the subsequent thawing, drastically reduces sludge dewaterability [35,36]. The decrease in freezing temperature did not show any response and did not correlate with any of the parameters (r^2 ranging from 0.12 to 0.25). This might be due to that sludge electro-dewatering process is not sensitive to sludge characteristic as discussed by Yoshida [37].

PC1 highly correlated with the highest current density, dry solid content in sludge, and negatively with the dry solid content at the anode and the cathode. PC2 was mainly determined by the energy input, freeze/thaw conditioning and polyelectrolyte doses. Also, it negatively correlated with the sludge loading rates (Fig. 3b). Therefore, a decrease in sludge loading rates reduced the distance between the anode and the cathode. Because of the same voltage application, the electrical field led to the higher DS content in the final sludge cake [3,6,38]. Furthermore, the decrease in the sludge loading rates (5.3, 10.8, 15.9, and 20.2 kg DS m^{-2}) significantly increased energy expenditure (0.60, 0.49, 0.33, and 0.30 kW h kg^{-1} DS), respectively, in Exps. 6, 7, 8, and 9 (Fig. 3b).
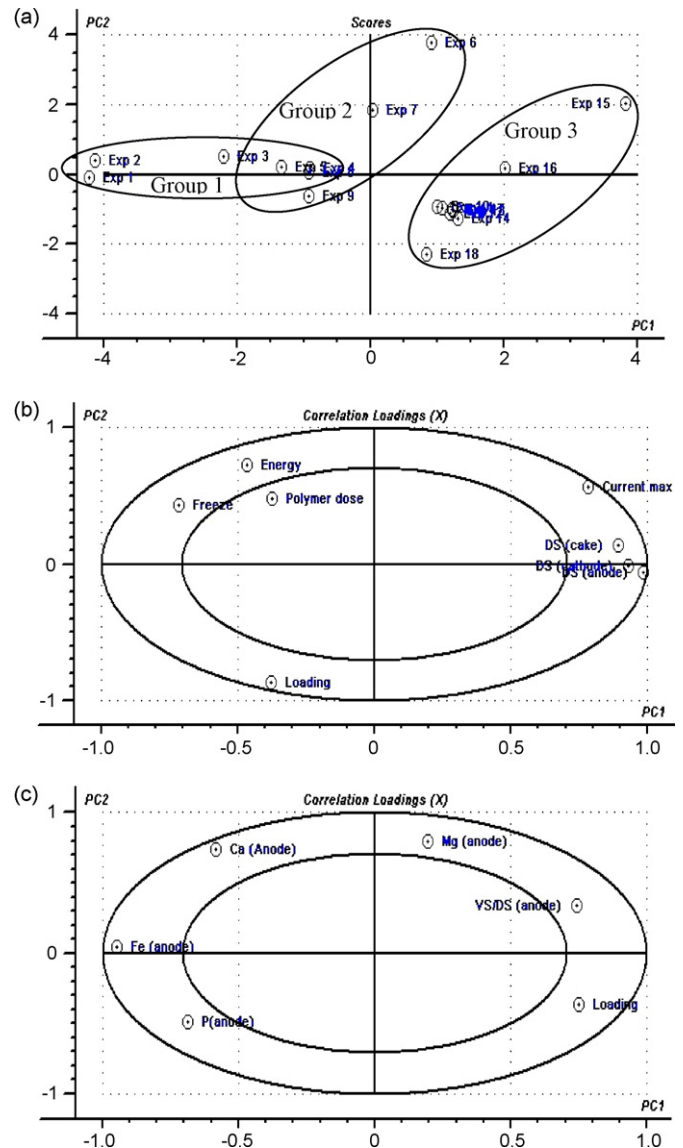

Fig. 3. Principal components analysis within various parameters (a) scores (b) loadings and (c) correlation (loading) of the VS/DS ratio, sludge loading rates and concentrations of macro-elements in sludge at the anode.

The decrease in sludge loading rates not only reduced the amount of the sludge feed but also increased the current density during the electro-dewatering process (Fig. 2c). Thus, the lower sludge loading rates resulted in higher energy expenditures.

3.3. Migration of organic matter during the electro-dewatering process

Hong et al. [39] reported that both, the COD and BOD values in water removed from sludge increased significantly after the freeze/thaw conditioning. This may be due to that freeze/thaw treatment caused cells disruption and released intra-cellular material to the sludge solution [27]. Therefore, concentration of TOC in water removed from sludge was lower in polymer conditioned sludge samples than in the freeze/thaw conditioned sludge (Fig. 4). After 5 h of the electro-dewatering process, TOC concentration increased in the removed water at the anode and decreased at the cathode in comparison to the blank experiment (Fig. 4). This indicates electro-migration of negatively charged organic matter from the cathode to the anode during the electro-dewatering pro-
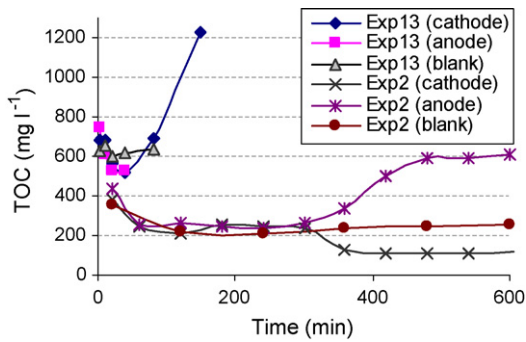
Fig. 4. TOC concentration in the removed water during electro-dewatering process (Exps. 2 and 13).

cess [29]. However, at the end of the dewatering experiment using freeze/thaw conditioned sludge (Exp. 13), TOC content significantly increased in the removed water at the cathode. It suggested the disruption of cells and release of un-charged intra-cellular materials that migrated towards the cathode under the applied electric current along with the electro-osmotic flow.

3.4. Migration of soluble ions during the electro-dewatering process

Figs. 5 and 6 present Na^+, K^+, Cl^-, NH_4^+ and IC distribution in the removed water at the anode and the cathode during electro-dewatering process. Na^+ concentration decreased at the anode in comparison to the blank experiments, however it fluctuated throughout the experiment at the cathode with a significant increase at the beginning and decrease at the end of the treatment (Fig. 5a). Similar fluctuation of Na^+ was also observed by Fernandez et al. [40] who investigated electrokinetic transport of Na^+ in kaolin. Moreover, a decrease in the sludge loading rate resulted in the shorter time to achieve the highest concentrations of Na^+ in the removed water at the cathode.

According to Acar and Alshawabkeh [9] and Fernandez et al. [40], the relation between electro-migration of ions and the electrical potential gradient can be explained by Eq. (2). Thus, the decrease in the sludge loading rates (from 20 to $5 \, kg \, DS \, m^{-2}$) increased the electrical potential gradient from 1.5 to $5.3 \, V \, cm^{-1}$. Moreover, it was assumed that an increase in electrical potential gradient also resulted in much faster electro-migration rates (Eq. (2)) and thus shorter time to reach the elevated concentration of ions at the cathode (Fig. 5a). The electro-migration of K^+ and NH_4^+ ions showed the
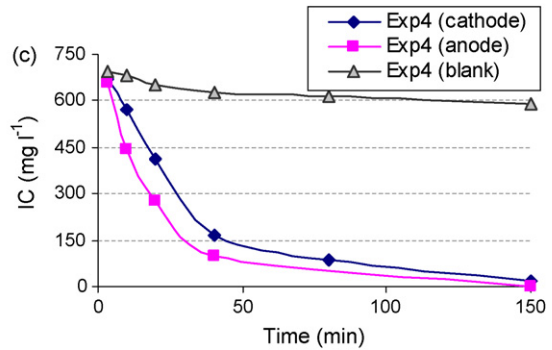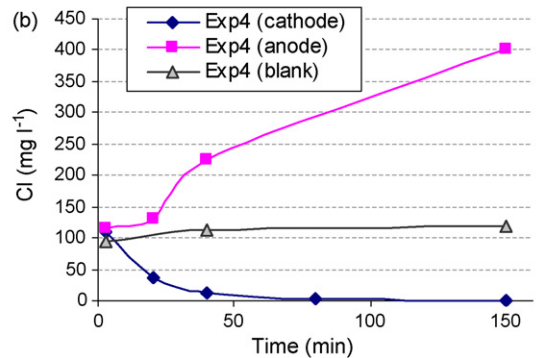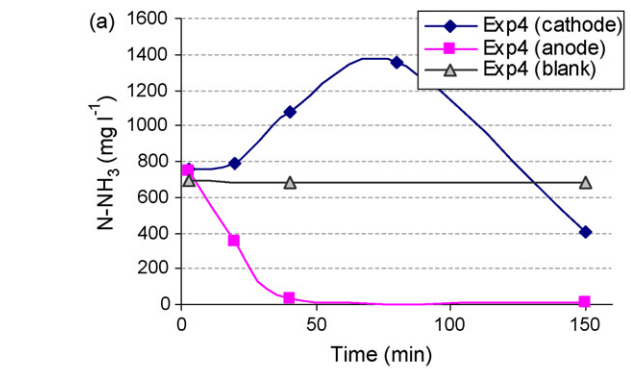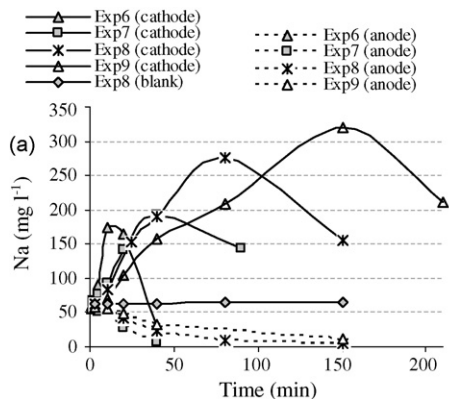

Fig. 6. Concentrations of N–NH3 (a), Cl (b), and IC (c) in the removed water at the anode and the cathode during electro-dewatering process.
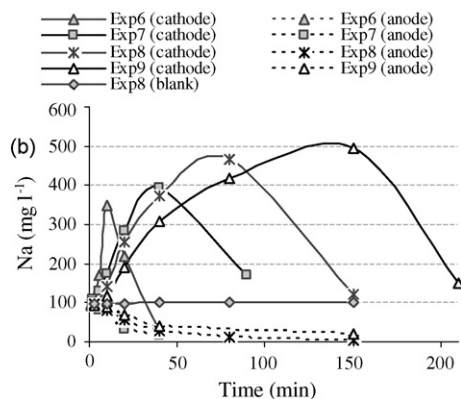

Fig. 5. Concentrations of Na (a) and K (b) in the removed water at the anode and the cathode during electro-dewatering process with different sludge loading rates (Exps. 6–9).
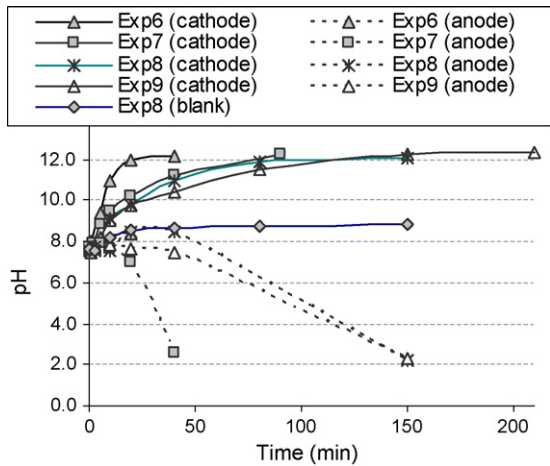
Fig. 7. pH of the removed water at the anode and the cathode during electro-dewatering process with different sludge loading rates (Exps. 6–9).

same trend as Na^+ (Figs. 5b and 6a).

$$J_j = u_j^* c_j \nabla(-E) \tag{2}$$
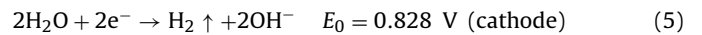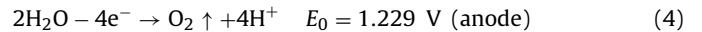
$$u_j^* = \frac{D_j z_j F}{RT} \tau n \tag{3}$$

where J_j is electro-migration flux of the species j (mol m^{-2} s^{-1}), u_j^* is an effective ionic mobility, c_j is molar concentration of the species j (M), E is electrical potential gradient (V m^{-1}), D_j is the diffusion coefficient of species j in the dilute solution (m^2 s^{-1}), z_j is charge of chemical species (dimensionless), F is Faraday's constant (96,487 C mol^{-1}), R is universal gas constant (8.314 J mol^{-1} K^{-1}), T is an absolute temperature (K), τ is the porosity of medium and n is the tortuous factor.

Under the applied electric field, anions usually move from the negatively charged cathode to the positively charged anode [9]. Thus, Cl^- concentration in the removed water increased at the anode and decreased at the cathode in comparison to the blank experiment (Fig. 6b). However, the decrease in IC concentration was observed in the removed water at both, the anode and the cathode (Fig. 6c). This may be explained that during the electro-dewatering process, pH significantly decreased at the anode due to electrolysis of water and H^+ production (Fig. 7). Electro-migration transported carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions from the cathode to the anode, which resulted in the reduction of IC concentration in the removed water at the cathode. Because of the acidic pH, carbonate and bicarbonate ions were demineralized to carbon dioxide (CO_2) at the anode. Thus, the IC concentration in the removed water at the anode subsequently decreased. The effect of mineralization was twofold; it stabilized pH in sludge [8] and also had a positive effect on the DS content in the final sludge cake [29]. Moreover, electro-migration of dissolved ions helped to reduce the concentration of Na^+ and K^+ in the sludge cake by 51 and 78% in comparison to the blank experiments.

3.5. Migration of Fe, Ca, Mg and P during the electro-dewatering process

The migration of Fe ions during electrokinetic soil and sludge remediation is widely discussed [11,41,42]. Low pH at the anode (Eq. (4)) facilitated the dissolution of Fe from the sludge particles into the solution [18]. Under the applied electrical gradient, Fe ions moved towards the cathode where they precipitated as hydroxides and oxy-hydroxides in the high pH environment (Eq. (5)). The increase in the sludge loading rates resulted in the significant reduction of Fe concentration in sludge at the anode (Fig. 8a). When the electric current was applied, a Fe-rich barrier comprised of FeOOH, Fe_2O_3 and Fe_3O_4 was formed between the electrodes at the boundary between the acid and alkaline fronts [43]. According to Cundy and Hopkinson [44], longer experimental time may cause a movement of the Fe barrier towards the cathode, thus, lower Fe concentration in sludge at the anode can be observed.

$$2H_2O - 4e^- \rightarrow O_2 \uparrow + 4H^+ \quad E_0 = 1.229 \text{ V (anode)} \tag{4}$$

$$2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^- \quad E_0 = 0.828 \text{ V (cathode)} \tag{5}$$

The dissolution and the subsequent migration of Ca^{2+} and Mg^{2+} ions resulted in their lower concentrations at the anode and higher concentrations at the cathode (Fig. 8b and c). During the electro-dewatering process, mineralization of carbonate and bicarbonate
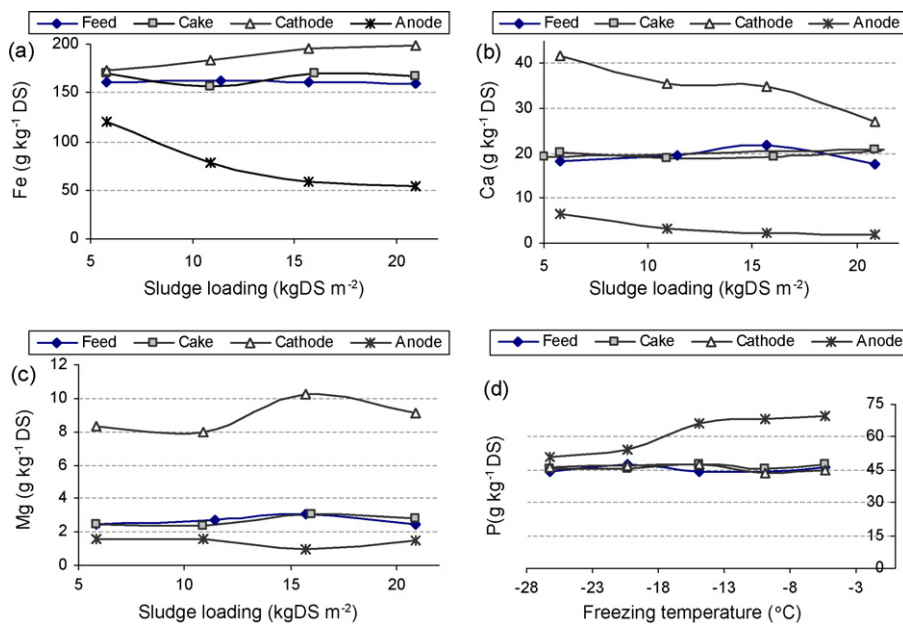

Fig. 8. Concentrations of Fe (a), Ca (b), and Mg (c) in sludge and the final sludge cake, sludge by the cathode and the anode after electro-dewatering process employing different sludge loading rates (Exps. 6–9) and (d) P concentrations in experiments using freeze/thaw conditioned sludge (Exps. 10–14).
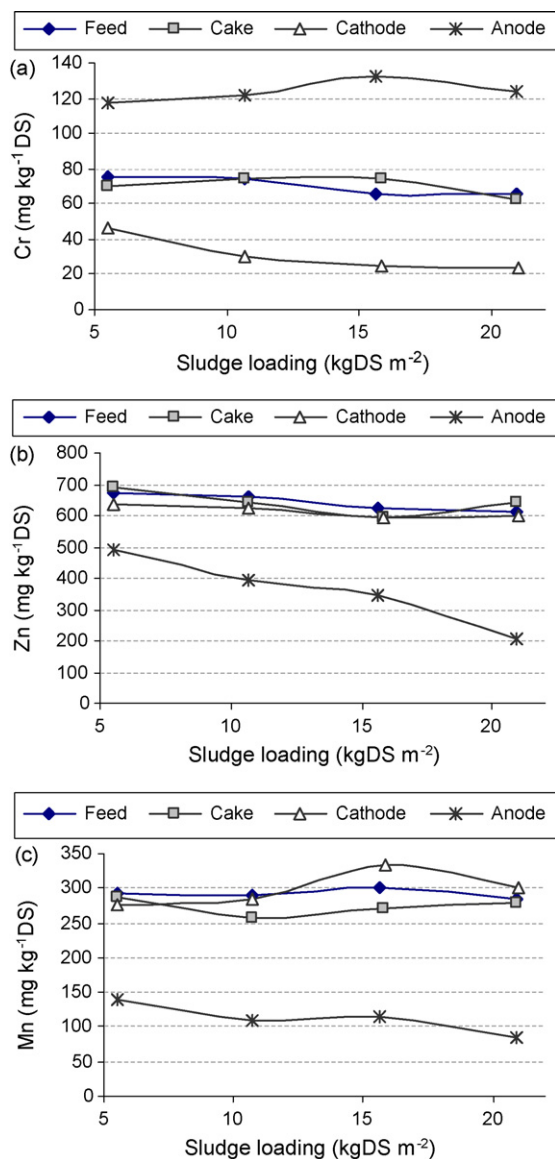
Fig. 9. Concentrations of Cr (a), Zn (b) and Mn (c) in sludge and the final sludge cake, sludge by the cathode and the anode after electro-dewatering process employing different sludge loading rates (Exps. 6–9).

ions reduced the concentration of IC and assisted in the release of calcium, which was predominantly bound to carbonates and bicarbonates in the sludge matrix (Fig. 6c). Therefore, at the end of Exps. 6, 7, 8 and 9 with the sludge loading rates of 5.3, 10.8, 15.9 and 20.2 kg DS m^{-2}, concentrations of Ca^{2+} in the removed water at the cathode were 453, 577, 987 and 830 mg l^{-1}, respectively. In addition, higher concentrations of Ca^{2+} in sludge at the anode were also observed (Fig. 8c).

Acidic pH at the anode assisted in the dissolution of Me$_n$(PO$_4$)$_m$ and the release of phosphorous that moved to the anode under the applied electrical gradient [8]. The concentrations of P in the removed water at the anode reached 91, 1153, 1785 mg l^{-1} after 40, 80, 150 min of the treatment, respectively, in comparison to the blank experiment, where the concentration of P remained constant at 5.4 mg l^{-1} (Exp. 4). According to Kim et al. [41], transport of phosphorous was retarded towards the cathode due to chemisorption on the surface of solid particles and electro-migration phenomenon. Moreover, phosphorous had a strong affinity for Fe oxides at low pH, thus acidic environment at the anode hindered P migration towards the cathode at the applied low-level electric current [45].

When electro-dewatering process was terminated, it was found that the VS/DS ratio increased in sludge at the anode. The PCA analysis was performed to establish the relationship between the VS/DS ratio, sludge loading rate and concentrations of Fe, Mg, Ca and P in sludge at the anode (Fig. 3c). At the end of the electro-dewatering process, the negative correlation between the VS/DS ratio and concentrations of Fe and Ca ions was found in sludge at the anode. The change of VS content in sludge may be attributed to the migration of inorganic matter/ions during the electro-dewatering process. Fe and Ca were the dominant metals in sludge (Table 1) and these positively charged ions predominantly migrated to the negatively charged cathode, where precipitation, co-precipitation, complexation and adsorption took place at high pH environment. Thus, according to Wang et al. [46], the migration and a subsequent decrease in the concentration of prevalent inorganic ions near the anode resulted in an increase of the VS content near the positively charged anode. Moreover, the positive correlation between the sludge loading rate and the VS/DS ratio in sludge at the anode was also observed.

3.6. Migration of trace elements Cr, Zn and Mn during the electro-dewatering process

Generally, Cr exists as Cr(III) and Cr(VI) in soils and sludge [11,12,47]. Under the applied electrical field Cr(III), which is cationic species tend to migrate towards the cathode [9]. Nonetheless, Cr(VI) that is anionic species and usually exists as hydrochromate (HCrO$_4^-$), dichromate (Cr$_2$O$_7^{2-}$) and chromate (CrO$_4^{2-}$), would migrate towards the anode when low level electric current is applied [11,48]. According to Reddy and Chinthamreddy [11], Cr(VI) can be absorbed by sludge particles at the low pH regions near the anode and undergo the reduction to Cr(III) at the cathode. During the electro-dewatering process, total Cr concentration significantly increased in sludge at the anode and decreased at the cathode indicating that Cr(VI) anionic species were prevalent during the treatment process (Fig. 9a). The same was observed by Cang et al. [49] who investigated the migration of Cr species during electrokinetic treatment of soil. The significant decrease in Zn and Mn concentrations in sludge at the anode was also found (Fig. 9b and c). Similar behavior of these metals was also observed by other scientists who researched electrokinetic heavy metal removal from soils and anaerobic granular sludge [50,51].

4. Conclusions

Decrease in the sludge loading rates (from 20 to 5 kg DS m^{-2}) resulted in an increase in the maximum current density (145–467 A m^{-2}). The statistical analysis showed correlations between the DS content in the final sludge cake, sludge loading rate, freezing conditions, energy consumption and the highest current density values. TOC increased at the anode and decreased at the cathode in experiments using polymer conditioned sludge samples. However, in experiments using freeze/thaw conditioned sludge samples, high concentration of TOC was observed in the removed water at the cathode. Concentration of Na$^+$ and K$^+$ were reduced by 51 and 78% in the sludge cake in comparison to blank experiments. Fe ions, Ca^{2+} and Mg^{2+} concentrations were found to be lower in sludge at the anode and higher at the cathode. There was a correlation between the VS/DS ratio in sludge at the anode, Ca^{2+} and Fe ions concentrations, and sludge loading rates observed. High P concentration in sludge at the anode was observed in experiments using freeze/thaw conditioned sludge samples. Migration and demineralization reduced concentrations of bicarbonate and carbonate ions in sludge, causing high concentration of Ca^{2+} ions in the removed water at the cathode. Lower concentrations of Zn^{2+} and Mn ions

and higher concentrations of Cr ions were found in sludge at the anode.

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