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SEWAGE SLUDGE ELECTRO-DEWATERING

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Abstract

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Original sludge from wastewater treatment plants (WWTPs) usually has a poor dewaterability. Conventionally, mechanical dewatering methods are used to increase the dry solids (DS) content of the sludge. However, sludge dewatering is an important economic factor in the operation of WWTPs, high water content in the final sludge cake is commonly related to an increase in transport and disposal costs. Electro-dewatering could be a potential technique to reduce the water content of the final sludge cake, but the parameters affecting the performance of electro-dewatering and the quality of the resulting sludge cake, as well as removed water, are not sufficiently well known. In this research, non-pressure and pressure-driven experiments were set up to investigate the effect of various parameters and experimental strategies on electro-dewatering. Migration behaviour of organic compounds and metals was also studied.

Application of electrical field significantly improved the dewatering performance in comparison to experiments without electric field. Electro-dewatering increased the DS content of the sludge from 15% to 40 % in non-pressure applications and from 8% to 41% in pressure-driven applications. DS contents were significantly higher than typically obtained with mechanical dewatering techniques in wastewater treatment plant. The better performance of the pressure-driven dewatering was associated to a higher current density at the beginning and higher electric field strength later on in the experiments. The applied voltage was one of the major parameters affecting dewatering time, water removal rate and DS content of the sludge cake. By decreasing the sludge loading rate, higher electrical field strength was established between the electrodes, which has a positive effect on an increase in DS content of the final sludge cake.

However interrupted voltage application had a negative impact on dewatering in this study, probably because the off-times were too long.

Other factors affecting dewatering performance were associated to the original sludge characteristics and sludge conditioning. Anaerobic digestion of the sludge with high pH buffering capacity, polymer addition and freeze/thaw conditioning had a positive impact on dewatering. The impact of pH on electro-dewatering was related to the surface charge of the particles measured as zeta-potential.

One of the differences between electro-dewatering and mechanical dewatering technologies is that electro-dewatering actively removes ionic compounds from the sludge. In this study, dissolution and migration of organic compounds (such as short-chain fatty acids), macro metals (Na, K, Ca, Mg, Fe) and trace metals (Ni, Mn, Zn, Cr) was investigated. The migration of the metals depended on the fractionation and electrical field strength. These compounds may have both negative and positive impacts on the reuse and recycling of the sludge and removed water.

Based on the experimental results of this study, electro-dewatering process can be optimized in terms of dewatering time, desired DS content, power consumption and chemical usage.

Keywords: Sewage sludge, biosolids, electro-dewatering, electro-osmosis, sludge dewatering

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Abbreviation

ATAD	Autothermal Aerobic Digestion Process
BFP	Belt Filter Presses
COD	Chemical Oxygen Demand
CST	Capillary Suction Time
DC	Direct Current
DLVO	Double Layer Theory or Overbeek
DS	Dry Solid
EPSs	Extracellular Polymeric Substances
F/M	Food to Microorganism
GC	Gas Chromatography
IC	Inorganic Carbon
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
NMR	Nuclear Magnetic Resonance
PCA	Principal Component Analysis
SRF	Specific Resistance to Filtration
SRT	Solid Retention Time
TOC	Total Organic Carbon
TTF	Time to Filter
VFAs	Volatile Fatty Acids
VS	Volatile Solids
WWTP	Wastewater Treatment Plants

List of original publications

The thesis consists of five original publications, which are referred by Roman numbers (**I-V**) in text, respectively.

I. Tuan P.A., Virkutyte, J. and Sillanpää M., Sludge dewatering by sand-drying bed coupled with electro-dewatering at various potentials, *International Journal of Mining, Reclamation and Environment,* 24 (2010) 151-162.

II. Tuan P.A., Virkutyte, J. and Sillanpää M., Electro-dewatering of sludge under pressure and non-pressure conditions, *Environ. Technol.,* 29 (2008) 1075-1084.

III. Tuan P.A. and Sillanpää M., Effect of freeze/thaw conditions, polyelectrolyte addition, and sludge loading on sludge electro-dewatering process, *Chemical Engineering Journal*, 164 (2010) 85-91.

IV. Tuan P.A. and Sillanpää M., Migration of ions and organic matter during electro-dewatering of anaerobic sludge, *Journal of Hazardous Material,* 173 (2010) 54-61.

V. Tuan P.A. and Sillanpää M., Fractionation of macro and trace metals due to off-time interrupted electro-dewatering, *Drying Technology,* 28 (2010) 762-772.

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1. Introduction

Activated sludge process is commonly used for purification of municipal and industrial wastewater. However, one of the drawbacks of this technique is the production of a huge amount of waste sludge. The annual production of sewage sludge is about 10.4 million tonnes of dry solids (DS) in 25 member states of the European Union (Table 1.1). The highest amounts of sludge are produced by Germany, the UK, French, Spain and Italy in this order. These five countries produce about 70% of the annual European sewage sludge production [1]. The annual sludge production in 13 EU states, not including Italy and Sweden increased from 5.5 million tonnes in 1992 to more than 9 million tonnes by 2006. In the USA, over 7 million tonnes of dry sewage sludge were produced in 1990. Japan produced 4.6 million tones of dry sludge in 1991. The central government of Japan projected that the number of sewer connections would increase to 54% in 1995 and to 70% by the year 2000. Therefore, a rapid increase in sludge production was expected in Japan [2]. All over the world, an increase in sludge production is expected to continue. This is because of an increase in percentage of household which connect to central WWTPs (Waste Water Treatment Plants) in developing countries and an update on WWTPs that is considered to be needed to achieve the stringent pollution limits on effluent discharge in developed countries.

Untreated sewage sludge has a high organic matter content ranging from 60 to 80%. After biological treatment, the organic matter content is significantly reduced (e.g. organic content is 60-70% of DS after aerobic digestion, 40-50% of DS after anaerobic digestion). However, biological stabilization reduces the calorific value of sludge from about 17.5 MJ/kg DS for raw sludge to about 10.5 MJ/kg DS for digested sludge [2].

High concentrations of plant nutrients, such as phosphorous (approximately 3%) and nitrogen (approximately 1.5%) in dewatered sewage sludge make it attractive to reuse as fertilizer. But, high contents of potential harmful substances such as organic contaminants, heavy metals, and pathogens may limit the reusability of sludge [3]. After banning the dumping of sewage sludge into the sea in 1998, landfilling, agriculture, and incineration have been the main disposal methods. Figure1.1 presents the sludge disposal routes in the EU member states. Landfilling of sludge is decreasing and incineration is increasing. Incineration is already widely practiced in Belgium, Denmark, France, and Germany [2].

Table 1.1 annual sewage sludge production in 25 member states of the European Union [1]

No	**EU member state**	**Sewage sludge production [tones DS]**	**percentage of total production in the EU [%]**	**Year of publication**
1	Austria	196,000	1.9	2000
2	Belgium	160,000	1.5	2000
3	Cyprus	12,000	0.1	2001
4	Czech Republic	200,000	1.9	2006
5	Denmark	200,000	1.9	2000
6	Estonia	53,000	0.5	2001
7	Finland	160,000	1.5	2000
8	France	1,172,000	11.3	2000
9	Germany	2,786,000	26.8	2000
10	Greece	99,000	1.0	2000
11	Hungary	230,000	2.2	2004
12	Ireland	113,000	1.1	2000
13	Italy	800,000	7.7	2000
14	Latvia	23,000	0.2	2001
15	Lithuania	48,000	0.5	2001
16	Luxembourg	14,000	0.1	2000
17	Malta	400	0.0	2001
18	Netherlands	401,000	3.9	2000
19	Poland	360,000	3.5	2000
20	Portugal	359,000	3.4	2000
21	Slovakia	86,000	0.8	2001
22	Slovenia	90,000	0.9	2001
23	Spain	1,088,000	10.4	2000
24	Sweden	180,000	1.7	2000
25	UK	1,583,000	15.2	2000
	EU total	**10,413,400**	**100**	

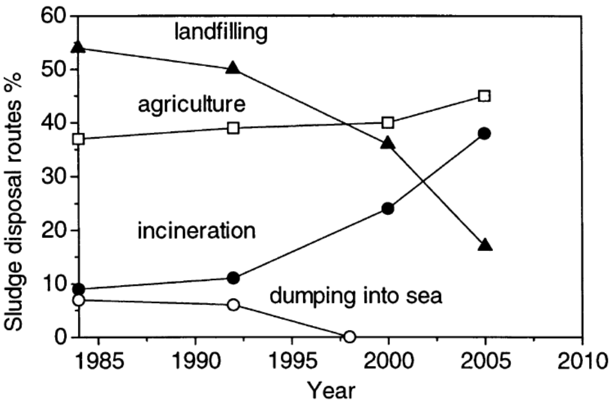

Figure 1.1 Sludge disposal routes in the European Community up to 2005 [2]

Commonly, sludge must be dewatered before transporting it to composting, incinerators, landfill or reuse as fertilizer. It is well known that the original sludge from WWTPs usually has a poor dewaterability. In order to successfully reduce water content, sludge conditioning by polymer addition is usually employed to increase the dewaterability of sludge. The main purpose of sludge conditioning is to enhance the effectiveness of a solid-liquid separation in mechanical dewatering processes such as centrifuge, diaphragm filter presses, and vacuum filter. However, the efficiency of sludge dewatering strongly depends on the polymer dosage and characteristics as well as the characteristics of the sludge. Moreover, mechanical methods cannot reach a sufficiently high potential to drive the interstitial water through the very narrow pore spaces, therefore dewatering using mechanical means is extremely limited and requires substantial further treatment [4]. Thus, sludge treatment and disposal requires over 50% of the operation budget for WWTPs [5].

Electric field application through the sludge segment causes electro-osmotic phenomenon which means a fluid flow in charged particle matrix. Electro-osmosis has been reported to reduce the interstitial water and some extent of the vicinal water, thus resulting in a dryer sludge cake [6]. The following literature review summarizes the existing knowledge of sludge dewatering characteristics, sludge conditioning methods and mechanical dewatering processes. Electro-dewatering process is discussed in detail based on recent research publications.

2. Review of the literature

2.1. Evaluation of sludge dewaterability

Common parameters using to evaluate sludge dewatering properties include capillary suction time (CST), time to filter (TTF) and specific resistance to filtration (SRF). The CST and TTF tests were standardized in an AWWA publication in 1998 but SRF measurement is not a standard method. In brief, the CST test determines the rate of water release from the sludge. The CST test consists of placing a sludge sample in a small cylinder on a sheet of chromatography paper. The paper extracts water from sludge by capillary suction. The time required for the water to travel a specified distance is recorded automatically by monitoring the conductivity change occurring at two contact points appropriately spaced and in contact with the chromatography paper. The elapsed time (seconds) is indicative of the water drainage rate.

The TTF is considered to be similar to SRF if the sludge content and filtrate viscosity do not vary among the compared samples. The TTF and SRF tests are measured by using the same facility. The test consists of a placing a sludge samples in a Buchner funnel with a paper support filter and applying vacuum. The funnel is connected to a graduated cylinder and the amount of filtrate is measured as a function of time. The time required (seconds) for 50% reduction in sample volume is TTF. On the other hand, SRF parameter is reported in m/kg and it can be calculated as:

$$SRF = \frac{2 \times A^2 \times \Delta P \times b}{\eta \times DS} \tag{2.1}$$

Where ΔP (N/m^2) is the pressure drop across the filter cake, A (m^2) is filtration area, η (kg/m/s) is dynamic viscosity, DS (kg/m^3) is solid content of sludge sample. The coefficient b (s/cm^6) is measured as the slope of the curve obtained by plotting the time of filtration to volume of filtrate ration (t/V) versus V itself.

In general, the main advantage of CST is a rapid and simple measurement in comparison to SRF. However, CST is far from realistic because of no pressure application. SRF is considered to be a realizable dewatering measurement. However, the coefficient (b) is difficult to calculate and large errors are encountered when dealing with low DS of content sludge samples [7]. The correlation and relationship between the CST and SRF measurements during sludge dewatering evaluation have been observed in several studies [7-9]. In studying alum sludge conditioning with polymers, it was found that the optimal polymer dosages which were determined by the CST test were higher than the dosages by the SRF test [10,11]. In a study on correlation between dewatering index and performance of centrifuge, belt press and filter press, Pan et al. [7] documented that the dewaterability through centrifuge dewatering was best predicted by the CST value, but CST was not a reliable index for belt press and filter press performance. SRF was reported to be a good index for the evaluation of filter press dewatering because of the similar filtration behavior.

Tests other than CST, TTF and SRF have also been used to evaluate sludge dewaterability. An arm-suspension centrifuge with rotational speed between 400 and 1000 rpm was employed in order to observe the filtrate amounts and cake thickness under the centrifugal field [12,13]. A constant head piston press with a hydraulic pressure of

1400–3000 psi was also used as consolidation tests to obtain solid density, time evolution for cake porosity [13,14].

2.2. Sludge characterization affecting dewaterability

2.2.1. Type of sludge

Types of sludge in a WWTP vary according to the treatment processes and method of operation. In typical WWTPs, sludge might be classified as primary, secondary and digested sludge (Figure 2.1). They are different in physical, chemical and biological characteristics which have an influence on to sludge dewaterability.

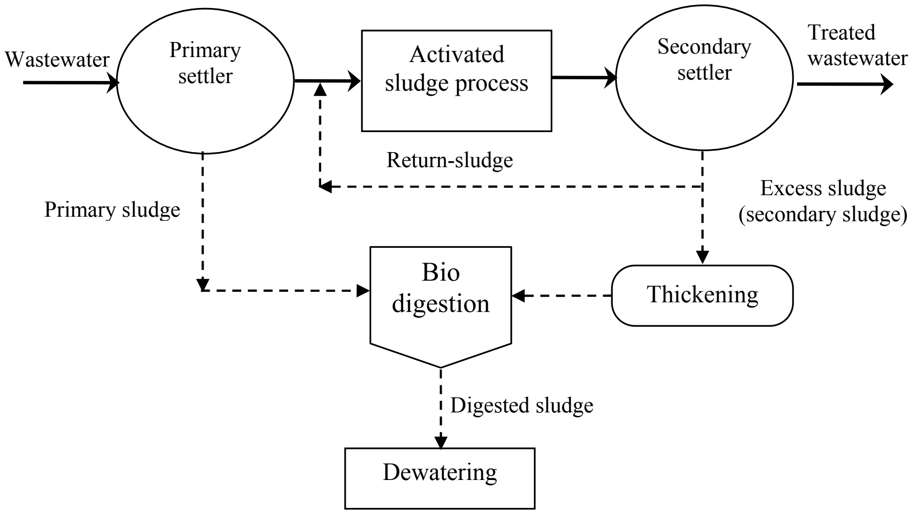

Figure 2.1 Sources and types of sludge generated in a typical WWTP

a) Primary sludge

Primary sludge is consisted of settleable solids which are removed from raw wastewater by using a physical process of primary settling. The main constituents of the primary sludge are non-cellular organic, components ranging from 70 to 75% of DS [15].

The highly bio-degraded organic matter in primary sludge results in unpleasant odor under storage. Due to composition of discrete particles, the primary sludge can easily be dewatered with lower conditioning requirements in comparison to secondary sludge [16].

b) Secondary sludge

Secondary sludge, also known as excess sludge, biological sludge or activated sludge, is produced aerobically in biological treatment. Secondary sludge mainly consists of micro-organisms and as well as adsorbed suspended solids and colloids. The organic content of biological sludge varies between 60 and 80%, with a typical value of 75%. In general, dewaterability of secondary sludge depends on numerous factors. A long solid retention time (SRT) improves flocculation resulting in an increase of sludge dewaterability [17]. This might relate to an increase of extracellular polymeric substances (EPSs) during long SRT [18,19].

Excessive growth of filamentous bacteria group is a common problem in activated sludge process. A term of bulking sludge is used to describe this problem. The bulking sludge causes poor settling and dewatering, which is widely reviewed and studied by many researchers [20-25]. Several factors may cause the over-growth of filamentous micro-organisms in activated sludge process: wastewater composition [26-28], low food to microorganism (F/M) ratio [29-34], low dissolved oxygen [33,35-38], nutrients deficiency [39-42] and high temperature [27,43,44]. In order to control the bulking sludge, oxidant chemicals such as chlorine and hydrogen peroxide have been added into the aeration tank or return sludge line to destroy the filamentous bacteria [25,45]. In addition, improvement of aeration system, control of F/M ratio and introduction of nutrients, minerals, and synthetic polymers effectively prevent the over growth of filamentous bacteria [23,38,45-47].

By increasing the concentration of divalent cations, particularly Mg^{2+} and Ca^{2+}, an improvement of settling properties and an increase in floc strength was observed, because these cations facilitate flocculation due to the cation bridging phenomena in which calcium ion is involved with polyelectrolyte system [48,49]. Thus, the high concentration of Ca^{2+} in sludge contributed to an improvement in sludge dewaterability and lower optimum polymer dosage [50].

It is important to note that the dewaterability of secondary sludge is significantly reduced during anaerobic storage [51,52]. This is due to the deflocculation of activated sludge when it is exposed to anaerobic conditions and shear [53].

c) Digested sludge

In municipal WWTPs, the primary and secondary sludge normally require stabilization and then dewatering prior to the final disposal to landfill or use for land application. The purposes of sludge stabilization are reduction of hazardous chemicals and microbes as well as odor. Biological digestion under aerobic or anaerobic conditions is commonly used for sludge stabilization. Bio-stabilization reduces the organic content in sludge from 75% to 50%. Anaerobic digestion is most widely used processes for sludge stabilization because the operation cost is low and the methane gas product is a potential source of energy. After aerobical and anaerobical digestion, the dewaterability of the digested sludge is decreaced in comparison to original excess sludge [15,54-57]. During digestion, both aerobic and anaerobic, the content of fine particles increases, which results in a decrease of sludge dewaterability. The decrease of sludge dewaterability is greater in the case of an aerobic process because of much higher bacterial growth following decay as well as mechanical stress, which leads to greater disintegration and formation of fine particles [15,58]. On the other hand, with respect to the power consumption for supplying the oxygen requirement, the operation costs of aerobic digestion are high, but a high level decrease in pathogen levels are obtained, particularly using the autothermal aerobic digestion process (ATAD). Digested sludge from ATADs has been found to dewater very poorly [59-61]. Dewaterability of ATAD sludge is also affected by the degree of mixing provided during digestion process because the intensive mixing destroys the structure of the solids floc [16]. Therefore, the ATAD sludge requires more polymer addition for sludge dewatering. However, dewaterability of ATAD sludge improves after post mesophilic aeration or anaerobic digestion [58,62]

2.2.2. Water distribution in sludge

There are different types of water in sludge. They all have different chemical and properties such as vapour pressure, enthalpy, entropy, viscosity and density [63]. Free and bound water are considered to be main types of water: free water represents the largest part of the sludge. Thermo-dynamically, it behaves like pure water. Bound water presents a very small proportion of the total water content in the sludge but it is generally greater in term of mass than the solid phase. Bound water can be distinguished as chemically bound water, physically bound water, and mechanically bound water [64].

The estimation of the amount of free water and bound water is based on their different behaviors; various techniques have been employed to measure the free water content such as vacuum drying, drying at atmospheric pressure, dilatometric test, centrifugal settling test, filtration test, differential thermal analysis, differential scanning calorimetry, water vapour sorption and nuclear magnetic resonance. The results presented in literature differ widely due to this large range of experimental techniques. It is often argued that the free water is an operationally defined value depending on the chosen methods of measurements [65]. Some authors consider that water vapour at 80 ^oC is free water while the others do the same measurement at 40 ^oC. Some researchers believe that a pressure higher than 28 MPa is required to remove all the free water from activated sludge. However, the most popular definition is that the free water is freezing at frozen point, but bound water remains unfrozen at frizzing point. Bound water is only frozen at -20 ^oC [64,66], or at -8^oC [67].

A simple way of dividing water in sludge into bound and free water is not sufficient to describe the physical and chemical mechanisms in dewatering process or pre-treatments used to improve dewatering process (such as coagulation, flocculation, physical condition, and chemical oxidation). In general, depending on their physical binding to sludge particles, Vesilind [6,67,68] divided water in sludge into four different types of water:

- Free water: water which is not bound to the particles or in the other words, free water is not associated with solid particles including avoid water not associated with capillary force. The free water content represents the largest part of sewage sludge (70-75%)
- Interstitial or capillary water: water which is bound by capillary forces between the sludge flocs or water trapped in crevices and interstitial spaces or flocs. This water

can be released when the floc is broken up. Some interstitial water might be removed by mechanical dewatering devices such as centrifuge.

- Surface or vicinal water: water that is associated with the solid particles. Multiple layers of water molecules help tightly to the particle surface by hydrogen bonding. This water is held on particle surfaces by virtue of the molecular structure of the water molecules and cannot be removed by mechanical methods.
- Intracellular water, water of hydration or chemically bound within the particle structure and can be released only by thermo-chemical destruction of the particles.

Recently, Mikkelsen and Keiding [69] gave a new term ‘water-holding’ to indicate water entrapped in proteins and polymers in sludge. The water-holding could be related to both surface bound and osmotic water. So far, no researches have been done on this kind of water.

It is quite difficult to get a clear picture of the distribution of water within activated sludge. According to Vaxelaire and Cézac [65], the choice of the best-adapted method of investigation is not easy. However, an extensive discussion about the different methods which are currently applied should facilitate the use of data reported in current literature, as well as provide a better evaluation of the information that each test can offer.

2.2.3. Extracellular polymeric substances

Extracellular Polymeric Substances (EPSs) are metabolic products accumulating on the surface of bacterial cells. They contain a variety of organic substances such as carbohydrates, exopolysaccharides, exoproteins, deoxyribonucleic acids, DNA, humic acid, uronic acid, etc. In sludge, proteins are predominant in the composition of EPSs

[70]. According to Liu and Fang [71,72], some of EPSs's functions are forming a protective layer for the cells against the harsh external environments such as toxicity and sudden change of pH, absorbing exogenous nutrients and organic molecules, aggregate bacterial cells in flocs and also serve as carbon and energy reserves during starvation. EPSs can form a negatively charged polymer network [73,74]. Thus, EPSs play an important role in flocculation, settling and dewatering of sludge [19,75-77]. In addition, by forming a polymeric network with pores and channels, they create a large surface area which is able to adsorb pollutants, nutrients and minerals [71,78].

An increase of EPSs in sludge results in a decrease in sludge dewaterability, as documented by several researchers [19,79,80]. However, during studies on the relationship of EPSs and sludge dewatering at eight municipal WWTPs, Houghton et al. [81] found that the optimum level of EPSs to give maximum sludge dewaterability was 35 mg EPS/gDS and at level under and above the optimum level, the sludge became more difficult to dewater. Moreover, many studies have reported the effect of the amount of EPSc (carbohydrate) and EPSp (protein) on sludge dewatering. The results are often inconsistent i.e. some researchers found the effect of EPSp to be positive [75,82] and some negative [81,83].

In addition, the impact of EPSs on sludge dewaterability seems to depend on the stage of the sludge treatment process. Biological sludge treatment under aerobic and anaerobic conditions reduces sludge dewaterability. A decrease in the amount of EPSs was found in sludge sample after anaerobic digestion [81,84]. Under aerobic digestion, an increase of dissolved EPSs was reported to reduce sludge dewaterability [85]. During thickening process, a change of EPSs composition in sludge resulting in reduction of sludge dewaterability was documented by several researchers [86-88]. Even though the amount of EPSs in sludge was significantly decreased, when sludge was storaged at 4 ^{o}C under anaerobic conditions for 24 h [86]. Nielsen et al. [88] reported that EPSp and EPSc of sludge rapidly decreased within the first two days of storage under anaerobic conditions.

It is important to notice that there are many conflicting results in literature about the effect of EPSs on sludge dewatering. The reason could be that there is no analyzed standard protocol for EPSs characterization, thus, the composition and amount of EPSs in sludge samples depend on the extraction methods. Moreover, the nature of sludge and EPSs are dependent on a large number of process variables such as type of wastewater, nutrient level, sludge retention time and dissolved oxygen [72].

2.3. Sludge conditioning

Sludge conditioning methods can be divided into two types: chemical conditioning, in which one or more chemicals are added to improve dewaterability, and physical conditioning, in which physical properties are used. The conditioning methods change the structure of the sludge and hence the solid and liquid portions become more easily separable.

2.3.1. Chemical conditioning

a) Sludge flocculation

Among chemical conditioning methods, flocculation process is the most commonly used in WWTPs. To explain the sludge particle aggregation under flocculation process, two models, charge neutralization and bridging model, are presented.

Charge neutralization model is based on Alginate Theory or Double Layer Theory. This theory is a classical colloidal theory that describes charged particles as having a double layer of counter-ions surrounding the sludge particle. The first layer is often referred to as the fixed layer which is comprised of a tightly associated layer of counter-ions, and the second layer is referred to as the diffuse layer which is made up of less tightly associated counter-ions. The concentration of ions in the diffuse layer decreases with distance from the fixed layer surface until the concentration of ions equals that of the bulk solution. The potential existing between the fixed layer and the bulk phase is the zeta potential (ζ). The zeta potential can be measured by using electrophoretic mobility or streaming potential, as most colloidal material. Sludge samples originated from WWTP usually have a negative value of zeta potential. This means that the sludge particles are negatively charged and the electrostatic repulsion between sludge particles prevents aggregation. An addition of an appropriate dosage of organic cationic polymers or inorganic flocculants at appropriate pH will eliminate the electrostatic repulsion, allowing short-range attractive forces to promote aggregation (Figure 2.2).

In bridging model, cationic polymers react as cationic sites to bind to more than one sludge particle, thus bridging the system of solid particles (Figure 2.3). The bridging improves flocculation and dewaterability. The bridging model can explain the effectiveness of conditioning during flocculation process using a high molecular weight polymer or dual polymers.

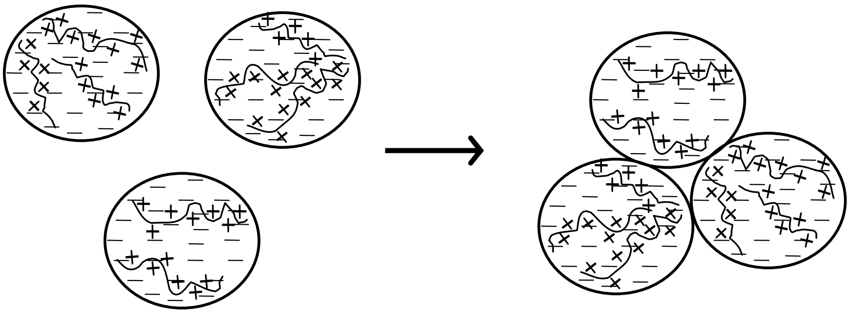

Figure 2.2 simplified depiction of the charge neutralization model

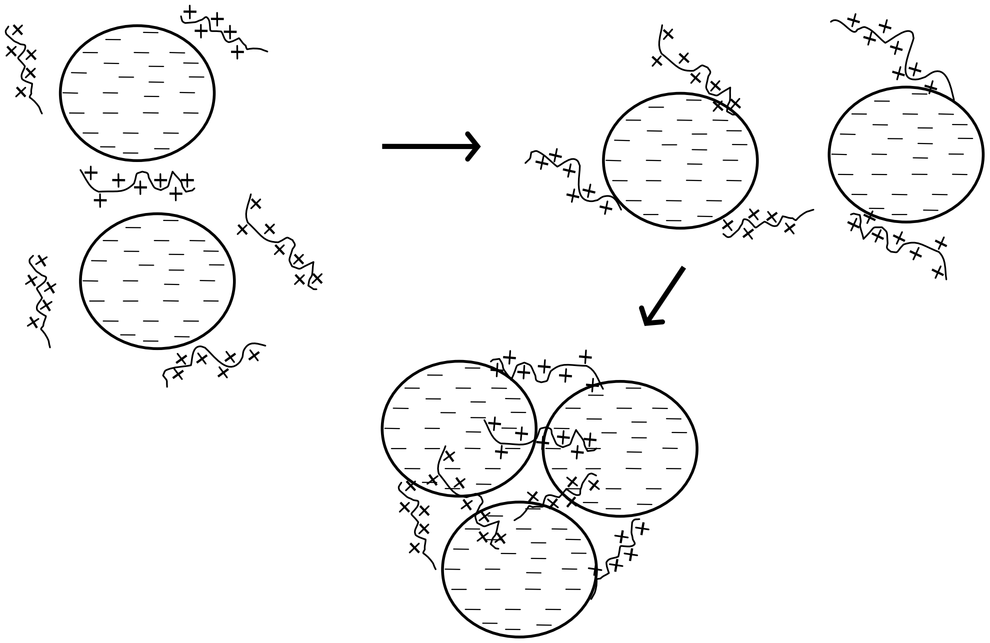

Figure 2.3 simplified depiction of bridging model

In general, the optimum flocculent dosage is close to the dose giving zero value of ζ and sludge conditioning using a high molecular weight polymer usually results in an increase of sludge dewaterability. Therefore, both charge neutralization and bridging models seem to be in operation in sludge flocculation process (Figure 2.3). According to Dentel [89], although the hypothesized combination of charge neutralization and bridging models explains many aspects of flocculation and the behavior of flocculated solids in subsequent solid-liquid separation processes, it should be regarded as a simplification. It has been noted that the addition of cationic polymers or other flocculants could increase dewaterability of sludge in company with increase in ζ value. But, in some cases, good sludge flocculation does not require charge neutralization. An excellent sludge dewatering could be achieved even when ζ value was positive [90]. Thus, after flocculation process, an easily dewaterable sludge sample may have a ζ value close to zero, but it does not mean that a ζ value close to zero leads to a easy dewatering sludge sample.

Ferric and aluminum salts and lime are commonly used as inorganic flocculants. However, mechanical dewatering methods, especially centrifuging, do not perform well using sludge samples conditioned with inorganic flocculants. To achieve high sludge dewatering, doses as high as 20-40% of the original dry weight of sludge are usually required [5]. Addition of the high dose flocculants can cause a significant increase of sludge volume which results in the impact the transport and disposal costs. Therefore, the use of inorganic flocculants is limited.

Organic polymers are widely used in sludge conditioning. Polymers can be classified by their ionic nature into groups with negative charge (anionic polymers), positive charge (cationic polymers), and neutral charge (non-ionic polymers). The polymers used for sludge conditioning are water soluble and mainly synthetic products. As mentioned above, cationic polymers are usually used in sludge conditioning. The most common cationic polymers are polyethylene imines (PEIs), epichlorohydrin/dimenthylamine (Epi/DMA), diallyldimethyl ammonium chloride (DADMAC), acrylamine (AM). The most important characteristics of polymeric flocculants are molecular weight and charge density. Molecular weights range from a few thousand up to tens of millions of daltons. Conventionally, polymers are regarded as having a low, medium or high molecular weight, corresponding to molecular weight values in the ranges: $<10^5$, 10^5–10^6 and $>10^6$, respectively [91]. Therefore, the polymers with the highest molecular weight (up to 30 million g/mole) may contain over 100,000 monomers.

Charge density of polyelectrolytes can be expressed in terms of mole per cent of charged groups or as milliequivalents per gram (meq/g). The technique of colloid titration can be used to determine charge density [92]. The charge density varies from 0 to 100% and is depended on polymer type and the pH of the solution. Polyelectrolytes are classified as low (10 mol%), medium (25 mol%), or high (50–100 mol%) charge equivalent compounds [91]. Product forms of polymers are liquid, emulsion, and dry. Liquids are true solutions of polymer in water. To provide enough viscosity for pumping and dilution, the concentration is limited to between 4 and 9%. Emulsions may very in concentration and dry forms (powder, granular, flake etc.) may contain 90 to 100% of the active product.

A typical polymer dose is about 1% of original sludge dry weight in comparison to 20 to 40% in sludge conditioning using inorganic flocculants. However, the costs of organic polymers usually cover almost half of the total sludge treatment and disposal costs [90,93].

b) Other chemical conditioning

Chemical oxidation techniques such as ozone, O_2 (wet oxidation) and hydrogen peroxide/ferrous ions (classic Fenton oxidation) can be used for sludge pre-treatment. Studies on the effect of ozonation on the characteristics of waste activated sludge have shown that ozone pre-treatment removes organic matter in the sludge. However, ozone has a negative effect on sludge dewaterability. Proteins released by cell lysis have a negative effect on sludge dewatering and the unsettled micro-particles may have an influence on sludge filtration leading to a more compact filtration layer with reduced permeation of liquids [94-96].The dewaterability of treated sludge decreases with an increase in ozone dose. Thus a higher polymer dose is required for sludge flocculation [96].

Hydrogen peroxide (H_2O_2) is a strong oxidant. Oxidation by H_2O_2 alone is not effective because of a slow reaction rate. Transition metal salts (such as Cu^{II}, Fe^{II}, Co^{II}, Ru^{III}, Ni^{I}), ozone and UV-light can activate the H_2O_2 resulting in formation of hydrogen radicals. The oxidant potential of hydrogen radicals is 2.8 V which indicates that hydrogen radicals are stronger oxidants than ozone (2.1 V) and H_2O_2 (1.8 V). Hydrogen radicals can completely decompose the organic pollutants to the final inorganic compounds such as CO_2, water, and inorganic salts. Fenton's reagent is a mixture of H_2O_2 and ferrous iron. The ferrous iron (Fe^{II}) initiates and catalyzes the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals as reflection on equation 2.1.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \qquad (2.1)$$

Improving sludge dewaterability by using Fenton's reagent has been investigated in many studies. A significant decrease in the water content of the final sludge cake has been observed. Due to the application of Fenton's reaction, advanced oxidation can help to improve sludge dewatering by degradation of EPSs [97]. The degradation of EPSs reduces their water retention properties releasing EPSs-bound water. The degradation of EPSs reduces cell stability but increases the size of sludge flocs, which results in an improvement of sludge filtration. Other authors have found that Fenton oxidation decreases the organic content and also sludge volume. In addition, the soluble COD and bio-degradability of the sludge increase due to the formation of smaller molecular weight compounds such as alcohols, aldehydes, organic acids, which are easily degradable by biological methods [98,99].

In Fenton oxidation, dewaterability of sludge is strongly depended on the reaction temperature and H_2O_2 dose [100]. At low temperature ($<40^oC$), a high H_2O_2 dosage and a long reaction are necessary to achieve satisfactory dewaterability of sludge. An increase in temperature results in shorter reaction time and lower H_2O_2 dosage requirements [99]. pH is also very important parameter in Fenton oxidation process. The optimal pH is around 3. Thus, it has been considered that low pH might contribute to influence the improvement of sludge dewatering in Fenton oxidation of sewage sludge [98].

Acid treatment in general improves sludge dewaterability. Low pH can cause EPSs to release from sludge particle surfaces which make it easy to pack the sludge aggregates and to reduce water content in dewatered sludge [101,102]. Moreover, low sludge pH increases ζ value, which reduces the electrostatic repulsion, allowing short-range attractive forces to promote aggregation of sludge particles. However, alkali treatment also improves sludge dewaterability. It is considered that at extreme pH, EPSs are solubilized [97].

2.3.2. Physical conditioning

Physical properties are also used to improve sludge dewatering properties. Among physical treatments, freeze-thaw conditioning shows high effect on improving sludge dewaterability. The freeze-thaw treatment is considered as a low-cost method at moderate to cold climates. The principle of freeze-thaw conditioning is that during freezing, ice crystals grow incorporating water molecules. Because the structure of ice crystals is highly organized and symmetrical, it cannot accommodate any additional atoms or molecules. Each ice crystal continues to grow as long as there are water molecules available. All other impurities and solid particles are forced to the boundaries of the ice crystal where they become compressed or dehydrated [103,104]. Freeze-thaw treatment transforms sludge into a compacted form and reduces the sludge bound water content. Thus, it makes sludge easier for settling and filtration [105].

In general, sludge freezing at slow freezing rates shows better dewaterability than fast freezing. When the freezing rate is high, sludge particles are entrapped in the continuous growing ice layer, which impairs the sludge dewaterability [106]. When the freezing rate is low, flocs are rejected instead of being trapped, thus they tend to migrate in front of the growing ice crystals, which relates to a remarkable increase in the sludge dewaterability rates. However, the difference between the morphology of the ice/water interfaces can be one factor that causes the difference in freeze-thaw conditioning effectiveness. At a slow freezing rate, ice crystals grow in columns, where the ice/water interface is flat or planar. At faster freezing rates, ice crystals grow in branching tree-like structures called dendrites [107]. The dendrite ice crystals are formed at the ice/water interface, sludge particles are trapped in the ice front, resulting in a decrease in effectiveness of sludge dewaterability. An addition of dissolved solids (NaCl) [107] or high concentrations of dissolved organic material [104] change ice crystals growth from columnar to dendrite which decreases the effectiveness of freeze-thaw sludge treatment. Long curing time was reported to be beneficial for the sludge dewaterability [108,109].

Furthermore, the release of ECPs during treatment may improve freeze-thaw conditioning. The action of ice front can cause cell disruption, which releases intracellular material resulting in an increase in concentrations of organic material in sludge filtration water [104]. In addition, the freeze-thaw treatment does not only increase the sludge dewaterability but also reduces pathogenic in sludge [110].

Another physical conditioning method is thermal treatment. Sludge heat treatment in temperature range from 40 to 180 ^oC was considered, and thermal hydrolysis refers to a process in which sludge is heated from 130 to 180 ^oC [111]. Pilot scale experiments performed at temperatures of 120 °C for 60 min showed that thermal treatment reduces the residual sludge amounts and enhances the dewaterability [97]. Under thermal treatment, EPSs are degraded and their natural properties are changed. Hydrolysis of the exocellular organic fractions leads to the destruction of the colloidal structure resulting in release of the bound water from the sludge particles. Both phenomena relate to the improvement of sludge dewatering. However, high temperature treatment destroys the cell walls and transforms some of the suspended organic solids into soluble compounds

[97]. Therefore, thermally treated sludge is easy for biological degradation and an increase of COD concentration in filtrate is also observed [111].

2.4. Mechanical dewatering processes

Dewatering is physical processes in which the water content and volume of sludge are reduced. After dewatering, sludge volume is reduced more than 80% and DS content increases from 4% to 20-40% depending on sludge type and dewatering method. The dewatering processes that are commonly used include mechanical processes (centrifuges, belt filter presses, and pressure filter presses) and natural processes (sand drying bed and drying lagoon). The main advantages and disadvantages of these dewatering processes are shown in Table 2.1. Because of a large area requirement and odor potential, natural dewatering processes are only applied at small WWTPs. A mechanical vacuum filter has also been developed, but the commercial application is limited. Sludge dewatering by centrifuges, belt filter presses, and pressure filter presses are presented in detail.

2.4.1. Belt filter press

Belt filter presses (BFP) have been used in Europe first for dewatering of paper pulp and later modified to dewater waste sludge from WWTPs. It was introduced in the mid- 1970s. A BFP is a continuous-feed sludge dewatering process in which sludge is pressed within two moving filter belts close to each other. The presses can be varied depending on number of rollers and the manner. There are three phases involved in a BFP. In the initial phase, conditioned sludge is fed into the BFP. In this phase, a majority of the free water in the sludge is removed by gravity. In the second phase, the sludge is squeezed by low pressure application between porous cloth filter belts. The low-pressure phase is followed by the high-pressure phase when the belts pass over a series of rollers.

Table 2.1 Comparison of dewatering processes [16,25]

Process	**Advantages**	**Disadvantages**
Belt Filter press	Relatively low capital, operating and power costs Easier to shut down the system Easier to maintain	Very sensitive to feed sludge characteristics Sensitive to polymer type and dosage rate Requires large quantity of belt wash water
Pressure filter press	High cake solid concentration Low suspended solids in filtrate A good dewatering process for hard-to-handle sludge Plates can be added to increase capacity without a significant increase in floor area	Batch operation High capital and labor costs Requires skilled maintenance personnel Often requires inorganic chemical conditioning that produces additional solids
Centrifuge	Relatively less space required Fast startup and shutdown capabilities Does not require continuous operator attention Clean appearance and good odor containment	Relatively high capital cost Consumes more direct power per unit of product produced Requires grit removal from feed sludge Requires periodic repair of scroll, resulting in long downtime Requires skill
Drying beds and drying lagoons	Low capital cost when land is readily available Low energy consumption Low to no chemical consumption Least operator attention and skill required	Large area requirement Requires sludge stabilization Design requires consideration of climatic effect Sludge cake removal is labor intensive Odor potential

In high-pressure phase, the sludge is subjected to squeezing and shearing force for additional water removal. At the last roller, the final dewatered sludge cake is removed from the belts by scraper blades. Normally, the belts are separately washed to remove the sludge particles which have been forced into the porous of the cloth filter belts.

Most of the water removal occurs in the gravity and low-pressure phases when pressure is first applied. For a successful operation of a BFP, the sludge feed must be flocculated to avoid blinding of the filter belt and to facilitate gravity drainage in the first phase. A higher feed sludge concentration than 3% DS has been recommended [112].

2.4.2. Pressure filter press

The pressure filter press is a batch process unlike belt filter presses and centrifuge. Among various types of pressure filter presses, a fixed-volume recessed plate filter press and a variable-volume recessed plate filter press (diaphragm press) are commonly used for sludge dewatering. A typical filtration for pressure filter press dewatering cycle is: (1) sludge feeding; (2) cake squeezing by inflating the filter cloth or application of high pressure air or water; (3) opening of the plates and sludge discharge; (4) filter cloth wash. Duration of a cycle varies from 30 minutes to several hours depending on the squeezing phase and pressure application. The pressure application is typically from 226 to 1550 kN/m^2 and is maintained from 1 to 3 hours for the fixed-volume recessed plate filter press in comparison to 1380 to 2070 kN/m^2 and 15 to 30 minutes for diaphragm press.

The pressure filter press can remove water from sludge which has a poor dewaterability. After pressure filter press dewatering, sludge cake is dryer in comparison to other mechanical dewatering processes. Solid content of greater than 35% can be commonly achieved. However, the disadvantages of pressure filter press include high investment costs, high labor costs and limitation on filter cloth life. Conditioning for the pressure filter press dewatering usually requires ferric chloride and lime addition instead of organic polymers. Solids, such as fly ash, incinerator ash, and diatomaceous earth are often added, and these solids contribute to the solids in the final sludge cake.

2.4.3 Centrifuge

The centrifuge process was first used in industry for separating liquids and solids of different density. At present, the centrifuge process is widely used in both the United States and Europe for dewatering of municipal sewage sludge. The imperforate basket and solid bowl are two main categories of centrifuge application for dewatering of sewage sludge. The third type is disk nozzle centrifuge which has been used for sludge thickening. Because of the improved design and efficiency of the solid bowl centrifuge in the past few years, the imperforate basket centrifuges are being replaced by solid bowl machines [16,41].

There are two types of solid bowl centrifuge, countercurrent and cocurrent. In principle, centrifuging is a process in which a high centrifugal force of 500 to 4000 g applied directly to feed sludge to accelerate the separation of the solids and the liquid. There are three operations taking place in a centrifuge: clarification of solids from the liquid; consolidation of the solids; and conveyance of the solids to the discharge point. These operations are not necessarily compatible, so that maximization or optimization of one of these operations can lead to a poor performance of the others. Therefore, the operation of a centrifuge requires balancing to find an acceptable performance for both cake solids and solids capture [5]. Capacities of centrifuge machines are available from 2.4 m^3/h to more than 180 m^3/h. Polymer conditioning of sludge is required and the dosages depend on the type of sludge. The polymer can directly be added to the sludge feed line or to the sludge within the bowl of the centrifuge. DS content of the final sludge cake varies from 10 to 35% also depending on the type of sludge.

2.5. Electro-dewatering process

2.5.1. Electrokinetic phenomena

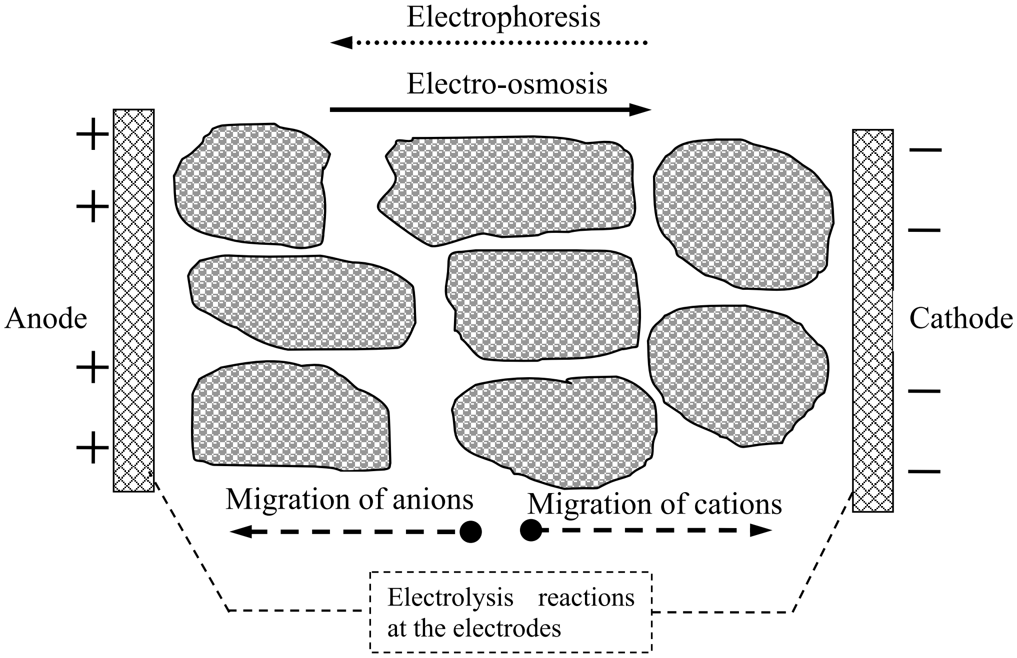

Figure 2.4 electrokinetic phenomena occur during electro-dewatering

Electro-dewatering is a process in which low direct current (DC) electric field is applied through the sludge segment to cause an electro-osmotic phenomenon that is fluid flow in a charged particle matrix. Electro-osmotic flow enhances extra water removal from sludge, resulting in an increase in solid content of the final sludge cake. When electrical field is applied, not only electro-osmosis but also electrophoresis, electro-migration and electro-chemical reactions at electrodes also occur (Figure 2.4) . These electrokinetic processes affect directly or indirectly the electro-dewatering of sludge and are therefore discussed in detail.

a) Electro-osmosis

Electro-osmosis was first described in 1809 by Ferdinand Friedrich Reuss, a professor at the University of Moscow. He used a system in which an electrolyte solution in a U-shaped cell was divided in two parts by a porous material. Two electrodes were placed in the boundary between electrolyte solution and the porous material. Under influence of electrical field application, the electrolyte solution started to flow through the porous material in direction of one of the electrodes. The discussion about the double layer theory considered that sewage sludge consists of charged particles having a double layer. When an electric field is applied to a sludge segment via electrodes, the net charge in the electrical double layer is induced to move by the resulting Coulomb force. The resulting flow is termed electroosmotic flow. The electroosmotic flow is expressed by Equation 2.2 [113,114].

$$\frac{dV}{dt} = \frac{\varepsilon_o \varepsilon_r \zeta}{\eta} EA \tag{2.2}$$

V; water volume (m^3)

t; time (s)

ε_o; dielectric permittivity of vacuum (8.854X10^{-12} CV^{-1}m^{-1})

ε_r; dielectric constant of the liquid

ζ ; zeta potential of sludge (V)

E; electrical field strength across the plug (Vm^{-1})

A; cross-sectional area (m^2)

η ; viscosity of the liquid medium ($kgm^{-1}s^{-1}$)

During electro-dewatering, electro-osmosis is considered to play the most important role to gain extra water removal from sludge. The zeta potential of sludge usually have a negative value, therefore, the direction of electro-osmotic flow is from the anode to the cathode. Recent studies from Saveyn et al.[115] using nuclear magnetic resonance (NMR) measurement technique to determine online the water content in sludge cake profile during electro-dewatering illustrated clearly picture of the transportation of water towards the cathode. A short interruption of power application enhances electro-osmotic flow resulting in 20 to 40% increase in water removal [116-118].

b) Electrophoresis

Electrophoresis and electro-osmosis were first observed by the same author, professor Ferdinand Friedrich Reuss in 1809. In solutions containing suspended material in a highly dispersed state, these suspended particles started to be displaced in the direction of one of the electrodes under the influence of electrical field. Thus, electrophoresis is the movement of charged particles in stationary liquid under electrical field. With particles of different shape, the electrophoretic velocity can be expressed by Equation 2.3 [119].

$$\upsilon = \gamma \frac{\varepsilon_o \varepsilon_r E \zeta}{\eta} \tag{2.3}$$

Where γ is a coefficient allowing for particle shape, for spherical particles $\gamma = \frac{2}{3}$

The influence of electrophoresis on enhanced water removal was described by Barton et al. [120]. During the initial stages of electro-dewatering, the sludge particles are still free to move in the fluid suspension. Because of negative charge of particles, they tend to migrate towards and locate at the anode, thus delaying the onset of cake formation on the lower filter medium and hence leading to enhanced water flow. When DS content in sludge segment becomes higher, sludge particles will be locked in position and are hence unable to move, only electro-osmosis plays an important role in transporting water from anode towards the cathode. However, the function of electrophoresis is still not fully understood during electro-dewatering and it is usually neglected in mathematic modeling.

c) Electro-migration

Electro-migration is the transport of ions in solution in which the movement of each ion species depends on its own ionic mobility. Under the applied electric field, anions usually move from the negatively charged cathode to the positively charged anode and *vice versa* for cations. Electro-migration flux of the species can be expressed by Equation 2.4 [121,122].

$$J_j = u_J^* c_j \nabla(-E) \tag{2.4}$$

$$u_j^* = \frac{D_j z_j F}{RT} \tau n \tag{2.5}$$

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.

Electro-migration is very important for electrokinetic remediation especially for the removal of metal contaminant. During electro-dewatering, electro-migration could occur, but there is limited discussion in the literature on this topic.

d) Electrolysis reactions at the electrodes

Due to the electrical field application, oxidation-reduction, corrosion and precifitation reactions occur at the electrode surface. These electrode reactions strongly depend on the material of electrode and the ions present in electrolyte. The possible electrode reactions could be:

At the anode:

$2H_2O - 4e^- \rightarrow O_2\uparrow + 4H^+$ $\quad E_o = 1.229$ V (2.6)

$M - ne^- \rightarrow M^{n+}$ (2.7)

At the cathode:

$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$ $\quad E_o = 0.828$ V (2.8)

$M^{n+} + ne^- \rightarrow M$ (2.9)

Where M denotes a metal

Reduction of water at the cathode releases hydroxide which results in an increase in the pH at the cathode. On the other hand, oxidation of water at the anode produces protons. The protons are transported towards the cathode by electro-migration and electro-osmosis. This causes a decrease in the pH in sludge cake profile from the cathode to the anode [118,123-125]. The low pH might dissolve metals and change sludge characteristics such as zeta potential and dewaterability. The gas evolution (oxygen and hydrogen) at surface of both electrodes leads to a reduction of contact within sludge segment and electrode. This may form an electrically resistant layer. In pressurized electro-dewatering device, the generated gases may cause extra driving force, which can result in an unsaturated final sludge cake [125]. Moreover, hydrogen gas might pose a potential risk of explosion. This risk can be prevented by extensive ventilation [126].

The oxidation of the anode material causes corrosion, which is a huge problem in electro-dewatering process. For example in full scale studies a filter belt press with electrokinetic facilities for sewage sludge dewatering, corrosion of stainless steel anode was reported [127]. Noble metals such as gold and platinum are not corrosive materials and have been used by many researchers [115,118,128]. However, noble metals are too expensive, therefore, they are only used in lab-scale experiments. Graphite is considered a low-cost material, and it is widely used as the anode in sludge electro-dewatering [123,124,129]. However, normal graphite does not withstand the mechanical stress and bending in pressure conditions. Recently, corrosion of the anode has effectively been suppressed by using titanium coated with mixed metal oxide (MMO) such as Ir_2O_3 [114,127,130]. Unlike the anode, corrosion is not a big problem for the cathode electrode material. Normal stainless steel mess or disks are widely used as the cathode.

In addition to the chemical impacts, the temperature of the sludge segment increases because high electric current generates a large amount of heat. Especially, at the end of electro-dewatering process, when water is depleted from the sludge cake, an increase of the electrical resistance results in Ohmic heating. Higher sludge temperature relates to reduction of viscosity which facilitates the extra water removal from the sludge cake [120].

2.5.2. Development of electro-dewatering process

Electro-osmosis has been used for soil drying after the First World War. Especially for building purposes, dryer soil strenghtens the bond between the foundation and the soil. Electro-osmosis is also used for removing water from clay, peat, and excavation mud. The earliest papers about electro-osmotic dewatering were presented in the works of Casagrande in 1950s [131-133].

In recent decades, some researches have investigated the use of electro-dewatering to remove water from different materials such as clay [134-136], tomato paste suspension [137,138], food processing [139], vegetable sludge, mine tailings [140], and organic humus [141]. Studies on the application of electro-dewatering to dry sewage sludge were started in the early 1990s. The main difference between sludge and other materials is that sewage sludge is composed of micro-organisms, mainly organic matters, and having high concentration of organic and inorganic material on porous water. Most studies in sludge electro-dewatering have investigated the effect of various parameters, improvement of the process design and operation, scale-up and commercialization. These will be discussed in detail in the following sections. Mathematical modeling of sludge electro-dewatering has been conducted by several authors [120,142-145]. In the past few years, commercial full-scale equipments of sludge electro-dewatering are available on the market such as CINETIK™ Linear Electro-Dewatering (Eimco Water Technologies), ELODE® electro-osmosis dehydrator (ACE Korea Incorporation), EDW (Water Technologies of Australia), and Electrokinetic (Electrokinetic Limited, UK).

2.5.3. Electro-dewatering set up and operation.

Most of the set up for electro-dewatering studies have been carried out with lab-scale devices. The devices vary in size, horizontal or vertical set up, non-pressure, pressure, and vacuum application etc. Cylindrical electro-dewatering cell with pressure application is commonly used. According to Yoshida [128], electro-osmosis can easily be combined with conventional mechanical dewatering methods to improve the rate and efficiency of water removal. There are several full and pilot scale electro-osmotic devices that have been used in conjunction with conventional dewatering devices such as belt filter press [4,127,146,147] and pressure filter press [130,148]. Durations of electro-dewatering have varied from several minutes [120,127,130,149-151] to few hours [123,149] or even some days [4,124]. The duration depends on the pressure and electrical field application.

Typically, direct electrical field has been applied in electro-dewatering process. However, interrupted DC electro-dewatering has been investigated in many studies [134,136,137,152]. It has been reported that a short interruption of power application enhances electro-osmotic flow [116-118]. However, there has been no further exploration on this topic in recent years. Use of AC electric field with periodic reversals of electrode polarity was tested by Yoshida [118].

In some experiments, a constant current at 100 A/m^2 has been applied [120,153]. However, a constant voltage from 5 to over 60 V has been used in most studies. Some researchers have reported electrical field strength as V/cm in their studies

[124,149,151,154]. Electrical field strength could accurately be calculated in horizontal experiments but it is not easy in vertical experiments, when the distance between the electrodes changes during the experiment.

The multi-stage electrode dewatering method was proposed by Yoshida [128] in which three perforated upper electrodes are vertically arranged at regular intervals within the sludge bed. This method can be expected to improve the efficiency of dewatering and reduce power consumption and it has been further investigated in Vijh's studies [155] using a term of "gate" electrode. Electro-dewatering using a flat plate rotated anode was designed by Ho and Chen [156]. In the lab-scale experimental device, the anode was able to rotate at different speeds. The rotating anode improves contact between the electrode and slurry material resulting in the dryer cake. A higher rotating speed of the anode was related to a decrease in water content of the cake.

2.5.4. Electro-dewatering of sewage sludge

In comparison to other materials, dewatering of sewage sludge is very difficult. Despite using a large amount of positively charged inorganic or organic polymers to neutralize a negatively charged polymer network of ESPs, the sludge remains hard to dewater by traditional dewatering processes. For more than 20 years, sludge electro-dewatering has been investigated in many laboratory, pilot and full scale studies. In most studies, pressure or non-pressure electro-dewatering significantly reduced water content in the final sludge cake. In some non-pressure electro-dewatering tests, electrical field was applied directly to the original waste sludge [4,123,157]. In other experiments, sludge was pre-dewatered by mechanical dewatering process, in which some of the water content was removed [124,158]. Despite a long experimental time (from several hours to several days), DS content in the final sludge cake up to 40% could be achieved.

In pressure electro-dewatering, duration of the process has ranged from several minutes to several hours. According to Saveyn et al. [130] electro-dewatering performance depends largely on the duration of electrical field application, which should be neither too short nor too long. Short electro-dewatering times were not able to induce a satisfactory dewatering effect [146,147]. However, extended application of the electrical field was not energy efficient [120,150]. In addition, an increase in the applied pressure resulted in a dryer sludge cake [149-151]. However, during electro-dewatering, sludge at the anode becomes dry. At some point, dry sludge layer is formed at the anodic site. This may deteriorate the electrical contact between the sludge and the electrodes and the increasing in contact resistance causes a drop in the electrical field. Thus, higher pressure application improves the electrical contact leading to more efficient electro-osmotic flow and dryer sludge cake.

Sludge electro-dewatering at different voltages has been presented in many studies [120,130,146,147,149-151]. Increase in voltage leads to higher water removal rates and dryer sludge cake. However, higher electrical field application consumes more energy.

The effect of polyelectrolyte conditioning on electro-watering performance has been studied by many researchers. In general, it is believed that polyelectrolyte addition is necessary to improve the solid-liquid separation by gravity or pressure filtration. Thus, polymer condition is needed to achieve smooth electro-dewatering. Smollen and Kafaar [146] considered that polyelectrolyte addition resulted in charge neutralization of sludge particles, which improves the efficiency of the electrical field application responsible for the electro-osmotic flow. Data from Snyman et al. [147] showed that the performance of electro-dewatering in conjunction with a belt filter press was not as sensitive to polymer dosages as conventional belt filter press. Laursen and Jensen [158] reported that electro-osmotic flow was not dependent on the polymer conditioning history. This finding is in line with the conclusion of Gingerich et al. [150] that excessive polymer addition was not a factor in increased DS content in the final sludge cake after electro-dewatering. Finally, Saveyn et al. [114] showed that the applied electric field improved the dewatering kinetics, regardless of the conditioning treatment. The conditioning polyelectrolyte characteristics and dose had a major effect on water removal during pressure dewatering of sludge, but did not have a significant effect on the electroosmotic water transport efficiency. Also it was found that even at high polyelectrolyte doses, leading to positively charged sludge flocs, negative surface charges are still present inside the sludge matrix. This was related to the hypothesis of Mikkelsen [159], who suggested that the total amount of charges present in activated sludge could be several orders of magnitude larger than the (external) amount that is neutralized during polyelectrolyte conditioning. A large amount of the charges is present in the relatively inaccessible exopolymer matrix between the individual sludge floc constituents.

The energy consumption of electro-dewatering has been calculated in several studies. However, the power consumption of sludge electro-dewatering method in the literature is multiform and difficult to compare and analyze. It depends on the electrical field application, operation, and unit expression. The electro-dewatering energy has been expressed as kWH/kgDS (kWh per kg of DS) by many researchers [120,147,148,150]. However, the energy consumption is strongly dependent on the initial DS content of the sludge which is different in each study. Perhaps, the best way is to calculate the energy per the additional amount of water removal in comparison to normal dewatering without electrical field application (kWh per m3 of removed water- kWh/m^3). By using this calculation, Gazbar et al. [149] and Saveyn et al. [130] showed that electro-dewatering consume from 46 to 445 kWh/m^3 depending on voltage application. This power consumption was lower than in conventional thermal evaporation methods, where the energy requirement was 617 kWh/m^3 based on a theoretical calculation [160] and up to 1200 kWh/m^3 in an industrial application [149]. Gingerich et al. [150] demonstrated that the energy consumption is not uniform during electro-dewatering process but it increases with the augmentation of cake dryness. This could be due to the fact that the last water fractions become increasingly difficult to remove because of the increasing binding strength. A linear relationship between the energy consumption and the amount of additional water removal was reported [114,158].

Gingerich et al. [150] and Yuan and Weng [124] made an economic analysis of the electro-dewatering process, taking into account of the additional energy costs and possible savings by transport and disposal, and came to the conclusion that electro-dewatering to intermediate moisture contents is the most cost-efficient. Based on a pilot-scale sludge electro-dewatering test in a diaphragm filter press, Saveyn et al. [130] considered that electro-dewatering method was very well suited to deliver dry filter cakes of sewage sludge at moderate energy consumption. Depending on local market prices for investments, operating and sludge disposal costs, this technology may lead to important savings in the sludge management process.

In recent years, the additional values of electro-dewatering have been studied by several researchers. Concurrent removal of oil and grease during dewatering of oily sludge was investigated by Yang et al.[123]. In additional, simultaneous disinfection of sewage sludge has been evaluated, showing that a high DS content can be achieved while removing fecal coliforms [161,162].

Although sludge electro-dewatering have been studied since early 1990s. However, some factors effecting sludge electro-dewatering have not received sufficient attention. For example, effect of biological, physical treatments such as anaerobic digestion and freeze/thawhas not been investitaged. On the other hand, not only electro-osmosis and electro-phoresis but also electrolysis and electro-migration occurred under electrical field application. The dissolution and migration of elements during sludge electro-dewatering can be related to the potential risk for the environment. However, only few works have been reported so far.

3. Aims of the study

In this study, the aims were:

- To study whether sludge dewatering with conventional sand-drying beds could be enhanced by applying electrical current.
- To investigate the effect of different operating conditioning on removal of water and water content in the final sludge cake. The operating conditions included sludge types, sludge pre-treatment (freeze/thaw and polyelectrolyte addition), different voltage, off-time interrupted application, and sludge loading rates.
- To study the electro-migration of organic and inorganic compounds from sludge in general and fractions of metals in particular.

4. Material and methods

4.1. Sludge samples

Sludge samples were taken from Mikkeli WWTP (SouthEastern Finland) with a capacity of 13000 m^3 d^{-1}, corresponding to 44000 population equivalent. The main treatment unit was activated sludge treatment for BOD removal and nitrification. Calcium hydroxide ($Ca(OH)_2$), ferrous sulfate ($FeSO_4$), poly aluminum chloride and polymers were added to stabilize pH, remove phosphorous and improve settling capacity. Two types of sludge were used for experiments. The most important sludge characteristics and concentrations of micro and trace metals are presented in Table 4.1. The first type of sludge (raw sludge) was collected from the influent of an anaerobic

Table 4.1 Main characteristics and concentrations of micro and trace metals of sludge samples from Mikkeli WWTP

Parameters	**Sludge before anaerobic digestion**	**Sludge after anaerobic digestion**
Temperature (^oC)	10.3 - 13.8	33.4 - 34.0
Electric conductivity-EC (mS cm^{-1})	2.46	7.16 – 7.50
pH	5.98-6.43	7.16 -7.38
Alkalinity (g kg^{-1} $CaCO_3$)	3.42 – 3.65	6.9-10.5
Total Solid- TS (%)	5.07 – 5.48	3.17 - 2.87
Volatile Solid –VS (%)	3.72 – 4.13	1.53 - 1.70
VS/TS (%)	73.3 – 75.2	55.1 – 53.4
Zeta Potential (mV)	-9.9 to -8.1	-15.9 to -14.0
Capillary Suction Time – CST (s)	385- 417	308 – 346
Fe (g kg^{-1}DS)	-	165 – 170
Ca (g kg^{-1}DS)	-	18.2 - 20.3
Mg (g kgDS^{-1})	-	2.58 – 3.32
P (g kg^{-1}DS)	-	43.6 – 46.4
Co (mg kg^{-1}DS)	-	8.6-8.8
Cu (mg kg^{-1}DS)	-	193-183
Cr (mg kg^{-1}DS)	-	51.6– 74.6
Mn (mg kg^{-1}DS)	-	294-433
Ni (mg kg^{-1}DS)	-	44 -47
Pb (mg kg^{-1}DS)	-	29.7-31.1
Ti (mg kg^{-1}DS)	-	660-766
Zn (mg kg^{-1}DS)	-	474– 615

(-) not measurement

digester, mainly composed of primary and secondary sludge mixture (**II**). The second type of sludge samples were collected from the effluent of anaerobic digested unit (**I-V**). The digester was continuously operated with 17 to 20 days retention time at mesophilic conditions (35-38°C). After sampling at the WWTP, the sludge was stored at 5 °C prior experiments. Before experiments, sludge was taken out of the cold room to reach the room temperature.

4.2. Sludge conditioning

The original raw and anaerobically digested sludge without any conditioning were used in many experiments (**I,II**). To study the effect of alkalinity on electro-dewatering, raw sludge with alkalinity ($NaHCO_3$) added to the same level as original anaerobically digested sludge (10 g kg^{-1} wet sludge as $CaCO_3$) was used for some experiments (**II**)

A deep freezing room was used to freeze the anaerobically digested sludge at -5, -10, -15, -20, and -25 (±1) °C (**III, IV**). The preliminary experiments (at -5 °C) showed that sludge was completely frozen within 36 h, therefore the freezing time of 36 h was adopted for all experiments. According to Ormeci and Vesilind [104], 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. In natural freezing treatments, sludge samples (5 l) were kept outdoors at the beginning of January to the end of March, 2008. The average temperatures in January, February, and March are - 9.3; -8.9 and -4.3 °C, respectively. However, the temperature fluctuated from +5 to -30 °C. (**III**).

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 [114]. 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. Then, various polymer dosages equivalent to 5, 10, 15, 20 kg ton^{-1}DS (kg polymer per ton of DS) (**III,IV**) or a fixed dosage of 15 kg ton^{-1}DS (**V**) were added. Sludge and polymer mixtures were 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 dewatering tests.

4.3. Experimental set up and procedure

Laboratory scale sand-drying beds coupled with electro-dewatering (**I,II**) were conducted in acrylic reactors (55 cm high, 17 cm wide and 31 cm long) as depicted in Figure 4.1a. A 10 cm thick gravel bed was placed on the bottom of the reactors, followed by a 10 cm thick sand bed. The particle size of the sand was 0.5 -1.0 mm (22.6%); 0.2 - 0.5 mm (77.4 %). A stainless steel mesh cathode (0.5 mm) was installed on the surface of the sand bed. The sludge was then fed into the reactors, and an anode made of inert titanium plate (2 mm thick) was placed on the top of the sludge cake. The reactors were covered with aluminum foil to minimize natural water evaporation, and removed water was collected from the bottom of the reactors. The electrodes were connected to a DC power supply providing a constant voltage.

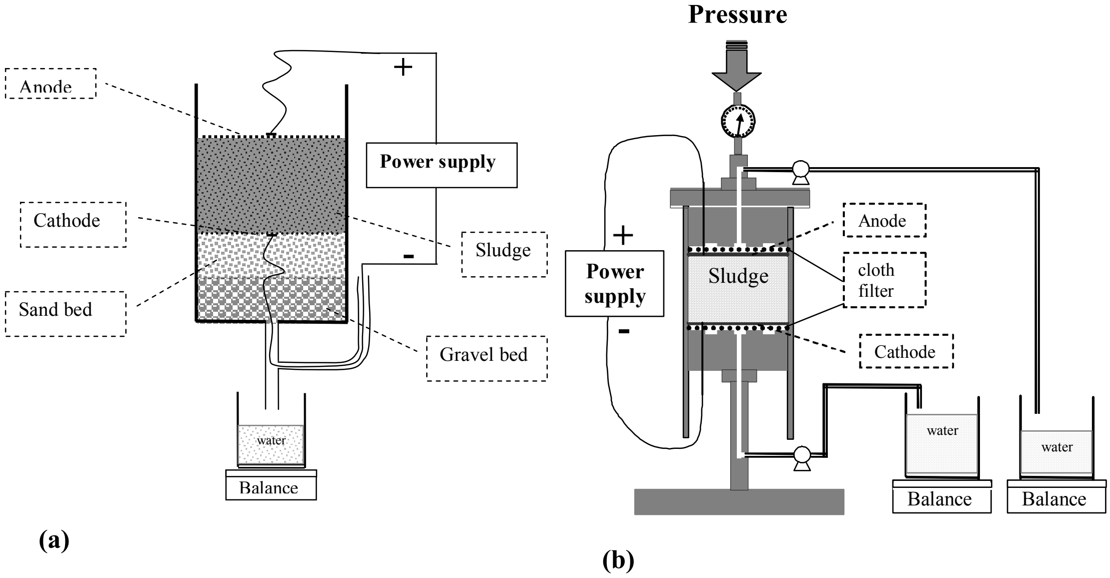

Figure 4.1 Schematic representation of the laboratory scale (a) electro-dewatering sand drying bed, (b) electro-dewatering reactor with applied pressure

Figure 4.1b shows a schematic representation of a pressure driven electro-dewatering reactor (**II-V**). The reactor was made of polyvinyl chloride (PVC) and it was 9.8 cm in diameter and 30 cm in length. The similar stainless steel mesh and titanium plate were used as the cathode and the anode, respectively. Polypropylene cloth filters (Z104256 PP, Sigma-Aldrich), with permeability factor of 7.62 (m^3 m^{-2} min^{-1}) were placed under sludge and the electrodes. Sludge was subjected to a constant pressure (**II-V**). Removed water was collected from both the anodic and the cathodic side. After every electro-dewatering experiment, the cloth filters in both the cathodic and anodic sides were replaced by the new ones.

All electro-dewatering experiments were performed at room temperature (22 ±1 ^{o}C). Table 4.2 shows experimental conditions in different studies. The different DC of 3, 5, 10, 15, 20 and 30 V were applied in sand-drying beds coupled with electro-dewatering experiments (**I**). In the other experiments, constant voltages were used (**II-V**). Besides of application of continuous DC voltage which is denoted as DC electro-dewatering. There was another mode of application: interrupted DC voltage, denoted as IS(t_1/t_2) electro-dewatering where t_1 was the on-time and t_2 was the off-time, both in seconds. In the study **V**, interrupted electro-dewatering was performed at IS(45/15), IS(30/30), and IS(15/45). To assess the effect of electrical treatment, the blank experiments were performed without the applied electricity in all studies.

Table 4.2 Overview of experimental conditions in electro-dewatering studies.

Study	**Sludge type**	**Pressure**	**Voltage**	**Loading rate (kg DS/m^2)**
I	Anaerobically digested sludge	None	3-30V	6
II	Anaerobically digested sludge Raw sludge Raw sludge with added alkalinity	None 4 bars	15 V	6
III	Anaerobically digested sludge freeze/thaw at different temperature and polymer adding with different doses	5 bars	20 V	3-20
IV	Anaerobically digested sludge freeze/thaw at different temperature and polymer adding with different doses	5 bars	20 V	3-20
V	Anaerobically digested sludge with added polymer at 15 kg/ ton DS	5 bars	40V off-time interruption	15

To investigate the effect of sludge loading rate on the final sludge cake, experiments were conducted using 3, 5, 10, 15, and 20 kg DS/m^2 sludge loading rates (**III, VI**). In the other studies, the amount of sludge introduction to electro-dewatering device was fixed to a constant sludge loading rate.

After electro-dewatering process, sludge cakes were removed from dewatering devices. Sludge samples were taken at the anode, the cathode, and the sludge cake for quantitative analysis. Moreover, to avoid discrepancies and ensure the reliability of data, all the pressure dewatering experiments were performed in duplicate.

4.4. Analytical methods

During electro-dewatering, current fluctuations were monitored with a multimeter (Fluke 110, The Netherlands) and electrical balances were employed to measure the amount of removed water from the anode and cathode. pH of sludge samples and removed water were measured with a pH meter (WTW pH730, Germany). The temperature of sludge cake was measured with an electronic thermometer (Fluke53 II, USA).

In order to measure the zeta potential, each sludge sample was first diluted with a supernatant that was obtained by centrifuging this sludge sample at 4000 rpm for 10 minutes. After that the zeta potential was determined with Malvern zeta sizer (Nano-Series Instrument, England). The concentrations of volatile fatty acids (VFAs) in removed water were analyzed with a gas chromatography (GC) (Agilent Technologies 6890 N) equipped with a capillary column (Agilent HP-FFAP) (**II**). The total organic carbon (TOC) and inorganic carbon (IC) were determined with a TOC analyzer (TOC-VCPH, Shimadzu, Japan) (**I,II,IV**). Chloride concentration (Cl^-) was measured by capillary electrophoresis system (Beckman Coulter, U.S.A) and nitrogen in form of ammonium ($N-NH_3$) was measured by Dr. Lange's test kits (LCK 302, Germany) (**IV**).

Other characteristics of the sludge and removed water such as alkalinity, dry solid (DS), volatile solids (VS), CST, and COD were determined by using Standard Methods [163].

*Pseudo-total metal digestion (***IV,V***)*

To determine the total amount of metal elements in the sludge, the samples were digested with aqua regia (HCl/HNO_3 1:3) using a microwave digester (Perkin Elmer, Anton Paar GmH, Austria) [164]. About 0.5 g DS of sludge samples were treated with 10 ml aqua regia in closed pressured vessels. The digestion procedure was programmed in three steps: 6 min of increase in temperature to 200 ^{o}C, 30 min of treatment at 200 ^{o}C and 30 min of cooling down to a room temperature. After cooling, the digested sample was transferred into a 100 ml volumetric flask and diluted to the mark with Milli-Q water. Before chemical analysis, the solution was centrifuged at 4000 rpm to remove small particles. Inductively coupled plasma optical emission spectrometry (ICP-OES) (ICAP-6000, Thermo, England) was used to determine the metal concentrations and that the experimental details are given in IV and V.

*Revised BCR sequential extraction (***V***)*

Revised BCR (Community Bureau of Reference in 1987) sequential extraction protocol was undertaken based on the method described by Mossop and Davidson [165]. Approximately 1g DS of sludge samples were used for the extraction of metal fractions.

- Step 1. (Exchangeable fractions): acetic acid extraction, this extraction step is related exchangeable metals and metals bound to carbonate species. The sludge sample was extracted with 40 ml of 0.11 M acetic acid (CH_3COOH) at pH 7 for 16 h.

- Step 2. (Reducible fractions): hydroxylamine hydrochloride extraction, the fraction is associated with iron and manganese oxides. In this step, the residual from step 1 was treated with 40 ml of 0.5 M hydroxylamine hydrochloride (NH_2OH-HCl) at pH 1.5 for 16 h.
- Step 3. (Oxidation fraction): hydrogen peroxide oxidation and ammonium acetate extraction, the metals species bound to organic matter and sulfides. The residual from step 2 was oxidized by 20 ml of 30% hydrogen peroxide (H_2O_2) at pH 2.0 and 85 ^{o}C for 2 h. Then, the oxidation fractions of metals were extracted with 50 ml of 1 M ammonium acetate (CH_3COONH_4) at pH 2.0 for 16 h.
- Step 4. (Residual fraction: microwave aqua regia extraction, species associated with mineral matter. The residual from step 3 was treated with 10 ml of aqua regia in microwave digestion as in Pseudo-total metal digestion protocol.

For pH adjustment, 6 M potassium hydroxide (KOH) and hydrochloric acid (HCl) solutions were used. The extraction liquids and solids were separated by using centrifuge at 4000 rpm for 20 min. ICP spectrometer was used to determine concentrations of metals in the extracts. After every step, sludge residual samples were thoroughly washed with Milli-Q water.

4.5. Statistics (IV)

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.

5. Results and discussion

5.1. Current density during electro-dewatering

Figure 5.1 shows the current density fluctuation during the electro-dewatering process under different experiment strategies. Current density in pressure driven experiments was significantly higher than in the non-pressure experiments using the same kinds of sludge (Figure 5.1a,b). This might be mainly due to the good contact between the anode and the sludge cake under pressure condition. Indeed, similar phenomenon was observed by Ho and Chen [156] who studied electro dewatering of bentonite with anode rotating at different speeds.

The EC of original sludge samples are shown in Table 4.1. After the addition of $NaHCO_3$ into the raw sludge, electrical conductivity increased from 2.5 to 10.9 mS cm^{-1}. Regardless of the experimental strategies, e.g. with or without applied pressure, the current density in the experiments using raw sludge with added alkalinity was always higher than during experiments with raw and anaerobically digested sludge without added alkalinity (Figure 5.1a,b) (**II**).

During initial stages of the electro-dewatering tests using polymer conditioned sludge samples, the current density sharply increased to the highest value (Figure 5.1c,d). In comparison to electro-dewatering experiments using original sludge samples, the highest current density was not observed in initial stages Figure 5.1a,b. Moreover, the highest current density was also observed with the lowest sludge loading rates (Figure 5.1c). It could be explained by Ohm's law (5.1)

$$J = \sigma \mathrm{E} \tag{5.1}$$

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}) (**IV,V**).

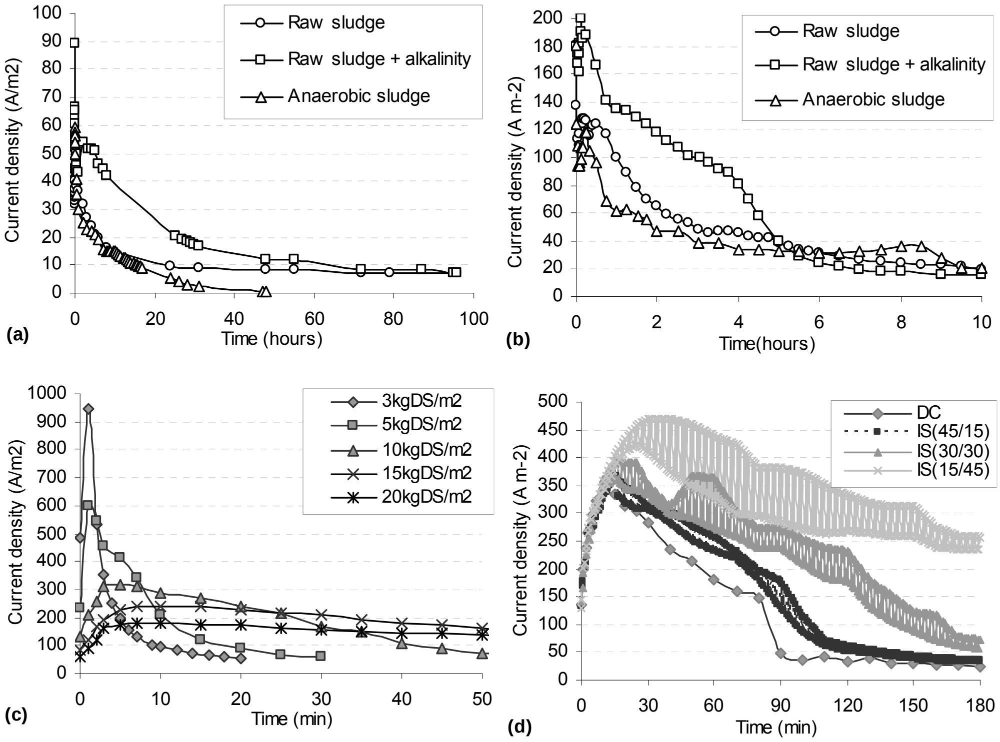

Figure 5.1 Current density fluctuations during electro-dewatering processes under (a) non-pressure, (b) pressure-driven, (c) pressure-driven with different sludge loading rate (d) pressure-driven with interrupted voltage application.

It can be assumed that the migration of ions and the amount of water in sludge did not have any effect on the conductivity (σ) during initial stages of electro-dewatering process. The lower sludge loading rate was related to the shorter distance between the electrodes because of the constant voltage application and the shorter distance between the electrodes resulted in an increase in electrical field (E). Therefore, the lower sludge loading rates resulted in shorter distances between the anode and the cathode, causing higher current density during electro-dewatering process with different sludge loading rates (**IV**).

Figure 5.1d, shows the current density fluctuation under the off time interrupted electro-dewatering process. According to Rabie et al. [117], during one cycle of interrupted electro-dewatering, the current was highest when the power was on. Thereafter, the current decreased until the end of cycle. Similar phenomenon was observed in IS experiments (**V**). Therefore, significant fluctuation in current density was shown in all off-time interrupted experiments. In addition, it was found that longer off-time resulted in higher current density and the fluctuation in current also extended over a wider range (Figure 5.1d). For example, after an hour of dewatering, in IS(45/15) electro-dewatering, the current density fluctuated in the range from 258 to 230 Am^{-2} in comparison to IS (15/45) experiment in which the fluctuation of current density ranged from 439 to 328 A m^{-2} (**V**).

Furthermore, the decline of the current density until the end of experiments was observed in all electro-dewatering tests. It may be associated with the decreased electrical resistance of sludge towards the end of the electro-dewatering process [166] and the loss of contact between the anode and dry sludge [156] (**II, IV,V**).

5.2. Effect of electrical field on electro-dewatering

The amount of the removed water and water removal rates during electro-dewatering process at various voltage applications is presented in Figure 5.2. In general, the applied electric current significantly increased the amount of the removed water

(Figure 5.2a). This was also observed by several other researchers [120,129,156], who investigated electro-dewatering of sludge and dredged sediments. An increase in the applied voltage resulted in higher water removal rates (Figure 5.2b). As expressed in Equation 2.2, electro-osmotic flow strongly depends on the electrical field strength (E). Because of the constant sludge loading rate, the distance between the cathode and the anode was the same in all the experiments. Therefore, an increase in the applied voltage resulted in a higher electrical field strength that led to a higher dewatering rate (Figure 5.2b) (**I**).

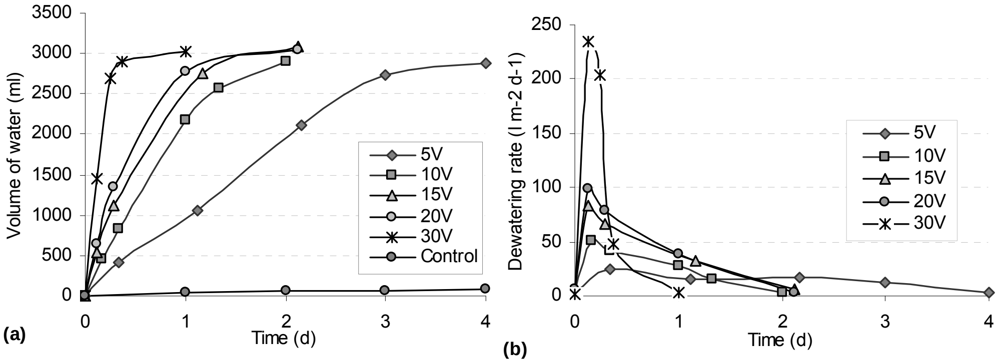

Figure 5.2 Amount of (a) removed water and (b) water removal rates as a function of time during the electro-dewatering process at different voltage application.

An increase in the applied voltage (from 3 to 10 V) resulted in an elevated DS content in the final sludge cake (Figure 5.3a). However, regardless of the subsequent increase in voltage (from 10 to 15, 20 and 30 V), the DS in the final sludge cake did not change (39 to 41 %). During electro-dewatering process, dry layer with high electrical resistance may be formed at the anode [156]. Thus, when sludge dried out at the anode because of the electro-osmotic flow, which transported water towards the cathode, it became hard and inflexible. Without the applied pressure, the contact between the anode and the dried sludge layer was inadequate for the efficient electro-osmotic flow to take place (**I**). On the other hand, due to pressure-driven electro-dewatering process with different sludge loading rates, it was observed that a decrease in the sludge loading rate significantly increased the DS content in the final sludge cake. In comparison to blank experiments without the applied electric field, the DS content in the sludge cake was the same regardless of the sludge loading rate (Figure 5.3b). When higher sludge loading rates were employed, the distance between the anode and the cathode increased. Because of the applied constant voltage, the lower sludge loading rate resulted in the higher electrical field strength (E), hence higher DS content in the sludge cake was observed. The similar result was reported by many researchers [123,130,167] (**III**).

In addition, Figure 5.3c shows the DS content in final sludge cake after DC and IS electro-dewatering. The low DS content in the final sludge cake was observed in IS experiments with longer off-times interruption. According to Rabie et al. [117], interruption with very short off-time application removed more water than DC in IS electro-dewatering of clay suspensions. However, if the off-time is too long, water from lower part was drawn upward by capillary force toward the dryer part [116]. Moreover, longer off-time interrupted electro-dewatering also had a negative effect on removal of water. Long off-time interruption limited the electrical field strength across the sludge segment and hence reduced electro-osmotic flow. Therefore, the DS content in the final sludge cake in long IS electro-dewatering was lower in comparison to DC electro-dewatering (**V**).

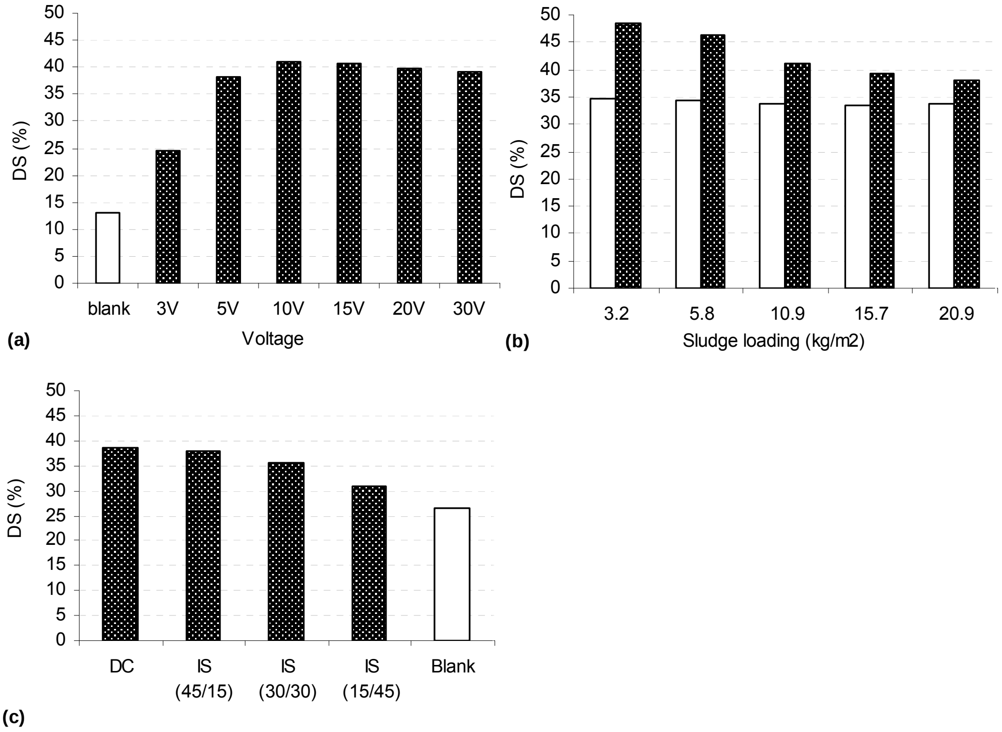

Figure 5.3 DS content in sludge cake after electro-dewatering processes with different (a) voltage, (b) sludge loading rate, and (c) interrupted voltage application (note that the duration of the experiments varied).

5.3 Effect of sludge type on electro-dewatering (II)

Due to non-pressure electro-dewatering, the DS content in the final sludge cake strongly depended on the sludge types used for experiments. In all the blank experiments after a month of dewatering process using natural sand drying bed with anaerobically digested, raw and raw sludge with added alkalinity, the DS of the final sludge cake was similar (about 13%). The sand drying bed coupled to electro-dewatering process resulted in an increase in the DS content of the final sludge cake in all the experiments (Table 5.1). In comparison to blank experiment, DS of the final sludge cake increased from 13.2% to 40.6% in experiment with anaerobically digested sludge after two days. These findings are similar to other research efforts to increase the DS content in a final sludge cake [123,157]. However, in experiments using raw sludge with and without added alkalinity, DS content in the sludge cake only increased from 13.5% to 17.7 and 16.3%, respectively. Moreover, water content in sludge samples at the anode was found higher than sludge samples the cathode (Table 5.1).

Table 5.1 Sludge solid content before and after electro-dewatering experiments

		Non-pressure electro Dewatering			**Pressure driven electro dewatering**		
sample point	**Type of sludge**	**DS (%)**	**VS (%)**	**VS/TS (%)**	**DS (%)**	**VS (%)**	**VS/TS (%)**
Initial feed	Anaerobic	7.5	3.7	49.1	6.9	3.7	52.7
	Raw sludge	8.6	6.3	73.7	6.7	4.9	73.3
	Raw sludge + alkalinity	8.3	5.7	68.2	7.3	5.1	69.6
Sludge cake	Anaerobic	40.6	22.0	49.2	40.2	21.2	52.7
	Raw sludge	16.3	12.4	76.3	36.0	26.7	74.2
	Raw sludge + alkalinity	17.7	12.0	67.9	34.9	24.4	70.0
By the anode	Anaerobic	44.1	25.5	57.8	43.8	30.1	68.8
	Raw sludge	14.4	11.8	82.0	31.6	28.0	88.4
	Raw sludge + alkalinity	15.0	12.7	84.1	36.4	30.4	83.5
By the cathode	Anaerobic	22.5	9.7	43.1	28.4	13.3	46.7
	Raw sludge	24.7	11.8	47.9	33.2	18.6	56.1
	Raw sludge + alkalinity	20.4	10.0	49.0	27.0	17.4	64.6

The acidic pH in sludge at the anode decreased electro-osmotic flow, which was in agreement with previous studies [125,168]. In non-pressure anaerobically digested sludge experiments, the pH of the final sludge cake at the anodic side was 4.0 and 2.3 as well as 2.0 in experiments using raw sludge with and without added alkalinity, respectively. The pH of sludge sample at the anode depends on pH buffering capacity of original sludge and current density due to electro-treatment [169]. It is well documented that the pH drop is related to the reduction of the absolute value of zeta potential, thus the decrease in pH reduced the electro-osmotic flow during DC application [122,125,170]. In the experiment with anaerobically digested sludge, low current density (Figure 5.1a) and high pH buffering capacity (Table 4.1) may have kept zeta potential constant or reduced it slightly, hence electro-osmotic flow may have transported water from the anode towards the cathode, which resulted in a lower water content in sludge at the anode in comparison to the cathode (Table 5.1). On the other hand, in the experiment using raw sludge with lower pH buffering capacity (Table 4.1), or in the experiment using raw sludge with added alkalinity with also high pH buffering capacity and high current density (Figure 5.1a), pH at the anode significantly decreased. Thus as argued by Eykholt [122,171], zeta potential may have become zero or slightly positive (Figure 5.4a), therefore, resulting in reverse electro-osmotic flow. Therefore, water content in sludge by the anode was higher than by the cathode (Table 5.1). Also, similar was observed by Yoshida et al. [118] who studied electro dewatering efficiency of sludge under direct and alternating currents.

In pressure-driven electro-dewatering, water was removed at both cathodic and anodic sites. Thus, the impact of sludge type on DS content in final sludge cake was reduced. After pressure driven electro-dewatering, DS content in the final sludge cake in the experiment using anaerobically digested sludge was 40%, and almost as high in experiments using raw sludge with (36%) and without (35%) added alkalinity (Table 5.1). In comparison to non-pressure electro-dewatering process when only raw and raw sludge with added alkalinity were used, pressure driven electro-dewatering significantly reduced water content in the final sludge cake. The effect of sludge type on the amount of water removed at the anode and the cathode are presented in Figure 5.4b. In experiment using anaerobically digested sludge, 81% of water was removed at the cathode in comparison to 60% in experiment with the raw sludge.

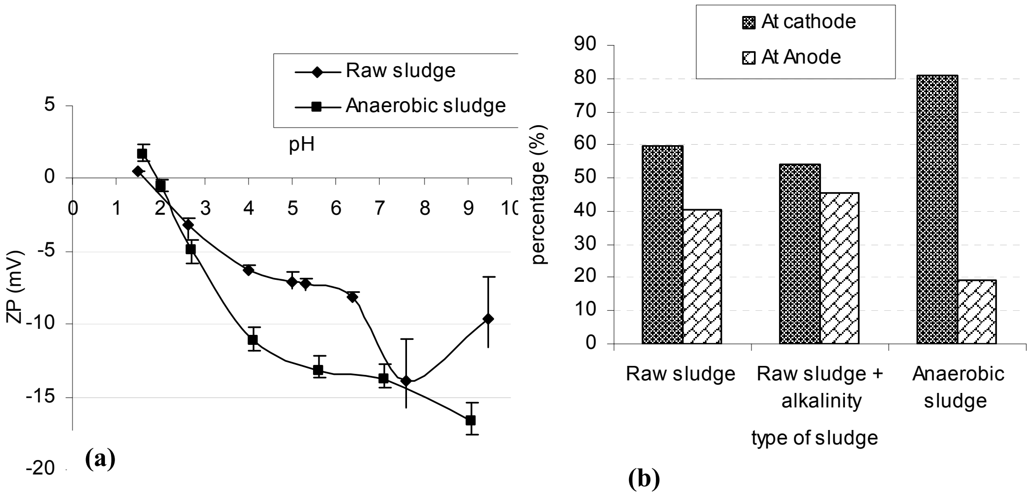

Figure 5.4 (a) Average zeta potential at different pH, (b) Water removal from the anode and the cathode during pressure driven electro-dewatering process

Furthermore, in comparison to original sludge, the VS/TS (Volatile Solid per Total Solid) ratio in sludge cake was always smaller by the cathode (48%) and higher by the anode (74 to 82%) regardless of the experimental strategy (Table 5.1).

5.4. Effect of polymer and freeze/thaw conditioning on electro dewatering (III)

Polyelectrolyte and freeze/thaw conditioning shows the increase in sludge dewaterability by reduction of CST (Figure 5.5). The decrease in freezing temperature was mainly associated with an increase in freezing rates. The slow freezing rate resulting in the significant improvement of the sludge dewaterability was reported by many researchers [108,109,172]. Therefore, higher freezing temperature related to the increase in sludge dewaterability (Figure 5.5a). However, in electro-dewatering experiments using sludge samples frozen at different temperatures, water content in the final sludge cake was found to be the same regardless the freezing temperature (Figure 5.6a). This could be due to the fact that electro-dewatering process seems to be less sensitive to sludge characteristic than other dewatering processes [128].

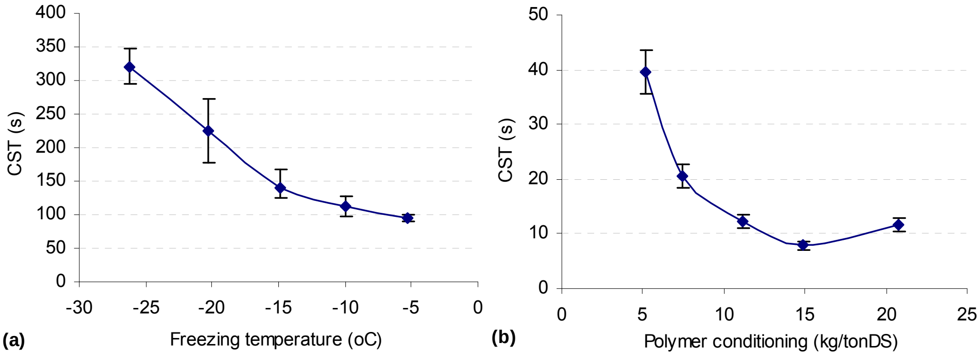

Figure 5.5 CST as a function of (a) freezing temperature and (b) polymer dosage.

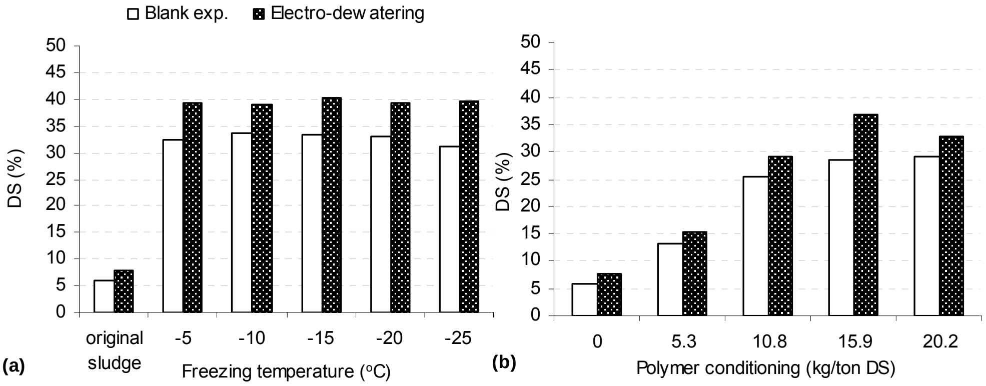

Figure 5.6 Solid content of the final sludge cake, sludge by the anode and the cathode due to electro-dewatering using freeze/thaw sludge at different temperatures (a) and different polymer dosage conditioned sludge (b).

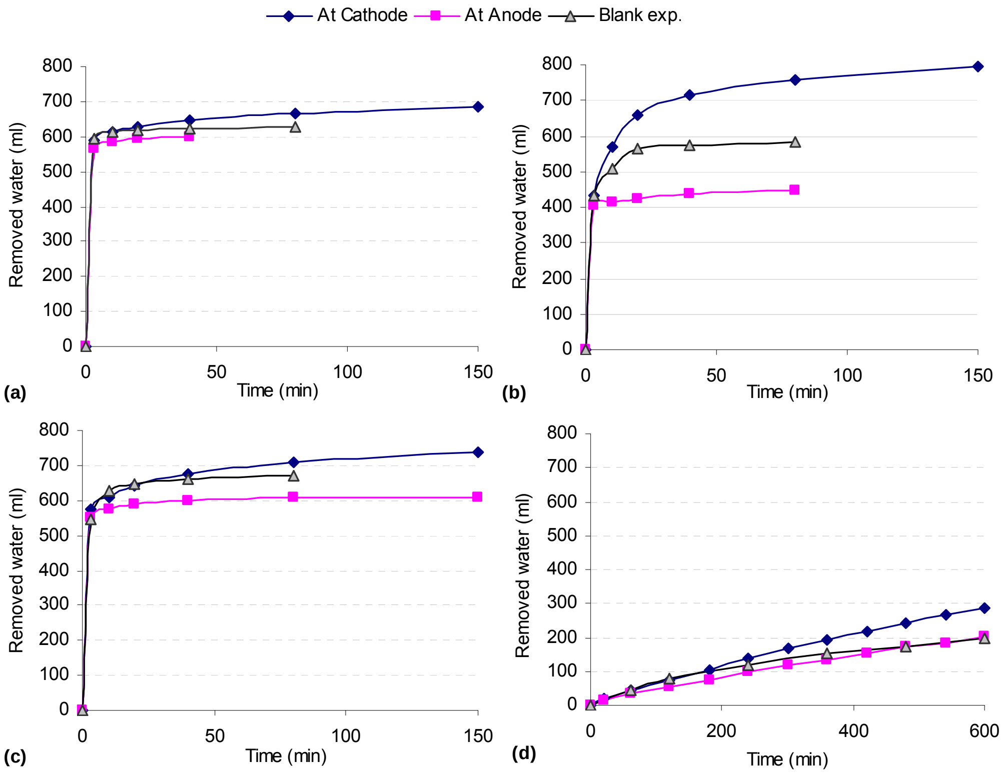

Figure 5.7 The amount of removed water at the anode and the cathode during pressure driven electro-dewatering process using sludge samples with different pre-conditioned methods (a) freezing at -5 ^{o}C, (b) freezing at -25 ^{o}C, (c) 15 kg/ton DS polymer addition, (d) original sludge without treatment.

Figure 5.7 shows the volumes of removed water as recorded at the anode and the cathode during electro-dewatering treatment of sludge samples with different conditioning methods. When the low level direct electric current was applied, electro-osmotic flow transported water from the anode to the cathode [120,173]. Therefore, the amount of water removed at the cathode was significantly higher than at the anode. A decrease in freezing temperature from -5 to -25 ^{o}C significantly increased the CST from 94 to 319 s (Figure 5.5a), which can be attributed to an increase in removed water at the initial state of the experiments. Indeed, during the experiments with sludge samples frozen at -5 ^{o}C (Figure 5.7a), 90% of water was already removed during initial 3 min in comparison to 68% during initial stages of experiment using sludge samples freezing at -25 ^{o}C (Figure 5.7b). However, the total amount of removed water in both experiments was the same at the end of the treatment. This might be related to similar water content in the final sludge cake regardless the freezing temperature in above discussion (Figure 5.6a).

An increase in the polymer dosage resulted in an improved sludge dewaterability (Figure 5.5b). Similar observations have been made by several authors [174-176]. In experiments using sludge samples with 5, 10 and 15 kg/ton of added polymers, electro-dewatering lasted for 10, 4, and 2.5 hours, respectively. This shows that an increase in polymer dose considerably reduces the dewatering time. Moreover, the increase in polymer dose from 5 to 15 kg/ton of DS not only reduced the dewatering time but also significantly decreased the water content in the final sludge cake in both, electro-dewatering and blank experiments (Figure 5.6b). After 10 min, the water removals at both sides in experiments using sludge samples with 0, 5, 10 and 15 kg/ton of added polymers were 2.3, 11, 46 and 57%, respectively. It was assumed that during the initial stage of electro-dewatering process, electrokinetic phenomenon did not significantly contribute to the removal of water from the sludge. The filtrate flow rate at the anode and the cathode may be expressed by the following Equation 5.2 [177,178]:

$$Q_p = \frac{dV_p}{dt} = \frac{\Delta p_H A}{\eta(r_c L + R_m)} \tag{5.2}$$

Where Q_p is the pressure-driven filtrate flow rate, V_p is the volume of filtrate, Δp_H is the hydraulic filtration pressure, A is the filter surface area, η the viscosity of the liquid medium, r_c is the filter cake resistance, L is the cake thickness, R_m is the filter medium resistance.

During the dewatering process, Δp_H and A were constant, because of the same experimental conditions with applied constant pressure. Due to the short time of experiments (10 min), the filter medium resistance (R_m) was assumed constant. During the dewatering process using original or polymer conditioned (5 kg/ton) sludge, the filter cake resistance (r_c) is high due to the applied pressure and the sludge cake thickness (L) subsequently increases, hence, the filter flow rate (Q_p) rapidly reduces, resulting in a small amount of removed water at beginning of experiments (Figure 5.7d). Therefore, in experiments using the original sludge samples, sludge cake was not formed, resulting in the high water content in the final sludge cake (Figure 5.6b). On the contrary, in experiments using polymer conditioned sludge (10 and 15 kg/ton of added polymers), the viscosity of the liquid medium may have increased and the filter cake resistance decreased. Because of that the filtrate flow rates did not rapidly decrease or even remained constant at the beginning of the experiment due to an increase in the sludge cake thickness, which consequently resulted in the higher initial water removal (Figure 5.7c). Furthermore, higher initial water removal significantly reduced the distance between the electrodes resulting in an increase in electrical field strength (E) which was discussed above. The higher electrical field strength facilitates the electro-osmotic follow which related to dryer sludge cake (Figure 5.6b) and shorter dewatering time.

5.5. Migration of organic and inorganic compounds during electro dewatering process

*5.5.1. Migration of organic matter (*II*)*

Migration of organic matter from the cathode to the anode was observed regardless of the sludge type (Table 5.2). Municipal sewage sludge, especially raw sludge, usually contains negatively charged organic substances such as fatty acids (acetic, propionic, butyric, vateric acids), humus and other organic materials that may be transported towards the anode during applied electric current. Indeed, acetate ions are also found to be moving towards the anode under the applied electric current in electrokinetic remediation process [179]. In non-pressure dewatering experiments, the organic matter accumulated at the anode. Therefore, the concentration of COD and TOC in removed water at the cathode decreased in comparison to blank experiments (Table 5.2). When pressure driven electro-dewatering process was applied, water was removed from both,

Table 5.2 COD and TOC concentrations in removed water after electro-dewatering experiments

Pressure condition	**Types of sludge**	**Blank experiments**		**At the cathode**		**At the anode**	
		COD ($g\ l^{-1}$)	**TOC ($g\ l^{-1}$)**	**COD ($g\ l^{-1}$)**	**TOC ($g\ l^{-1}$)**	**COD ($g\ l^{-1}$)**	**TOC ($g\ l^{-1}$)**
Non-pressure electro dewatering	Anaerobic	1.29	0.37	0.74	0.25	-	-
	Raw sludge	8.24	2.78	5.66	2.00	-	-
	Raw sludge + alkalinity	10.21	3.87	9.67	3.37	-	-
Pressure driven electro dewatering	Anaerobic	0.94	0.30	0.69	0.24	1.57	0.62
	Raw sludge	11.68	4.06	2.12	0.70	25.91	8.36
	Raw sludge + alkalinity	14.02	4.78	5.28	3.54	28.49	9.47

- : water not removed

the anodic and the cathodic sides, thus, organic matter did not only accumulate in sludge at the anode but was also removed from sludge by the water flow. Therefore, the COD and TOC concentrations in removed water were higher at the anode and lower at the cathode (Table 5.2).

5.5.2. Migration of soluble ions (**IV,V**)

Figure 5.8 presents Na^+ concentrations in the removed water at the anode and the cathode during electro-dewatering process with different sludge loading rates and interrupted voltage application. Na^+ concentration decreased at the anode in comparison to the blank experiments. At the cathode, there was a significant increase in Na^+ concentration to a peak value at the beginning, followed by a decrease until the end of the treatment (Figure 5.8a). Similar fluctuation of Na^+ was also observed by Fernandez et al. [121] who investigated electro-kinetic transport of Na^+ in kaolin. Moreover, a decrease in the sludge loading rate resulted in the shorter time to achieve the peak concentrations of Na^+. Similar phenomenon was also observed with off-time interrupted electro-dewatering, in which the longer off-time interruption led to a longer delay in reaching the peak concentration of Na^+ (Figure 5.8a). According to Acar and Alshawabkeh [122] and Fernandez et al. [121], the relationship between electro-migration of ions and the electrical potential gradient can be explained by Equation 2.3. Thus, the decrease in the sludge loading rates (from 20 to 5 kgDS m^{-2}) increased the electrical field strength from 1.5 to 5.3 V cm^{-1}. On the other hand, due to IS electro dewatering, long off-time interruption might reduce the amount of electrical field strength through the sludge segment. Therefore, it was assumed that an increase in electrical potential gradient also resulted in much faster electro-migration rates and thus shorter time to reach the elevated concentration of ions at the cathode (Figure 5.8b). The electro-migration of K^+ ions showed the same trend as Na^+ (**IV,V**).

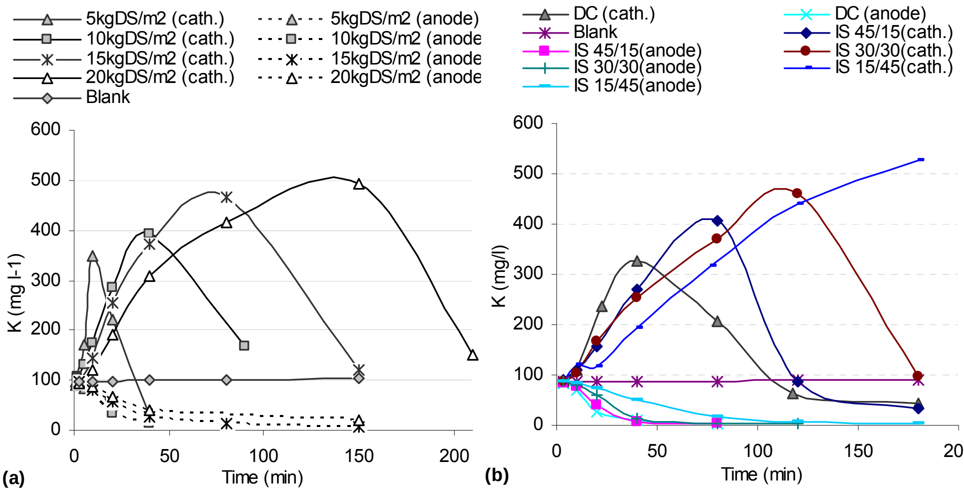

Figure 5.8 Concentrations of Na in the removed water at the anode and the cathode during electro-dewatering process with different (a) sludge loading rates and (b) off-time interrupted voltage application.

Electro-migration of dissolved ions reduced the concentration of Na^+ and K^+ in the sludge cake by 51 and 78 % in comparison to the blank experiments. In IS electro-dewatering, longer off-time interrupted voltage application also affected the reduction in Na^+ and K^+ concentration in the sludge cake. For example, in DC electro-dewatering experiments, concentration of K^+ in the final sludge cake was reduced 74% in comparison to control experiments, on the other hand, the concentration of K^+ was only reduced 23% in IS(45/15) experiments.

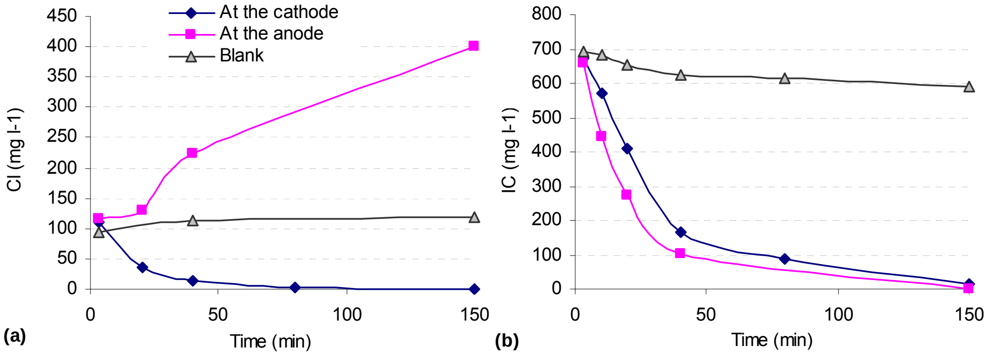

Figure 5.9 Concentrations of Cl (a), and IC (b) in the removed water at the anode and the cathode.

Under the applied electric field, anions usually move from the negatively charged cathode to the positively charged anode [122]. Thus, Cl^- concentration in the removed water increased at the anode and decreased at the cathode in comparison to the blank experiment (Figure 5.9a). However, a decrease in IC concentration was observed in the removed water at both, the anode and the cathode (Figure 5.9b). This may be explained by the fact that during the electro-dewatering process, pH significantly decreased at the anode due to electrolysis of water and H^+ production. Electro-migration transported carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions from the cathode to the anode, which resulted in a reduction in IC concentration in the removed water at the cathode. Because of the acidic pH, carbonate and bicarbonate ions were converted 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 two-fold; it stabilized pH in sludge [173] and also had a positive effect on the DS content in the final sludge cake (**II**).

5.5.3 Migration of macro and trace metal fractions

a) Migration of macro metals

During electro-dewatering, electrolysis of water releases H^+ ions at the anode and electro-migration transports the H^+ ions from the anode to the cathode. Thus, a decrease of pH in the sludge profile from the cathode to the anode is well documented [123,124]. Under low pH conditions, some of the metals associated with the sludge matrix might be dissolved. Under the applied electrical gradient, the metallic cations moved from the anode to the cathode by both electro-migration and electro-osmosis [122,173].

In conditioned sludge samples, exchangeable and reducible species were the predominant fractions of Ca, which indicated that Ca was highly mobile. Moreover, mineralization of carbonate and bicarbonate ions during electro-dewatering was reported to assist in the release of Ca (**IV**). The exchangeable and reducible fractions of Ca might be dissolved and migrated to the cathode. Therefore, in comparison to the control experiments, a decrease in concentrations of Ca in sludge at the anode and an increase in concentrations of Ca in sludge at the cathode were observed (Figure 5.10a). Due to DC and IS electro-dewatering, in comparison to the control experiments, the exchangeable and reducible fractions of Ca in the sludge at the anode were decreased by 81 and 96%, respectively. However, an increase of the exchangeable and reducible species of Ca in sludge at the cathode significantly depended on the duration of the off-time in IS experiments (Figure 5.10b). Longer off-time interrupted electro-dewatering resulted in lower concentrations of the exchangeable and reducible fraction of Ca in sludge at the cathode. Similar effect of longer off-time interrupted electro-dewatering on migration of Mg was also observed in Figure 5.10c,d (**V**). Moreover, high concentrations of Ca were observed in removed water at the cathode and the concentrations were depended on sludge loading rate (**IV**).

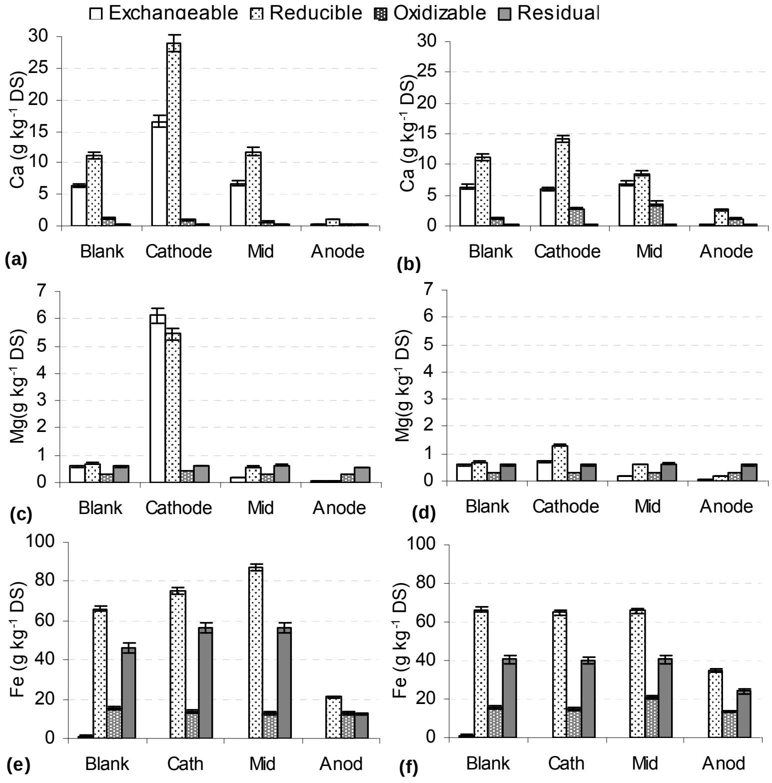

Figure 5.10 Fractionation of Ca, Mg and Fe in sludge due to DC (a, c, e) and IS$_{(15/45)}$ (b, d, f) electro-dewatering

For Fe, the reducible fraction was found to be predominant, comprising about 66.4% of total Fe. During electro-dewatering, low pH at the anode facilitated the dissolution of Fe from the sludge particles into the pore water, then Fe ions moved towards the cathode. Therefore, a significant decrease in the residual fraction in sludge at the anode was found, but an increase at the cathode, was observed (Figure 5.10e,f).

Moreover, the reducible fraction of Fe increased in middle of the final sludge cake. The increase in reducible fraction of Fe in the middle of the sludge and the decrease of the reducible fraction in sludge at anode depended on the duration of off-time in IS experiments. Due to electrical field application, a decrease of the pH in sludge at the anode depends on the amount of current [169]. Longer off-time interrupted electro-dewatering might reduce the amount of current through the sludge segment. Consequently, in long off-time IS experiments, pH of removed water at the anode slowly reduced in comparison to short IS or DC experiments (**V**). In long off-time IS experiments, the dissolution of Fe in sludge matrix at anode might be limited by a slow decrease of pH. In addition, the reduction of electro-osmosis and electro-migration due to longer off-time interrupted electro-dewatering were discussed above. Therefore, dissolution and migration of Fe was restricted in IS(15/45) experiments which resulted in higher reducible fraction of Fe in sludge at the anode than in other experiments (Figure 5.10f). During electro-dewatering, Fe ions moved towards the cathode. At the boundary between the acid and alkaline fronts in sludge segment, a Fe-rich barrier which comprised of FeOOH, Fe_2O_3 and Fe_3O_4 was probably formed as observed in previous studies of Narasimhan and Ranjan [180]. Consequently, high concentration of reducible fraction of Fe was observed in the middle of the sludge cake. The Fe-rich barrier moves towards the cathodic site depending on current and experimental time [181]. Thus, in long off-time IS experiments, the increase in reducible species of Fe in the middle of the sludge cake was not significant in comparison to DC and short off-time IS experiments (Figure 5.10e,f).

Moreover, the VS/DS ratio was found to increase in sludge at the anode after electro-dewatering. The PCA analysis performing to establish the relationship between the VS/DS ratio and metal concentrations showed the negative correlation between the VS/DS ratio and concentrations of Fe and Ca ions in sludge at the anode. This could be related to 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 [182] (**IV**).

b) Migration of heavy metals

Figure 5.11 shows the fractions of Ni, Mn, Zn and Cr in sludge cake after DC and IS(15/45) electro-dewatering. Due to electro-dewatering, the reducible fraction of the Ni, Mn, and Zn decreased in the sludge sample at the anode. Similar observations were also documented by Virkutyte et al. [183] during electrokinetic treatment of methanogenic anaerobic granular sludge. As discussed above, these metals might have been dissolved in the sludge at the anode and migrated towards the cathode. Then, they precipitated at particular points in the sludge segment, where pH changed from acidic to alkaline. This phenomenon is the so-called cathode hindering of contaminant migration [184,185]. Therefore, in DC electro-dewatering experiments, the reducible fraction of Ni, Mn and Zn significantly increased in the sludge samples in the middle of the sludge cake (Figure 5.11a,c,e). However, an increase in the reducible fraction of these trace elements in the sludge samples in the middle of the final sludge cake was not significantly observed in IS(15/45) experiments (Figure 5.11b,d,f). This might be the effect of long off-times interrupted voltage application which resulted in a slowdown in electrolysis, electro-migration and electro-osmosis (**V**).

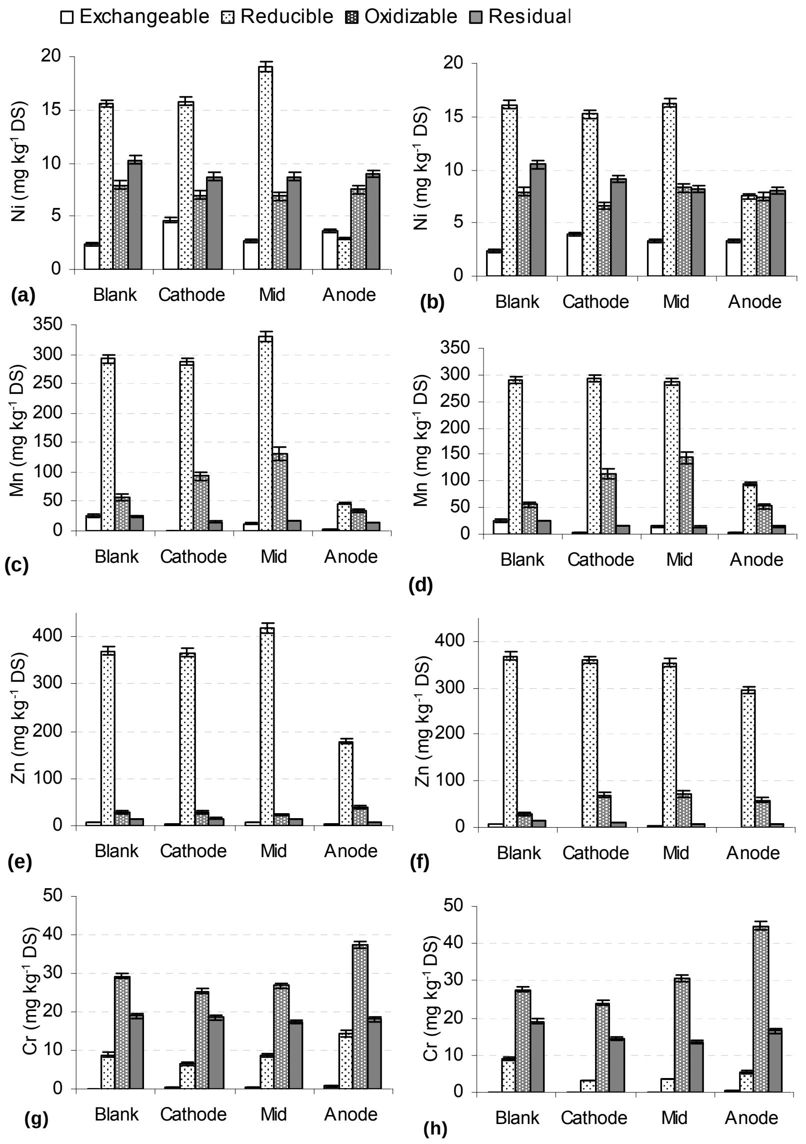

Figure 5.11 Fractionation of Ni, Mn, Zn and Cr in sludge due to DC (a, c, e, g) and $IS_{(15/45)}$ (b, d, f, h) electro-dewatering.

The main fraction of Cr was oxidizable species. During electro-dewatering, instead of migration to the cathode, an increase in oxidizable fraction of Cr was observed in sludge at the anode and long off-time interrupted voltage application did not affect the increase in oxidizable fraction of Cr at the anode (Figure 5.11g, h). In sludge, Cr exists as Cr (III) and Cr (VI) valances. Cr (VI) is anion species and usually present as hydrochromate ($HCrO_4^-$), dichromate ($Cr_2O_7^{2-}$) and chromate (CrO_4^{2-}). Under an applied electrical field, the anion species migrate to the anode [186,187] and become adsorbed by sludge particles at acidic pH regions near the anode [188]. Therefore, high concentration of Cr in sludge samples at the anode (Figure 5.11g, h) might be associated with migration of Cr (VI). However, Cr not only adsorbed in sludge but also leaked out into the removed water at the anode. The increase of Cr concentration in removed water was more significant in DC and short off-time IS experiments than in long off-time IS experiments (**V**).

6. Conclusion and recommendation

Pressure driven electro-dewatering resulted in higher current density than non-pressure experiment. The fluctuation of current density depended on sludge types, conditioning methods and sludge loading rates. The high current density and intensive fluctuation was observed in electro-dewatering with long off-time interrupted voltage application. High current density could be considered in power supply capacity.

In general, the electro-dewatering process significantly decreases water content in the final sludge cake. In non-pressure electro-dewatering, higher voltage application reduced the electro-dewatering time and resulted in the higher water removal rates. An increase in voltage from 3 to 10 V increased the DS content in the final sludge cake, but an increase in voltage from 10 to 30 V, did not significantly affect the DS content in the final sludge cake. However, an increase in voltage application reduced dewatering time. On the other hand, in pressure driven pressure, Because of high electrical field strength in low sludge loading rate experiments, an increase of DS content in the final sludge cake was observed. However, long off-time interrupted voltage application had a negative effect on transportation of water in sludge segment resulting in a high water content in sludge cake.

Due to electro-dewatering using different sludge types, sludge characteristics such as pH buffering capacity and conductivity can influence on electro-osmotic flow. Reverse electro-osmotic flow resulting in high water content in sludge at anode was observed in non-pressure experiments using raw sludge samples. Polyelectrolyte addition and freeze/thaw conditioning increased the dewaterability of sludge resulting in smooth electro-dewatering and dryer sludge cake.

Electric field application induced the migration of negatively charged organic matter from the cathode to the anode and organic matter was removed from sludge by the water flow in pressure driven experiments. This was proven by the fact that the COD and TOC concentrations in removed water were higher at the anode and lower at the cathode in comparison to the blank experiments.

Migration of Na^+ and K^+ resulted in a decrease of these metals in removal water at the anode and an increase at the cathode. The fluctuation of Na^+ and K^+ concentrations in removed water depended on sludge loading rate and modes of voltage application. The concentrations of Na^+ and K^+ were reduced in sludge cake in comparison to blank experiments. In addition, electro-dewatering could remove water and salt at the same time. This could be an additional benefit of electro-dewatering, because in some WWTPs, high salt concentration in sewage sludge limits reuse of sludge as fertilizer. Migration and mineralization of IC ions at the anode helps stabilization of pH in sludge and also had a positive effect on the DS content in the final sludge cake.

Application of long off-time interrupted voltage causes a decrease of electrolysis, electro-migration and electro-osmosis which reduced dissolution and migration of macro (Ca, Mg, and Fe) and trace (Ni, Mn, and Zn) metals in sludge cake. Migration of Ca and Fe was responded for an increase of VS/DS ration in sludge at the anode. An increase of Cr concentration in sludge at anode was observed, but the increase did not depend on experimental strategy. Moreover, high concentration of Cr was found in removed water at the anode. It can be a potential risk for the environment when removed water is returned to the wastewater treatment processes.

In brief, pressure application, an increase of voltage, a decrease of sludge loading rate or short off-time interrupted voltage application significantly reduced the water content in the final sludge cake and also shortened dewatering time. Polyelectrolyte addition and freeze/thaw conditioning had a positive effect on sludge dewatering. Migration of elements during electro-dewatering was investigated.

However, due to the complicated interactions of sludge properties in electro-dewatering process, laboratory tests with different sludge types and different conditioning methods are recommended. The effect of total dissolved solids on sludge electro-dewatering was not investigated. Pilot or full cale are recommended in order to accurately calculate energy comsumption of sludge electro-dewatering at different sludge loading rate,.

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Paper I

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Sludge dewatering by sand-drying bed coupled with electro-dewatering at various potentials

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Large amounts of water in sludge from wastewater treatment plants directly translate into high transport and handling costs. In this study, a laboratory scale sludge sand-drying bed was coupled with an electro-dewatering process to investigate the trends of dewatering at variable voltage potentials. There was a two-fold increase of dry solid (DS) content in final sludge cake when the applied voltage was increased from 3 to 10 V. Although applied voltages greater than 10 V did not result in any significant increase of the final DS content, they increased the maximum water removal rates and reduced electro-dewatering time by 75% when voltage increased from 10 to 30 V. There was a linear relationship between maximum water removal rates and applied voltage for the conditions studied. The final DS content of sludge cake and water removal rates significantly depended on the initial water loading in the sludge. When the voltage was increased through to 20 V, there was a steady decrease in the Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) of the effluent to a maximum of 43% when compared with the control experiment (0 V). However, when the sludge was subjected to a 30 V potential, there was a simultaneous increase in the temperature (24°C), COD (44%) and TOC (31%) of the effluent over the control experiment.

Keywords: electro-dewatering; electro-osmosis; sludge; sand-drying bed

1. Introduction

Activated sludge processes that are extensively used in municipal wastewater treatment plants have a major drawback of producing huge amounts of waste sludge with high (from 95 to 97%) water content. Usually, sludge treatment and disposal costs account for about 25–50% of the whole wastewater treatment plant operation budget. Therefore, high water content in sludge presents a key technical and economical problem in sludge handling and disposal processes [1]. In the medium and large scale wastewater treatment plants, flocculation coupled with mechanical dewatering methods such as centrifugation, vacuum and belt filtration are commonly used to remove water from sludge. However, even after the

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consumption of high amounts of expensive polymers, the dry solid (DS) content of the final sludge cake remains relatively low (20–25% in raw and 25–30% in anaerobic-digested sludge) [2]. If sludge requires further treatment, e.g. incineration, low DS content usually translates into larger energy expenditure for water evaporation during the subsequent drying process. Thus, high water content in sludge is always proportional to an increase in transport and sludge handling costs [3].

During the electro-dewatering process, the applied direct electric current results in increased water removal from the sludge. Electro-osmosis, which is the movement of capillary water because of the formation of the electrical double layer at the interface of water and the solid surface, is the major phenomenon occurring during such treatment. Usually, sludge has a negative zeta potential, thus the direction of the electro-osmotic flow is always towards the cathode.

Previous scientific attempts were mainly directed towards the use of electro-dewatering in combination with conventional mechanical dewatering processes. Electro-dewatering coupled to a belt filter was studied at various scales [4–6]. Full-scale dewatering of sludge utilising electro-belt filtration produced a 3.5-fold increase (from 4% to 14%) of the DS content in sludge when a stainless steel anode and a 30 V electrical potential was applied [4]. Additionally, another full-scale application of electro-dewatering in combination with a filter belt press showed the applicability (increased DS content from 17% to 24%) and technical feasibility of such an approach to dewater aluminum coagulated drinking water sludge with energy expenditure of 60 kWh per ton of DSs [5]. However, the major drawback of such a process was anode corrosion, which significantly impaired the dewatering process.

A pilot-scale sludge electro-dewatering process using a diaphragm filter and various voltage applications demonstrated a nearly two-fold (from 36 to 64%) increase of the DS content in the sludge cake [7]. It has also been reported that an increase in pressure resulted in better dewatering performance and significantly dryer sludge cake [8]. On the other hand, non-pressure electro-dewatering of sludge in a horizontal setup using municipal waste sludge [9], and in a vertical setup using oily sludge [10] also resulted in relatively dry sludge cake (from 44 to 54% DS). Taking into account the required energy costs and potential savings offered by the reduced transport and disposal costs, a cost/benefit analysis performed by Gingerich et al. [8] and Yuan and Weng [9] showed that the electro-dewatering process may be regarded as a cost efficient process viable for industrial applications.

A sludge sand-drying bed is a conventional technique still being used in small-scale wastewater treatment plants especially in developing countries [11]. The main advantages of this technique are easy handling and low operation costs. However, the main disadvantages are associated with long operation times (7–27 days) and low solid content in the final sludge cake (6.5%–25%) [11,12]. To further develop sludge dewatering methods, several approaches were investigated to reduce energy expenditure and to improve the final sludge quality by adding polymers [13] and by using solar power-driven sludge drying beds [14].

In this study, laboratory scale sludge sand-drying beds coupled with an electro-dewatering method were used to reduce the dewatering time and to assess the effect of various voltage applications on the sludge dewatering ability as well as the initial water content in sludge on the DS content in the final sludge cake. The reduction of organic matter in the removed water and energy consumption are also discussed in detail.

2. Materials and methods

2.1. Sludge

Laboratory scale electro-dewatering experiments were conducted with anaerobically digested sludge from Mikkeli Wastewater Treatment Plant (SE Finland), having a capacity of 13,000 m^3 d^{-1} or a population equivalent (p.e.) of 44,000. The main treatment unit of this plant is activated sludge for BOD removal and nitrification. Calcium hydroxide ($Ca(OH)_2$), ferrous sulfate ($FeSO_4$), Poly Aluminum Chloride and polymers are added to stabilise pH, remove phosphorous and improve settling capacity. Sludge samples were taken from the effluent of the anaerobic digestion unit. The digester was continuously operated with 17–20 days solids retention time at 35°C–38°C. The main characteristics of the sludge are presented in Table 1. After sampling at the wastewater treatment plant, sludge was taken to the laboratory and stored at 4°C. Before the experiments, the sludge samples were kept out of the cold room to reach the ambient temperature.

2.2. Experimental setups

Laboratory scale sand-drying beds coupled with low-level direct electric current were used in this study as described by Tuan et al. [15]. The reactors consisted of the acrylic vessels (height 55 cm, width 17 cm and length 31 cm) as depicted in Figure 1. In each vessel, a 10 cm gravel bed was filled at the bottom, followed by the 10 cm sand bed. The sand particle size was distributed accordingly: 0.5–1.0 mm, 22.6%; 0.2–0.5 mm, 77.0%. The stainless steel mesh (thickness 0.5 mm) used as the cathode was installed directly on the surface of the sand-bed. The original sludge sample was filled into the reactors, and the titanium plate anode (thickness 2 mm) was placed on the top of the sludge cake. The top of the vessels was covered with aluminum foil to minimise the evaporation of water. The electrodes were then connected to the DC power supply (GW Instek, Taiwan) to provide a constant voltage throughout the experiments. Removed water was collected at the bottom of the vessels and its amount was measured by the electrical balance.

2.3. Electro-dewatering tests

Experiments were performed at room temperature (22 ± 1°C). Sludge loading was 6 kg DS m^{-2} of a sand-bed in all the experiments. Before the actual start of the

Table 1. Main characteristics of anaerobically digested sludge from Mikkeli Wastewater Treatment Plant (SE 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} $CaCO_3$)	6862–10,487
Total solids – TS (%)	3.17–2.87
Volatile solids –VS (%)	1.53–1.70
VS/TS (%)	55.1–53.4
Zeta potential (mV)	14.0–15.9
Capillary suction time – CST (s)	307.7–345.8

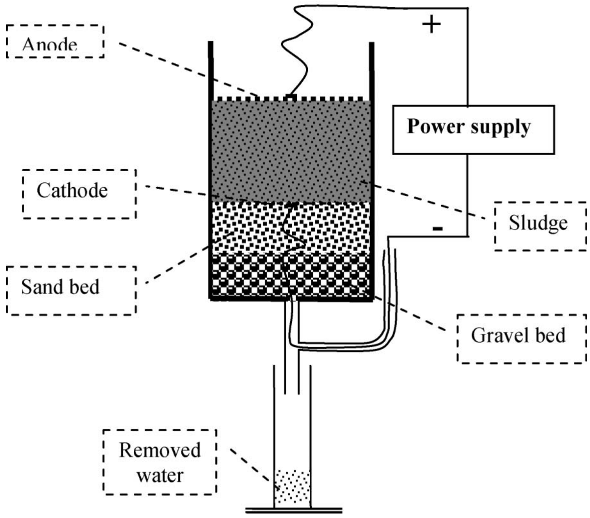

Figure 1. Schematic representation of the laboratory scale electro-dewatering sand-drying bed.

electro-dewatering experiments ($t_{\mathrm{exp}} = 0$), sludge was pre-dewatered by using natural sand-drying beds. A mass balance model was used to calculate the DS content of the sludge in the reactors. When the DS content reached 7–8%, constant direct electric current of 3, 5, 10, 15, 20 and 30 V was applied ($t_{\mathrm{exp}} = 0$) to the experimental system.

To investigate the effect of initial DS content on the dewatering ability of sludge, un-altered sludge samples that have been subjected to 30 days of natural dewatering using sand drying beds were subjected to 15 and 10 V treatments, respectively. Control experiments were performed in the absence of electricity for comparison and to test the reliability of data. At the end of the electro-dewatering process, sludge samples were taken at the anode and the cathode to analyse for the DS content of the sludge cake.

2.4. *Analytical methods*

A Multi-meter (Fluke 110, the Netherlands) was used to monitor current fluctuations. The DS content of the sludge samples was determined by drying samples at 105°C for 24 h according to the European Standards [16]. The characteristics of the removed water such as pH, electric conductivity (EC), COD, TOC, alkalinity and capillary suction time (CST) were determined using Standard Methods [17]. To ensure reliability of data, all the measurements were performed in duplicate. Zeta potentials were measured by electro-phoretic light scattering method (Malvern zeta sizer Nano-Series Instrument). Sludge was centrifuged at 5000 rpm for 10 min, and the supernatant liquid was used to dilute the original sludge samples for Zeta potential measurements.

3. Results and discussion

3.1. *Effect of voltage on the dry solid in the final sludge cake and water removal rates*

Figure 2 shows that the DS content of the final sludge cake, sludge at the anode and at the cathode, after various voltage applications, varied considerably from 25% to

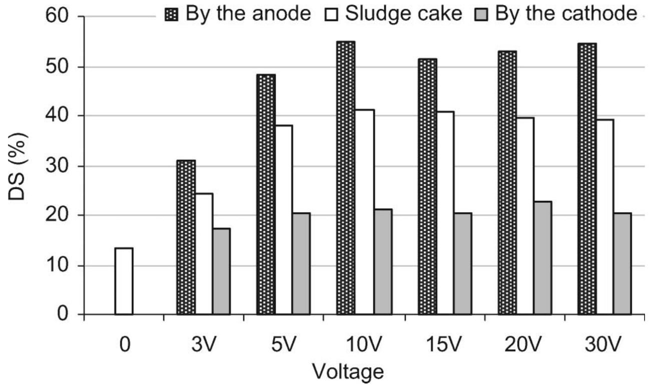

Figure 2. Solid content in the final sludge cake, sludge by the anode and the cathode during the electro-dewatering process at differed voltage applications.

41%. The DS content was relatively high in comparison to the control experiment (13%) conducted for 30 days using only a natural sand bed dewatering process.

It has been reported that anaerobically digested sludge has a negative zeta potential (−15 mV), therefore electro-osmotic flow plays a significant role in transporting water from the anode to the cathode [18,19]. In this study, water content in sludge at the anode was found to be lower than in sludge at the cathode (Figure 2). Also, an increase in the applied voltage (from 3 to 10 V) resulted in an elevated DS content in the final sludge cake. Indeed, this observation was similar to the findings of other researchers who studied pressure driven electro-dewatering and non-pressure dewatering processes [4,7,10]. An increase in voltage from 10 to 15, 20 and 30 V did not result in any significant change (39–41%) of the DS content in the final sludge cake. According to Ho and Chen [20], dry layer with high electrical resistance may be formed at the anode during electro-dewatering process. Thus, electro-osmotic flow transports water from the anode towards the cathode, thereby drying out considerably the sludge at the anode. Without the applied pressure, the contact between the anode and a dried sludge layer was inadequate for the occurrence of an efficient electro-osmotic flow.

The amount of the removed water and water removal rates during the electro-dewatering process at various voltage applications are shown in Figure 3. In general, the applied electric current significantly increased the amount of water removed (Figure 3a). Similar trends were also observed by several other researchers [18,21,22], who investigated electro-dewatering of sludge and dredged sediments. Figure 3b shows that applied electric current drastically increased water removal rates (10–20 times) during the first hours of the experiments, regardless of the applied voltage potential. However, a 30 V application resulted in 87% water removal during the first 6 h of the experiment, reaching a maximum dewatering rate of 234 $\mathrm{l\,m^{-2}\,d^{-1}}$.

The effect of electro-osmosis on water removal during the dewatering process can be estimated by assuming that 7% of the initial DS content in the sludge was in the solid form and, therefore, the effect of the electro-phoretic phenomenon becomes negligible. Then, according to Bagotsky [23] and Reddy et al. [21], the electro-osmotic flow can be expressed by the Equation (1) as follows:

$$\upsilon = \frac{\varepsilon_0 \varepsilon_r \zeta}{\eta} E, \qquad (1)$$

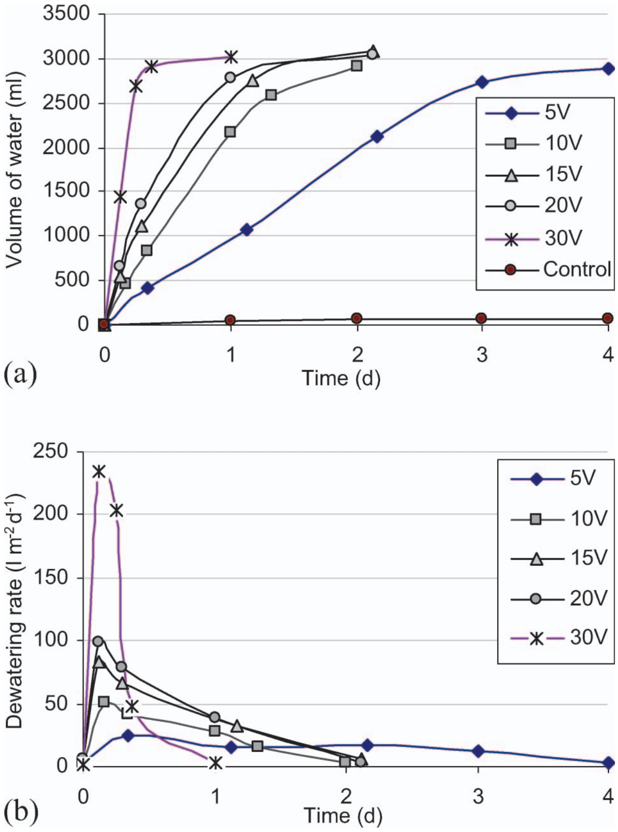

Figure 3. Amount of (a) removed water and (b) water removal rates as a function of time during the electro-dewatering process at different voltage applications.

where υ is the electro-osmotic flow, ε_o is the dielectric permittivity of vacuum, ε_r is the dielectric constant of the liquid, ζ is the zeta potential of sludge, E is the electrical potential gradient across the plug and η is the viscosity of the liquid medium.

The dielectric permittivity of vacuum (ε_o) and the dielectric constant of the liquid (ε_r) remained unchanged in all the experiments because the sludge samples were of the same origin. It was assumed that at the beginning of the electro-dewatering process, zeta potential of sludge (ζ) and the viscosity of the liquid medium (η) remained constant. Therefore, the electro-osmotic flow only depended on the electrical potential gradient (E). As a result of the distance between the cathode and the anode being the same at the beginning of the experiments, increasing the applied voltage resulted in higher electrical potential gradients that induced increased maximum dewatering rates (Figure 3b). There was a gradual decrease of water removal rate with time after the maximum rate was reached (Figure 3b). This is because of the limitation of water content in the sludge cake as reported by Larue et al. [24] from their investigation on the electro-dewatering of bentonite. It must be noted from the same figure that increasing voltage significantly reduced the electro-dewatering time; for applied voltages of 5–30 V, the dewatering process lasted 4 days to 1 day, respectively. Meanwhile, at a lower potential of 3 V the dewatering process took 14 days to complete. Figure 4 shows that the maximum water removal rate increased linearly with the applied voltage.

3.2. Effect of initial dry solid content and water removal rate

Table 2 shows the relationship between the initial and final DS content of the sludge. At an applied voltage of 10 V, the electro-dewatering process utilising the sand-bed with an initial 7% DS content in sludge, resulted in 41% of the solid content, whereas experiment with initial 13% DS in sludge only resulted in 21% of the DS content in the final sludge cake. On the other hand, the DS content in the final sludge cake of the original un-altered sludge sample was nearly twice lower than obtained during the same experiments using initial 7% DS content sludge.

When the original un-altered sludge was used, the DS in sludge adjacent to the anode was lower than that of the sludge adjacent to the cathode (Table 2). Similar trends have been discussed in detail by Tuan et al. [15] and Yoshida et al. [25]. This may be explained by the formation of H^+ ions at the anode leading to a decrease in sludge pH. The measured pH at the anode decreased from 7.1 to 4.9, 3.1 and 2.7 after 6, 24 and 30 h, respectively. The decrease in pH at the anode related to an increase in zeta potential (Figure 5). At some point during the experiment, zeta

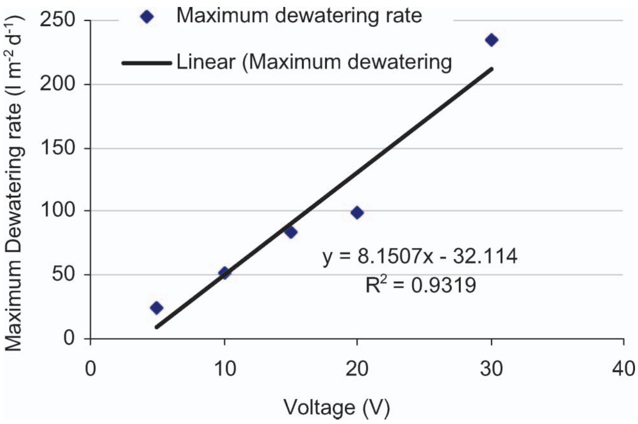

Figure 4. Relationship between the maximum water removal rates and voltage applications.

Table 2. Dry solid content in the final sludge cake at the anode and the cathode before and after electro-dewatering process, using different initial DS content in sludge.

	DS content (%)			
		Sludge after the electro-dewatering process		
Voltage (V)	Initial DS in sludge	Sludge cake	By the anode	By the cathode
10	13.2	20.6	41.6	13.7
10	7.1	41.1	54.8	21.2
15	3.1	25.3	20.3	25.8
15	7.1	40.6	49.5	20.2

potential became positive, which resulted in the reversed osmotic flow from the cathode to the anode. A similar phenomenon was observed by Yeung et al. [26] and Alshawabkeh et al. [27], who researched the application of electrokinetics in soil treatment.

The highest water removal rates were achieved at 15 V with 3% (253.3 $\text{l}\,\text{m}^{-2}\,\text{d}^{-1}$) and 7% (83.3 $\text{l}\,\text{m}^{-2}\,\text{d}^{-1}$) of the initial DS content in sludge (Figure 6). However, when the sludge was subjected to 10 V direct electric current, the water removal rates significantly decreased to 51.2 and 15.4 $\text{l}\,\text{m}^{-2}\,\text{d}^{-1}$ at 7% and 13% initial DS content, respectively. According to Barton et al. [18], both electro-osmotic and electro-phoretic migration may contribute to water removal from sludge, with major influence on the rate and the extent of the dewatering process. At the beginning of the electro-dewatering process using low DS sludge, sludge particles were mainly suspended in water; hence they were free to move in the solution. Therefore, the negatively charged (zeta potential −15 mV) sludge particles migrated towards the cathode because of electrophoresis, resulting in their lower concentration at the cathode. Additionally, electro-osmosis also contributed towards an increased water transport from the anode to the cathode. However, when the sludge has a

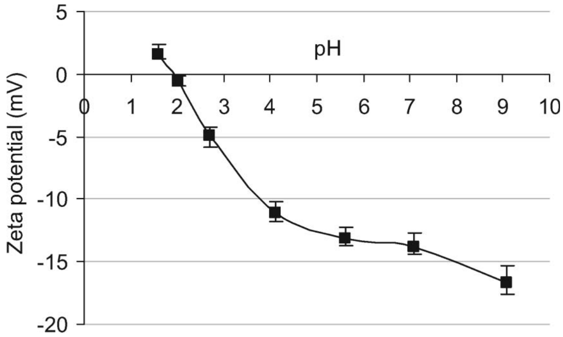

Figure 5. Average zeta potential at different pH.

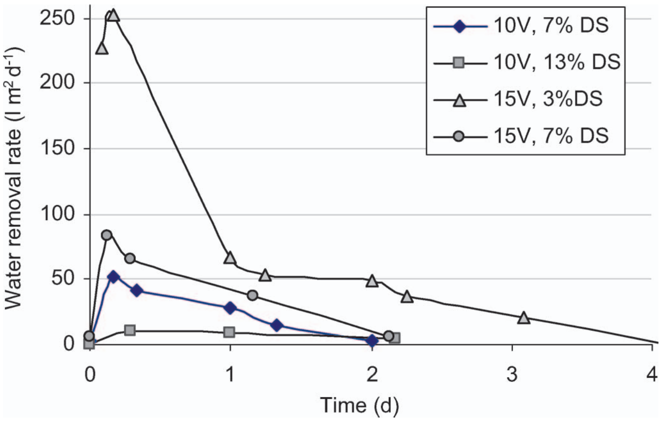

Figure 6. Dewatering rates during the electro-dewatering process at different voltage application and initial DS content in sludge.

high DS content, mobility of the fine particles is severely reduced by lock-up within the sludge matrix. Hence, electrophoretic flow becomes negligible and electro-osmotic flow becomes prevalent. Also, hydrogen and oxygen gases are produced at the cathode and the anode, respectively, during the electrical treatment. Oxygen could easily escape into the atmosphere because the anode was directly installed on the surface of the sludge segment and not within the matrix. However, as the cathode was directly immersed into the sludge segment, hydrogen remained in the reactor. These tiny gas bubbles have a very large surface area and attract fine particles inducing sludge floatation [28–30]. Meanwhile, gas bubbles at the cathode could assist with effluent removal rate by reducing sludge filter cake resistance.

3.3. Reduction of organic matter in the removed water during the electro-dewatering process

The COD and TOC concentrations in the removed water (effluent) at various applied voltages are shown in Figure 7. This figure reveals that an increase in voltage from 10 to 20 V significantly reduced the COD and TOC concentrations in the effluent. The COD and TOC concentrations were reduced by 43% and 41%, respectively, when sludge was subjected to 20 V direct electric current, in comparison to the control experiment in the absence of electricity. During the electro-dewatering process, H^+ ions were formed at the anode and migrated towards the cathode throughout the sludge cake, leading to the significant pH decrease throughout the sludge profile [9]. Thus, such a low pH (2.1–3.7) ionised negatively charged organic matter such as volatile fatty acids [10] that moved and accumulated in the sludge cake at the anode during the electro-dewatering process [15].

On the other hand, the COD and TOC concentrations increased by 45% and 31%, respectively, in the effluent when 30 V was applied to the experimental system. The electric potential at the cathode was -1.50 V while at the anode was $+3.03$ V, thus a large voltage loss resulted in heat generation at the anode [31]. Meanwhile, the

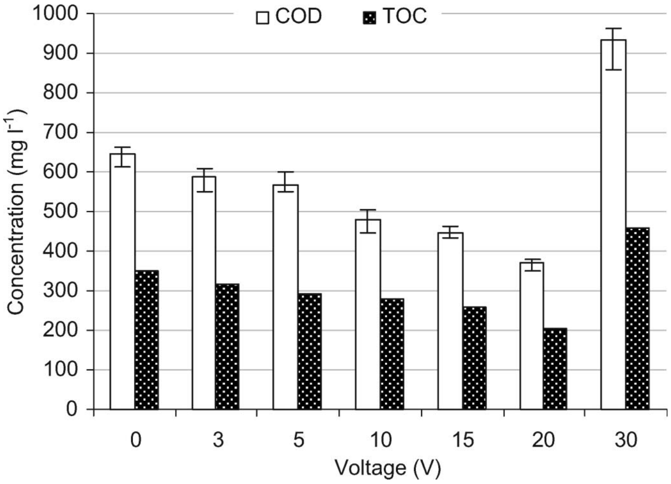

Figure 7. COD and TOC concentrations in the removed water at various voltage applications.

amount of water in the sludge cake decreased. This may be attributed to the combined effect of increased electrical resistance and Ohm heating, which elevated the sludge temperature from 22°C to 46°C. High temperature and low pH environments destroy cell walls, leaking out intra cellular substrates [32], which generate higher COD and TOC values in the electro process effluents when compared to the control experiment (Figure 7).

3.4. Energy consumption

Energy consumption was calculated as kWh per kg of dry solid (kWh kg^{-1} DS) or kWh per m^3 of removed water (kWh m^{-3}) and plotted against applied voltage as shown in Figure 8. Energy utilisation increased with voltage as also observed by Gingerich et al. [8] who investigated the technical and economical feasibility of pressure driven electro-dewatering processes. Higher voltage applications may not be economical from the perspective of energy consumption because the residual water content in the final sludge cake was independent of voltage from 10 to 30 V (Figure 2). However, higher voltages resulted in much shorter dewatering times, which must be considered in project decision-making processes. At 10 and 20 V, energy consumption to remove one cubic meter of water was similar to the results obtained by Saveyn et al. [7], who combined electro-dewatering with a diaphragm filter press process. Nevertheless, a 30 V application consumed less energy (150 kWh m^{-3}), than electro-dewatering combined with the diaphragm filter press (203 kWh m^{-3}). Energy consumption in this study, depending on the applied voltage, was four to six times less than the theoretical thermal evaporation of water, where the energy requirement is about 627 kWh m^{-3} of water [33].

Energy consumption expressed as kWh kg^{-1} DS for an applied voltage was lower at low initial DS loading when compared with the high initial DS loading. However, when energy consumption was expressed as kWh m^{-3} of effluent, it was independent of the initial DS content in the sludge cake. Moreover, energy consumption at 15 V using the original sludge (3% DS) was 2.52 kWh kg^{-1} DS, and decreased two-fold when 7% DS sludge was introduced (1.19 kWh kg^{-1} DS).

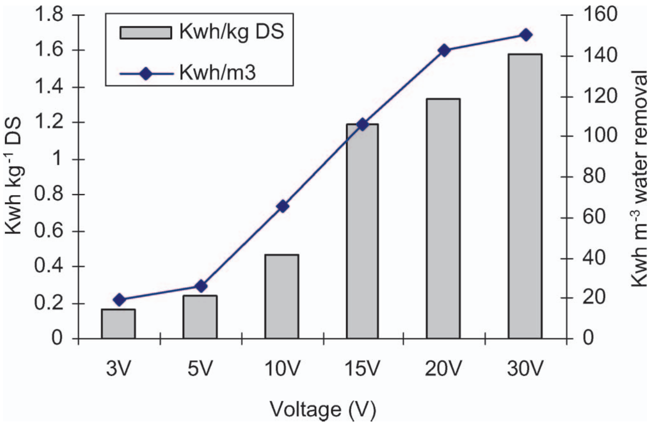

Figure 8. Energy consumption at different voltage applications during the electro-dewatering process.

4. Conclusions

The electro-dewatering process efficiently reduced water content in the final sludge cake. An increase in voltage from 3 to 10 V increased the DS content in the final sludge cake from 25 to 41%. However, an increase in voltage from 10 to 30 V did not significantly affect the DS content in the final sludge cake. Higher voltage application reduced the electro-dewatering time and also resulted in the higher water removal rates. Water removal rates and the DS content in the final sludge cake significantly depended on the initial water loading of the sludge. The increase or decrease in the COD and TOC in the effluent depended on voltage application. Finally, the studies reveal that the electro process uses four to six times less energy than the conventional thermal evaporation method, proving it to be an energy-efficient sludge dewatering method.

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Paper II

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ELECTRO-DEWATERING OF SLUDGE UNDER PRESSURE AND NON-PRESSURE CONDITIONS

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ABSTRACT

The electro-dewatering method is regarded as a promising approach to reduce the water content in sludge. Laboratory scale non-pressure and pressure-driven dewatering reactors were set up to study the dewatering rate in different types of sludge and the water content in the final sludge cake after electro-dewatering process. It was observed that in non-pressure experiments, the water removal rate was highly dependent on sludge pH buffering capacity and the type of sludge; the highest water removal rate (83.2 $lm^{-2}day^{-1}$) was achieved with anaerobic sludge. When pressure was applied, the rate of removal of water from the anode and the cathode depended on alkalinity as well as current density. During the electro-dewatering process, pressure had a significant contribution to water reduction in the final sludge cake in experiments using raw sludge and raw sludge with added alkalinity in comparison with non-pressure experiments using the same types of sludge. However, experiments using anaerobically digested sludge in non-pressure and pressure-driven reactors resulted in the same water content in the final sludge cake (40%). In general, different types of sludge with various amounts of alkalinity affected sludge electro-dewatering capacity by changing zeta potential and pH. Migration of negatively charged organic substances occurred during the applied low-level direct current (15 V), and chemical oxygen demand and total organic carbon concentrations in removed water were found to be higher at the anode and lower at the cathode in comparison with control experiments.

Keywords: Electro-dewatering, electro-osmosis, sewage sludge, alkalinity

INTRODUCTION

Waste sludge from municipal wastewater treatment plants contains a large percentage of water. Conventional mechanical techniques such as centrifuge, vacuum, and belt pressure filtering are usually used to remove water from sludge. Despite the consumption of large amounts of costly polymers, the remaining water content in sludge is still high, usually ranging from 67–87%. Four different types of water in sludge were described by Versilind and co-authors [1, 2].

- Free water: water that is not associated with solid particles, including void water, which, at the same time, is not associated with capillary forces.
- Interstitial water: water that is bound by capillary forces between the sludge flocs or water trapped in crevices and interstitial spaces or flocs. This water can be released when the flocs are broken up.
- Surface or vicinal water: water that is associated with the solid particles. This water is held on particle surfaces by virtue of the molecular structure of the water molecules.
- Intracellular water: water chemically bound within the particle structure that can only be released by thermo-chemical destruction of particles.

Mechanical dewatering methods can only remove free water and an insignificant amount of interstitial water [3], resulting in a high water content (65–80%) of the sludge cake. Therefore, to further reduce water content, thermal drying and other methods must be employed [4].

Recent studies have shown that electro-osmosis is a promising method to reduce interstitial and some of the vicinal water in sludge [3], and it also considered a cost-effective method [5, 6]. It is well documented that electro-osmosis causes the double layer associated with the surfaces to move towards an oppositely charged electrode [7, 8]. However, according to Barton *et al.* [9], in addition to electro-osmosis, electrophoresis and Ohmic heating also contribute to increased water removal from sludge under an applied electric current.

Several laboratory and pilot-scale studies have been conducted to assess the feasibility of sludge for electro-dewatering. Buijs *et al.* [10] argued that polymer addition before the electro-dewatering process may cause a bridging coagulation in a stable suspension, despite increasing the absolute value of the zeta potential. This observation enabled an increase in the efficiency of electro-osmotic dewatering, without blocking of filters, by a higher driving force of electro-osmosis and a larger repulsion between the negatively charged sludge particles and the negatively charged electrode. The belt filter press method coupled with electro-dewatering did not show significant results, because of insufficient contact time [11–13]. However, it was found that electro-dewatering significantly reduced filter fouling [10, 13]. Sludge electro-dewatering, by using a diaphragm filter press with a longer contact time, has resulted in low water content in the final sludge cakes [14]. It was observed that an increase in voltage application resulted in a dryer sludge cake, but at the same time consumed more energy. Nevertheless, such a process still uses less energy than drying sludge by conventional evaporation methods. In addition, Gingerich *et al.* [5] observed that increased applied pressure during electro-dewatering resulted in lower water content in the final sludge cake. However, there is a lack of research on electro-dewaterability of sludge before and after anaerobic digestion, and the role of pressure in electro-dewatering process using different types of sludge is still not fully understood.

In the current study, non-pressure and pressure-driven electro-dewatering reactors were set up to investigate the effect of sludge types on the dewatering rate and the subsequent water content in the final sludge cake.

MATERIALS AND METHODS

Laboratory-scale experiments were conducted with sludge taken from the Mikkeli Wastewater Treatment Plant, which has a capacity of 13,000 m^3 day^{-1}, an amount equivalent to the sludge produced by a population of 44,000. The main treatment unit is activated sludge for biochemical oxygen demand removal and nitrification. Calcium hydroxide ($Ca(OH)_2$), ferrous sulfate ($FeSO_4$), poly aluminum chloride and polymers are added to stabilize pH, remove phosphorous and improve settling. The most important sludge characteristics are presented in Table 1. The first type of sludge was collected from the influent of anaerobic digester, and was mainly composed of primary and secondary sludge mixture. Samples of the second sludge type were collected from the effluent of anaerobic digestion unit. The digester was continuously operated with 17–20 days retention time at mesophilic conditions (35–38°C). After sampling at the wastewater treatment plant, the sludge was stored at 5°C prior to experiments. Before the experiments were conducted, the sludge samples were taken out of the cold room and allowed to reach room temperature.

The non-pressure experiments were conducted in acrylic reactors (55 cm high, 17 cm wide and 31 cm long) as depicted in Figure 1(a). The 10 cm gravel bed was placed on the bottom of the reactors, followed by the 10 cm sand bed. The particle size of the sand bed was 0.5–1.0 mm (22.6%); 0.2–0.5 mm (77.4 %). The stainless steel mesh (0.5 mm) cathode was installed on the surface of the sand bed. It has been reported that the main problem during the electro-dewatering process is anodic corrosion [13], therefore an inert titanium plate electrode (2 mm thickness) was used as the anode. The sludge was then fed into the reactors, and the anode was placed on top of the sludge cake. The reactors were covered with aluminum foil to minimize natural water evaporation. The electrodes were connected with a direct current power supply (GW Instek, Taiwan) to provide a constant (15 V) voltage. Removed water was collected at the bottom of the reactors, and the amount of water was measured by electrical balance.

Figure 1(b) shows the schematic representation of a pressure-driven electro-dewatering reactor. The reactor was made of polyvinyl chloride and was 9.8 cm in diameter and 30 cm in length. Stainless steel mesh and titanium plates were used as the cathode and the anode, respectively. The cloth filter (Z104256 PP, Sigma-Aldrich), with a permeability factor of 7.62 (m^3 m^{-2} min^{-1}) was placed by the electrodes. Sludge was subjected to a constant pressure of 4.0 bars. Removed water was collected from both the anodic and the cathodic sides. The amount of removed water was also measured by electrical balance.

Table 1. Main characteristics of sludge from the Mikkeli Wastewater Treatment Plant.

Parameters	Sludge before anaerobic digestion	Sludge after anaerobic digestion
Temperature (°C)	10.3–13.8	33.4–34.0
Electric conductivity (µs cm^{-1})	2458	7160–7500
pH	5.98–6.43	7.16–7.38
Alkalinity (mg kg^{-1} $CaCO_3$)	3415–3650	6862–10,487
Total solid (%)	5.07–5.48	3.17–2.87
Volatile solid (%)	3.72–4.13	1.53–1.70
Volatile solid/Total solid (%)	73.33–75.29	55.1–53.4
Zeta potential (mV)	8.07–9.87	14.0–15.9
Capillary suction time (s)	384.7–416.8	307.7–345.8

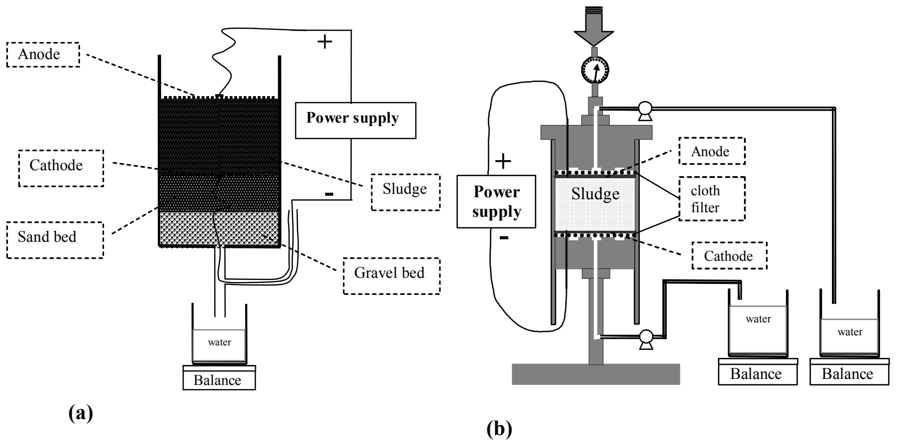


Figure 1. Schematic representation of the laboratory scale: (a) electro-dewatering sand drying bed; and (b) electro-dewatering reactor with applied pressure.

Three types of sludge were used in these experiments: from the influent and the effluent of the anaerobic digester, and sludge with added alkalinity. To increase dewaterability, the third type of sludge was a raw sludge with added alkalinity ($NaHCO_3$) to the same level as conventional anaerobically digested sludge (10 g kg^{-1} wet sludge as $CaCO_3$).

The laboratory-scale experiments were performed at room temperature (22°C ± 1°C). The raw and anaerobically digested sludge had a low initial dry solid (DS) content (3%), thus the sludge was pre-dewatered prior to the experiments. In non-pressure experiments, the water mass balance model was used to determine the DS of sludge in reactors during natural sand drying bed process, until the solid content of sludge was in the range of 7–8%. The second phase of dewatering process was performed by applying a low-level electrical current (15 V). In pressure-driven experiments, sludge was pre-treated by a vacuum in a funnel to increase sludge DS to 7–8 %. After pre-treatment, sludge was fed into the reactors. The sludge loading rate for all the experiments was 6 kg DS m^{-2} filter medium. Control experiments without electricity were performed to evaluate the effect of electricity in enhancing water removal rates from sludge.

A multimetre (Fluke 110, The Netherlands) was used to monitor fluctuations in current. At the end of the experiments, sludge samples were taken at the anode, the cathode and from the sludge cake for solid content analysis based on the European Standard method [15]. Characteristics of removed water such as pH, electrical conductivity (EC), chemical oxygen demand (COD), total organic carbon (TOC), inorganic carbon (IC), alkalinity and capillary suction time of sludge were analysed using Standard Methods [16]. Volatile fatty acids (VFAs) were analysed by gas chromatography (Agilent Technologies 6890 N) with capillary column (Agilent HP-FFAP). The zeta potential was measured using the electrophoretic light scattering technique (Malvern zeta sizer Nano-Series Instrument). To measure the zeta potential, sludge was centrifuged at 5000 rpm for 10 minutes, after which the liquid in the upper layer was used to dilute the original sludge sample.

RESULTS AND DISCUSSION

Current Density Fluctuation during Electro-dewatering

Current density in pressure-driven experiments was significantly higher than in the non-pressure experiments using same kinds of sludge, mainly because of a good contact between the anode and sludge cake (Figure 2). Indeed, a similar observation was made by Ho and Chen [17] who studied electro-dewatering of bentonite under a rotation anode at different speeds. After the addition of $NaHCO_3$ into the raw sludge, EC increased from 2.46 to 10.91 mS cm^{-1}. Regardless of experimental strategy, that is, with or without applied pressure, current density in experiments using raw sludge with added alkalinity was always higher than during experiments with raw and anaerobically digested sludge without added alkalinity (Figure 2).

Current density fluctuations during the non-pressure electro-dewatering process are presented in Figure 2(a). A similar trend of electric current decrease during electro-dewatering was also discussed by other researchers [18, 19]. Such a decrease may be explained by a dry layer formation at the anode, formed because of the repulsion of water from the anode to the cathode [17]. In the current study, the decrease in current density was highly dependent on the types of sludge used for experiments. During the first 10 hours, current densities were similar to experiments using both raw and anaerobically digested sludge (Figure 2(a)). However, after 10 hours, current density in experiments using anaerobically digested sludge decreased and finally reached zero at

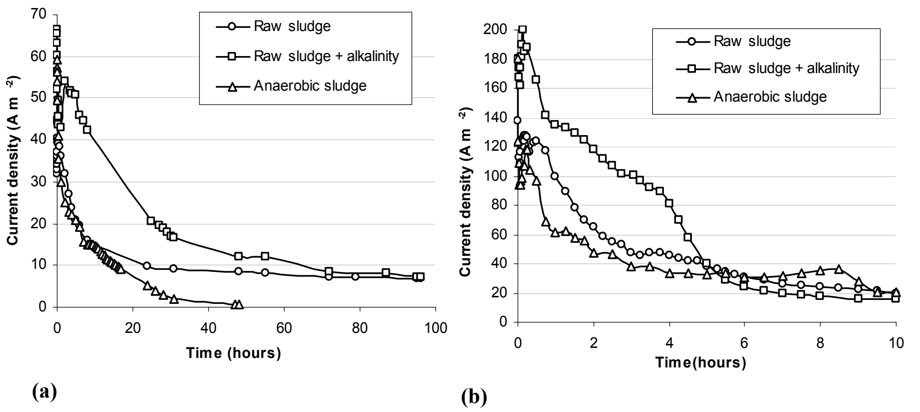


Figure 2. Current density fluctuation during (a) non-pressure and (b) pressure-driven electro-dewatering processes.

the end of the electro-dewatering process. On the other hand, when using only raw sludge, the current density was only slightly reduced and remained constant at 10 A m^{-2} until the end of the experiment. After 48 hours, the current density in experiments using both raw sludge with and without added alkalinity almost equalized and remained constant until the end of the electro-dewatering process.

During the pressure-driven electro-dewatering experiments, current density varied in different types of sludge. Thus, it started to fluctuate immediately upon initiation of the experiments, and gradually decreased after one hour. The current density in raw sludge with added alkalinity was the highest in comparison with raw and anaerobically digested sludge (Figure 2(b)). After 5 hours, current density reached the same level in all the experiments (35 A m^{-2}). In anaerobic sludge, current density was almost constant, with a small increase between 7.0 and 8.5 hours, caused by decreased electrical resistance of sludge towards the end of the electro-dewatering process [20]. Consequently, the current density significantly decreased and remained nearly constant at 20 A m^{-2}, until the end of the process. During first 5 hours of the pressure-driven electro-dewatering process, current density in raw sludge was higher than in anaerobically digested sludge (Figure 2(b)). This could be explained by the formation of acid at the anode due to the electrolysis of water during the electro-dewatering process. The concentration of IC in pore water of anaerobically digested sludge was 530.8 mg l^{-1}. At nearly neutral pH, bicarbonate and carbonate anions are present in large amounts and, having a negative charge, they moved to the anode due to the electromigration phenomenon [7, 12]. At low pH, bicarbonate and carbonate ions in sludge at the anode were mineralized to carbon dioxide (CO_2) gas and escaped from sludge, an effect which might be attributed to the reduced EC in the sludge at the anode. In addition, pore water in the raw sludge (COD concentration of 11,677 mg l^{-1}) contained large amounts of organic anions such as VFAs (Table 2). Therefore, VFAs may have moved towards the anode without mineralization, remaining in the sludge matrix. This may have resulted in a relatively constant EC, and may therefore explain why the current density was higher in a raw rather than in an anaerobically digested sludge (Figure 2(b)).

Removal of Water with Non-pressure Electro-dewatering Process

Under applied constant voltage, in all the experiments the water removal rate increased from 6.0 l m^{-2} day^{-1} (litres

Table 2. Volatile fatty acid concentrations in removed water after pressure-driven electro-dewatering experiments using raw sludge with and without added alkalinity.

Type of sludge		Acetic acid (mM l^{-1})	Propionic acid (mM l^{-1})	Isobutyric acid (mM l^{-1})	Butyric acid (mM l^{-1})	Isovaleric acid (mM l^{-1})	Valeric acid (mM l^{-1})
Raw sludge	Control	51.84	22.93	4.62	14.45	4.30	3.90
	At cathode	10.02	3.81	0.65	2.17	0.56	0.52
	At anode	299.37	55.56	10.27	34.72	9.14	8.54
Raw sludge added alkalinity	Control	70.85	29.16	5.23	19.36	4.9	4.30
	At cathode	14.5	6.53	1.82	4.92	1.67	1.55
	At anode	157.13	59.53	10.72	37.21	9.33	8.05

removed water per square metre filter media per day) to the maximum dewatering rate after 4 hours of experiments (Figure 3). The maximum water removal rate was highly dependent on the sludge types used for experiments. Hence, the maximum water removal rate was 83.2, 60.5 and 43.2 l m^{-2} day^{-1} in experiments using anaerobically digested sludge, raw sludge with added alkalinity and raw sludge, respectively. Adding alkalinity to the raw sludge increased the maximum water removal rate by 40%.

Average zeta potentials of anaerobically digested sludge, raw sludge with added alkalinity and raw sludge were −14.1, −10.4 and −8.2 mV, respectively. It has been reported that electroosmosis plays an important role in removing water from sludge [9]. It may be assumed that the porosity of sludge is constant during electro-dewatering process, and the flow of liquid due to electroosmosis could be expressed by [8, 19]

$$\upsilon = \frac{\varepsilon_o \varepsilon_r \zeta}{\eta} E \qquad \text{(i)}$$

where υ is the liquid flow due to electroosmosis (m s^{-1}), ε_o is the dielectric permittivity of vacuum (8.854×10^{-12} CV^{-1} m^{-1}), ε_r is the dielectric constant of the liquid, ζ is the zeta potential of sludge (V), E is the electrical potential gradient across the plug (V m^{-1}), and η is the viscosity of the liquid medium (kg m^{-1} s^{-1}). According to Equation (i), a higher absolute value of zeta potential of sludge relates to a higher maximum water removal rate, which may be observed in Figure 3.

However, during the course of the experiments, the water removal rate decreased with time, due to the limitation of the water content in the sludge cake. A similar effect was observed by Larue *et al.* [21] where bentonite electro-dewatering was researched. After 48 hours, the water removal rate in all the experiments was the same (7.0 l m^{-2} day^{-1}), and in the experiment using anaerobically digested sludge, the electro-dewatering process was complete. In addition, experiments using raw sludge with and without added alkalinity lasted 2 days longer than the experiment using anaerobically digested sludge.

Removal of Water during Pressure Driven Electro-dewatering Process

At the anodic side, the water removal rate in experiments using raw sludge with and without added alkalinity was similar, that is, the dewatering rate was initially high (7.2 and 6.2 l m^{-2} h^{-1}, respectively), gradually decreased with time and reached almost zero at the end of the experiments (Figure 4(a)). However, in the experiment using anaerobic sludge, the water removal rate was initially low (1.1 l m^{-2} h^{-1}), reaching a maximum (4.9 l m^{-2} h^{-1}) in 4 hours, and then decreasing to zero at the end of the dewatering period. It is assumed that protons (H^+) were formed due to the electrolysis of water, which reduced the pH of sludge at the anode. Low pH has been reported as having a positive effect on dewatering, because it may cause extra-cellular polymer (ECP) to detach from the sludge surface and therefore increase the zeta potential (Figure 5(a)), facilitating the formation of sludge aggregates [22, 23]. Raw sludge had lower pH buffering capacity in comparison with anaerobic sludge (Table 1). Moreover, low pH at the anode contributed to higher water removal from the sludge. Added alkalinity not only increased the pH buffering capacity, but also increased the EC, which related to higher current density in comparison with the experiments using other types of sludge (Figure 2(b)). According to Hamed and Bhadra [24], high current density related to the decrease in pH at the anode. Therefore, water removal at the anodic side was similar to experiments using raw and raw sludge with added alkalinity (Figure 4(a)). Also, anaerobic sludge had a high pH buffering capacity (Table 1) and a lower current density during the electro-dewatering process; thus, the pH at the anode may have decreased more slowly than in the experiments using

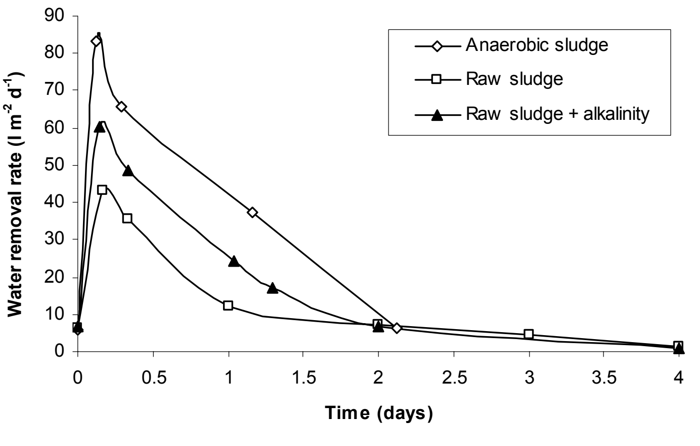
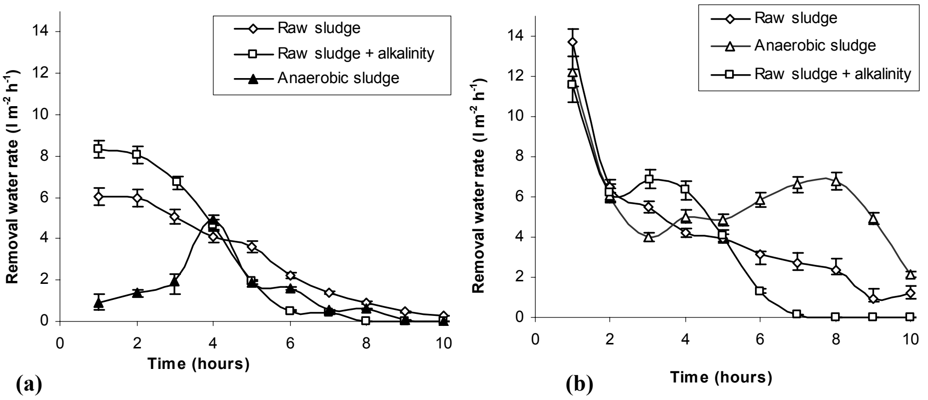


Figure 3. Water removal rate for different sludge types during non-pressure electro-dewatering process.



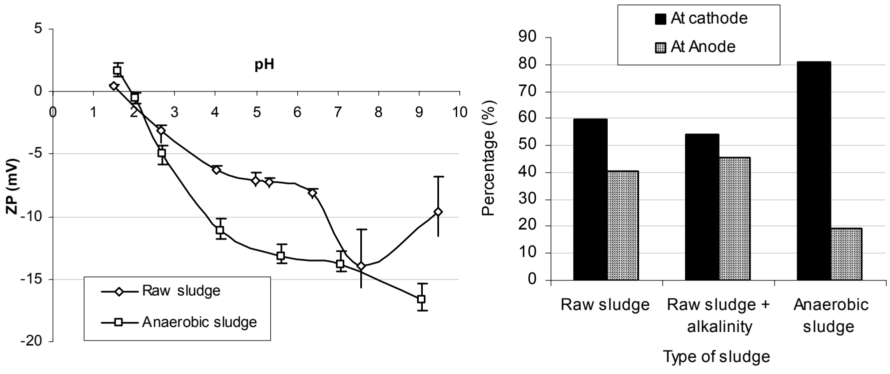
(a) (b)

Figure 4. Water removal rate during pressure driven electro-dewatering process using different sludge types: (a) at the anode; (b) at the cathode.

raw sludge with and without added alkalinity. Moreover, this may have affected water removal during initial four hours of the experiment (Figure 2(b)).

Variation in water removal at the cathode is shown in Figure 4(b). At the beginning of experiments, the pressure-driven electro-dewatering process was similar to a simple pressure filtration. Therefore, in all experiments the water removal rates had a significant drop during first 30 minutes, because increasing resistance of the sludge cake decreased the filtration flow rate [25].

According to Equation (i), dielectric permittivity of vacuum (ε_0) and the dielectric constant of the liquid (ε_r) are constant during the electro-dewatering process. According to Barton *et al.* [9], during the initial stage of the electro-dewatering process, the electrical resistance of the sludge does not increase, hence the sludge temperature is not influenced by Ohmic heating. Thus, the viscosity of a medium (η) is also assumed to be constant. Therefore, the liquid flow by electro-osmosis depends entirely on the electrical potential gradient (E) and zeta potential (ζ). During the electro-dewatering process, the volume of sludge decreased; hence, the distance between the anode and the cathode also decreased. Owing to the applied constant voltage, the electrical potential gradient increased with time. On the other hand, the sludge pH decreased with time due to the applied electric current [18, 26, 27]. It is also well documented that the pH drop relates to the reduction of the absolute value of the zeta potential (Figure 5(a)), thus the decrease in pH reduced the electro-osmotic flow during direct current application [28–30]. In the anaerobically digested sludge and raw sludge with added alkalinity, there was a high pH buffering capacity, which resulted in a constant or slightly increased



(a) (b)

Figure 5. (a) Average zeta potential at different pH; (b) water removal from the anode and the cathode during the pressure-driven electro-dewatering process.

zeta potential. As a consequence, an increasing potential gradient may facilitate higher water removal at the cathode. In the experiment using raw sludge with a low pH buffering capacity, the absolute zeta potential decreased faster than the increase in electrical potential gradient. Therefore, the water removal rate was gradually reduced during the electro-dewatering process (Figure 4(b)).

The amount of water removed at the anode and the cathode are presented in Figure 5(b). In the experiment using anaerobically digested sludge, 81% of the water was removed at the cathode in comparison with 60% in the experiment using raw sludge. The addition of alkalinity into the raw sludge increased the amount of removed water at the anode from 40% to 46%. This may be regarded as a consequence of the decrease in sludge pH due to the high current at the anode, which facilitated sludge dewatering under applied pressure.

Effect of Sludge Types on Dry Solid of the Final Sludge Cake in Non-pressure Electro-dewatering Process

In experiments without pressure, electro-dewatering significantly reduced water content in the sludge cake. However, the amount of DS of the final sludge cake was strongly dependent on the sludge types used for experiments. In all the control experiments, after a month of dewatering processing using a natural sand drying bed with anaerobically digested, raw and raw sludge with added alkalinity, the DS of the final sludge cake was similar (about 13%). The sand drying bed coupled to the electro-dewatering process resulted in an increase of the DS content of the final sludge cake in all the experiments (Table 3). In comparison with the control experiments, DS of the final sludge cake increased from 13.2% to 40.6% in the experiment with anaerobically digested sludge under the applied electric current. These findings are similar to other research efforts to increase the DS content in a final sludge cake [18, 26]. However, in experiments using raw sludge with and without added alkalinity, DS content in the sludge cake only increased from 13.5% to 17.7% and 16.3%, respectively.

The acidic pH in sludge at the anode decreased electroosmotic flow [27, 29]. In non-pressure anaerobically digested sludge experiments, the pH at the anodic side was 4.0, and 2.3 and 2.0 in experiments using raw sludge with and without added alkalinity, respectively. In the anaerobically digested sludge, low current density (Figure 2(a)) and high pH buffering capacity (Table 1) may have kept the zeta potential constant or slightly reduced, hence electro-osmotic flow may have transported water from the anode towards the cathode, which resulted in a lower water content in sludge at the anode in comparison with the cathode (Table 3). On the other hand, in experiment using raw sludge with low pH buffering capacity (Table 1), or in raw sludge with added alkalinity, high pH buffering capacity and high current density (Figure 2(a)), pH at the anode significantly decreased. Thus, as argued by Eykholt [28, 31], the zeta potential may have become zero or slightly positive, resulting in reverse electro-osmotic flow. Therefore, the water content in sludge by the anode was higher than by the cathode (Table 3). A similar result was observed by Yoshida *et al.* [32] who studied the electro-dewatering efficiency of sludge under direct and alternating currents.

Effect of Pressure on the Final Sludge Cake during Electro-dewatering Process

In the control experiments, the sludge cake was not formed during the initial 10 hours of the experiment. The DS was 8% in anaerobically digested sludge and about 15% in experiments using raw sludge with and without added alkalinity. Applying an electric field significantly increased (to 40%) DS in the final sludge cake of anaerobically digested

Table 3. Sludge solid content before and after electro-dewatering experiments.

		Non-pressure electro-dewatering			Pressure-driven electro-dewatering		
Sample point	Type of sludge	DS (%)	VS (%)	VS/TS (%)	DS (%)	VS (%)	VS/TS (%)
Initial feed	Anaerobic	7.5	3.7	49.1	6.9	3.7	52.7
	Raw sludge	8.6	6.3	73.7	6.7	4.9	73.3
	Raw sludge + alkalinity	8.3	5.7	68.2	7.3	5.1	69.6
Sludge cake	Anaerobic	40.6	22.0	49.2	40.2	21.2	52.7
	Raw sludge	16.3	12.4	76.3	36.0	26.7	74.2
	Raw sludge + alkalinity	17.7	12.0	67.9	34.9	24.4	70.0
By the anode	Anaerobic	44.1	25.5	57.8	43.8	30.1	68.8
	Raw sludge	14.4	11.8	82.0	31.6	28.0	88.4
	Raw sludge + alkalinity	15.0	12.7	84.1	36.4	30.4	83.5
By the cathode	Anaerobic	22.5	9.7	43.1	28.4	13.3	46.7
	Raw sludge	24.7	11.8	47.9	33.2	18.6	56.1
	Raw sludge + alkalinity	20.4	10.0	49.0	27.0	17.4	64.6

sludge, and to 36% and 35% in experiments using raw sludge with and without added alkalinity, respectively (Table 3). In comparison with the non-pressure electro-dewatering process, when only raw and raw sludge with added alkalinity were used, pressure-driven electro-dewatering significantly reduced water content in the final sludge cake. However, electro-dewatering using anaerobically digested sludge with or without applied pressure resulted in the same DS of the final sludge cake. This is in contrast to the findings of Gingerich *et al.* [5], who argued that an increase in pressure reduces water content in the final anaerobically digested sludge cake.

In comparison with the initial sludge, the volatile solid per total solid (VS/TS) ratio in sludge cake was always smaller by the cathode (48%) and higher (74–82%) at the anode, regardless of experimental strategy (Table 3). In addition, the pressure-driven electro-dewatering process resulted in a thinner sludge cake (7 mm) in comparison with 15–20 mm in non-pressure experiments.

Migration of Organic Matter during the Electro-dewatering Process

The migration of organic matter from the cathode to the anode was observed regardless of sludge type (Table 4). Usually municipal, and especially raw, sludge contains negatively charged organic substances such as fatty acids (Table 2), humus and other organic materials that may be transported towards the anode during applied electric current. Also, in, for example, the electrokinetic remediation process, acetic acid is usually added to depolarize cathodic reactions [28, 33]. Thus, acetate ions are also found to be moving towards the anode under the applied electric current [34]. In non-pressure dewatering experiments, the organic matter accumulated at the anode. Therefore, the concentration of COD and TOC in removed water at the cathode decreased in comparison with control experiments (Table 4). When pressure-driven electro-dewatering process was applied, water was removed from both the anodic and the cathodic sides; thus, organic matter did not only accumulate in sludge at the anode but was also removed from sludge by the water flow. Therefore, the COD and TOC concentrations in removed water were higher at the anode and lower at the cathode in comparison with control experiments (Table 4).

CONCLUSIONS

The addition of alkalinity to raw sludge increased the current density in comparison with experiments using raw sludge and anaerobically digested sludge. Pressure-driven electro-dewatering resulted in higher current density and a shorter dewatering time than in solely pressure-driven experiments.

In non-pressure electro-dewatering, the water removal rate and the DS of the final sludge cake were highly dependent on sludge types. The addition of alkalinity to raw sludge increased the maximum water removal rate but did not significantly reduce the water content in the final sludge cake. Reduction of sludge pH at the anode increased the zeta potential to a positive value, which resulted in a reversed electro-osmotic flow. Therefore, in experiments using raw sludge with and without added alkalinity, the water content in sludge at the anode was higher than at the cathode.

During the pressure-driven electro-dewatering process, current density and sludge pH buffering capacity affected the water removal rate both at the anode and the cathode. Pressure-driven electro-dewatering using raw sludge with and without added alkalinity significantly increased the DS of the final sludge cake in comparison with non-pressure experiments using the same types of sludge. However, experiments using anaerobically digested sludge with and without applied pressure resulted in the same water content in the final sludge cake.

Electric field application induced the migration of negatively charged organic matter from the cathode to the anode, and it was removed from sludge by the water flow in pressure-driven experiments. Therefore, the COD and TOC concentrations in removed water were higher at the anode and lower at the cathode in comparison with control experiments.

Table 4. Chemical oxygen demand (COD) and total organic carbon (TOC) concentrations in removed water after electro-dewatering experiments.

		Control experiments		At the cathode		At the anode	
Pressure condition	Types of sludge	COD (mg l^{-1})	TOC (mg l^{-1})	COD (mg l^{-1})	TOC (mg l^{-1})	COD (mg l^{-1})	TOC (mg l^{-1})
Non-pressure electro-dewatering	Anaerobic	1286	368	740	248	–	–
	Raw sludge	8238	2783	5660	2000	–	–
	Raw sludge + alkalinity	10,206	3870	9666	3370	–	–
Pressure-driven electro-dewatering	Anaerobic	936	304	694	242	1568	616
	Raw sludge	11,677	4064	2116	695	25,912	8363
	Raw sludge + alkalinity	14,017	4780	5281	3543	28,493	9470

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Paper III

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Effect of freeze/thaw conditions, polyelectrolyte addition, and sludge loading on sludge electro-dewatering process

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ABSTRACT

Laboratory scale pressure-driven electro-dewatering reactor was set up to study the effect of polyelectrolyte addition and freeze/thaw conditions on solid content in the final sludge cake at different sludge loading rates. An increase in freezing temperature and extended natural freezing periods resulted in a significant increase in sludge dewatering ability. However, dry solid (DS) content in the final sludge cake after electro-dewatering was similar (39.3–41.5%) regardless the experimental strategies. The reduction in sludge loading rate from 20 to 3 kg DS/m^2 resulted in the increase in DS content of the final sludge cake (35.8–48.7%) using both, the polyelectrolyte addition and freezing condition sludge samples. During electro-dewatering using sludge amended with polymers, the DS content in the final sludge cake by the anode and the cathode was similar or a bit higher at the cathode either at high sludge loading or using high amount of polymers. It was found that polymer addition had a negative effect on the electro-osmotic flow.

1. Introduction

The most important disadvantage of aerobic municipal wastewater treatment is the generation of large amounts of waste sludge. Original biological sludge from wastewater treatment plant such as activated sludge and anaerobically digested sludge are well known to have a poor dewaterability. It is known that freeze/thaw conditioning is a highly effective sludge dewatering technique. The main principle of this technique is that during freezing, ice crystals grow incorporating water molecules [1,2]. Because the structure of ice crystals is highly organized and symmetrical, it cannot accommodate any additional atoms or molecules. Each ice crystal continues to grow as long as there are water molecules available. All other impurities and solid particles are forced to the boundaries of the ice crystal where they become compressed or dehydrated. This technique changes sludge floc into a compacted form, reduces sludge bound water content and makes sludge more apt for settling and filtration [3]. In general, sludge freezing at slow freezing rates shows better dewaterability than fast freezing. Nonetheless, it has been reported that even fast freezing significantly improves sludge dewaterability [4]. Ormeci and Vesilind [2] who studied freeze/thaw conditioning effect on alum and activated sludge, concluded that freeze/thaw conditioning effectively dewatered alum and activated sludge, however, alum sludge was likely to freeze/thaw better than activated sludge due to its low dissolved ion and organic matter content. High concentrations of dissolved ions and organic material present in activated sludge promote particle entrapment during freezing and decrease the effectiveness of freeze/thaw conditioning. Alum sludge ice crystals predominantly grow in columns, whereas activated sludge ice crystals grow in dendrite [5]. The addition of dissolved solids (NaCl) to alum sludge changes ice crystals growth from columnar to dendrite. Because the dendrite ice crystals are formed at the ice/water interface, sludge particles are trapped in the ice front, resulting in a decrease in sludge dewaterability. The freeze/thaw conditioning does not only increase the sludge dewaterability but also reduces pathogenic microorganisms in sludge [6]. It is also considered as a low-cost sludge treatment technique at moderate to cold climates [7].

Electrically assisted treatments have gained popularity in environmental engineering in recent years [8–13]. Electro-dewatering method, when low level electric field is applied to the sludge cake to induce the migration of water, has been reported to significantly reduce water content in the final sludge cake [14,15]. However, the effectiveness of electro-dewatering process strongly depends on electric field strength and the contact time [16–18]. Moreover, an increase in voltage application subsequently results in reduced water content in the final sludge cake as reported by numerous researchers [14,19–21]. During electro-dewatering process, sludge type and alkalinity plays an important role in water removal rate and the final dry solid (DS) content of the sludge cake [22]. The effect of different types of polyelectrolyte and doses on electro-

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Table 1
Main characteristics of sludge from Mikkeli Wastewater Treatment Plant.

Parameters	Sludge after anaerobic digestion
Temperature (°C)	33.4–34.0
EC (electric conductivity) (s/cm)	7160–7500
pH	7.16–7.38
Alkalinity (mg/kg $CaCO_3$)	6862–10487
DS (dry solid) (%)	3.17–2.87
VS (volatile solid) (%)	1.53–1.70
VS/DS (%)	55.1–53.4
Zeta potential (mV)	−14.0 to −15.9
CST (capillary suction time) (s)	307.7–345.8

dewatering was investigated by Saveyn et al. [23]. However, there was lack of studies in influence of freeze/thaw conditioning on electro-dewatering of sludge.

In this study, a laboratory scale pressure-driven electro-dewatering reactor was set up to investigate the effect of polyelectrolyte and freeze/thaw conditioning on water content in the final sludge cake at different sludge loading rates.

2. Materials and methods

2.1. Sludge samples

Laboratory scale experiments were conducted with anaerobically digested sludge taken from the effluent of anaerobic digestion unit of Mikkeli Wastewater Treatment Plant (SE Finland). The anaerobic digester was continuously operated and treated mixing primary and secondary sludge with 17–20 days retention time at 35–38 °C. The main characteristics of sludge are shown in Table 1. Because the DS content of this sludge was low (3.1%), the samples were pre-treated by settling to increase the sludge DS to 5%. The sludge was stored at 4 °C prior treatments. Before sludge conditioning, the sample 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. The samples were frozen 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 chosen for all the experiments. During natural freezing treatments, 5 l of the digested sludge samples were kept in 8 l plastic buckets placed outdoors at the beginning of January until the end of March, 2008. The average temperatures in January, February, and March are −9.3, −8.9, and −4.3 °C, respectively. However, the temperature can be fluctuated from +5 to −30 °C. Long term thawing results in altered sludge characteristics due to the anaerobic reactions in the sludge [2]. Thus, all the freezing sludge samples were thawed for 10 h at a room temperature.

Granular polyelectrolyte from Praestol (Praestol 855BS, Germany) was used for sludge conditioning. The polymer had a medium cationic charge, effective at the pH range from 1 to 10. Polymer solutions 4 g/l (0.4%) were prepared at least 24 h before the use [23]. A conventional Jar Test was used to mix the anaerobically digested sludge and polymer. 500 ml of sludge samples were placed in 1000 ml beakers, and then different doses of polymer solutions equivalent to around 5, 10, 15, and 20 kg/ton of DS (kg polymer per ton of DS) were added. Sludge and polymer mixture was then intensively mixed at 300 rpm for 1 min, following by 10 min of slow mixing at 50 rpm. After that sludge samples were fed into the reactor for dewatering.

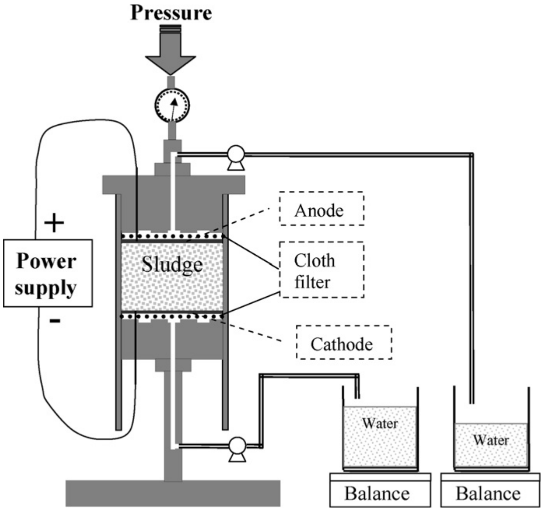


Fig. 1. Schematic representation of the laboratory scale pressure-driven electro-dewatering reactor.

2.3. Electro-dewatering tests

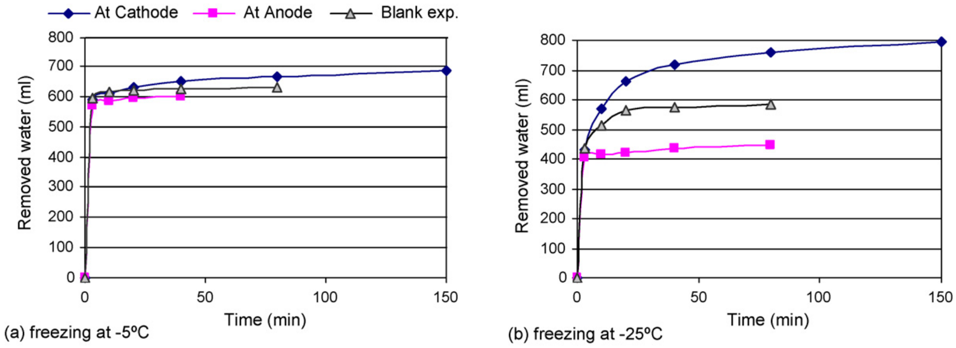
The electro-dewatering experiments were conducted in a pressure-driven reactor [24] (Fig. 1). The reactor was made of plastic (9.8 cm in diameter and 30 cm in length). The stainless steel mesh (0.5 mm thickness) and titanium plate electrode (2 mm thickness) were used as the cathode and the anode, respectively [22]. The electrodes were connected to the DC (Direct Current) power supply (GW Instek, Taiwan) to provide a constant (20 V) voltage. The cloth filter (Z104256 PP, Sigma–Aldrich), with permeability factor of 7.62 ($m^3/(m^2$ min)), was placed by the electrodes. The laboratory scale experiments were performed at a room temperature (22 ± 1 °C).

After the sludge samples were introduced into the reactor, sludge was subjected to a constant pressure of 5.0 bars and 20 V throughout the experiments. Removed water was collected from both, the anodic and the cathodic sides. 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) (liters removed per square meter filter per hour). Sludge was removed from the reactor and sampled at the anode, the cathode and the sludge cake.

Sludge loading rate was 15 kg DS/m^2 (kg DS per m^2 filter) for the experiments using natural and controlled freeze/thaw conditions and different polyelectrolyte dosages. To investigate the effect of sludge loading rate on the final sludge cake, experiments were conducted using about 3, 5, 10, 15, and 20 kg DS/m^2 sludge loading rates with sludge frozen at −20 °C and 15 kg/ton DS of added polymer. Blank experiments applying pressure only without electricity were performed to ensure the comparability of data. Moreover, to avoid discrepancies and ensure reliability of data, all the experiments were performed in duplicates.

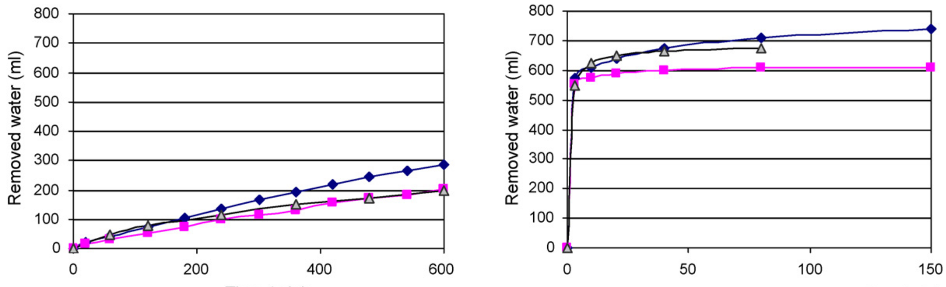
2.4. Analysis

Multimeter (Fluke 110, The Netherlands) was used to monitor current fluctuation. The amount of removed water was measured by electrical balances. Temperature of sludge was measured by electronic thermometer (Fluke53 II, USA). Characteristics of sludge, such as pH, alkalinity, DS (dry solid) VS (volatile solid), and CST (capillary suction time) were determined using Standard Methods



(a) freezing at -5ºC

(b) freezing at -25ºC



(c) original sludge

(d) 15 kg/tonDS of added polymers

Fig. 2. The amount of removed water at the anode and the cathode during electro-dewatering process using different conditioned sludge samples: (a) freezing at −5 °C, (b) freezing at −25 °C, (c) original sludge without treatment, and (d) 15 kg/ton DS of added polymers.

[25]. Zeta potential was determined by Malvern zeta sizer (Nano-Series Instrument, England). To measure zeta potential, the sludge sample was centrifuged at 4000 rpm for 10 min, after that liquid in the upper layer was used to dilute the original sludge sample [21,22]. The average temperature data from January to March, 2008 was taken from automatic weather station at Mikkeli Airport (61°41′14.0″N, 27°12′35.7″E).

3. Results and discussion

3.1. Effect of different freezing temperatures on electro-dewatering efficiency

After freeze/thaw conditioning, the sludge floc structure was altered and became more compacted as also observed by Vesilind et al. [3]. Increased floc size is directly proportional to the improved filterability and settleability of the sludge [26]. In comparison to the CST of the original sludge, freeze/thaw conditioning significantly reduced the CST of the treated sludge samples. During electro-dewatering process using freeze/thaw conditions at different temperatures, electro-dewatering was over after 150 min of the experiment (Fig. 2a and b). On the contrary, electro-dewatering using the original sludge samples lasted approximately 600 min (Fig. 2c) and the sludge cake was not formed at all. Therefore, sludge conditioning was necessary to improve the solid–liquid separation by pressure filtration, resulting in smooth electro-dewatering was achieved.

The freezing rate was found to be an important parameter in the performance efficiency of the freeze/thaw process. The slow freezing rate results in the significant improvement of the sludge dewaterability [4,27,28]. When the freezing rate is high, sludge particles are entrapped in the developed ice layer, which impairs the sludge dewaterability [29]. Moreover, when the freezing rate is low, flocs are rejected instead of being trapped, thus they tend to migrate in front of the growing ice crystals, which relates to a remarkable increase in the sludge dewaterability rates. The decrease in freezing temperature was mainly associated with an increase in freezing rates, therefore the CST of freezing sludge samples at −5, −10, −15, −20, and −25 °C were 94.2, 111.7, 141.1, 226.2, and 319.2 s, respectively. However, in electro-dewatering experiments using sludge samples frozen at different temperatures, water content in the final sludge cake was found to be the same regardless the freezing temperature (Fig. 3a). This could be due to the fact that electro-dewatering process was discussed being less sensitive to sludge characteristic by Yoshida [30].

Fig. 2 shows the amount of removed water as recorded at the anode and the cathode during electro-dewatering treatment of sludge samples with different conditioning methods at the same sludge loading rate. When the low level direct electric current was applied, electro-osmotic flow transported water from the anode to the cathode [31,32]. Therefore, the amount of water removed at the cathode was significantly higher than at the anode. As above discussion, a decrease in freezing temperature increased dewaterability of sludge, which can be attributed to an increase in removed water at initial state of experiments. Indeed, during experiments using sludge samples freezing at −5 °C (Fig. 2a), 90% of total removed water was already taken out during initial 3 min in comparison to 68% during initial stages of experiment using sludge samples freezing at −25 °C (Fig. 2b). However, the total amount of removed water in both experiments was the same at the end of the treatment. This might be related to similar water content in the final sludge cake regardless the freezing temperature in above discussion (Fig. 3a).

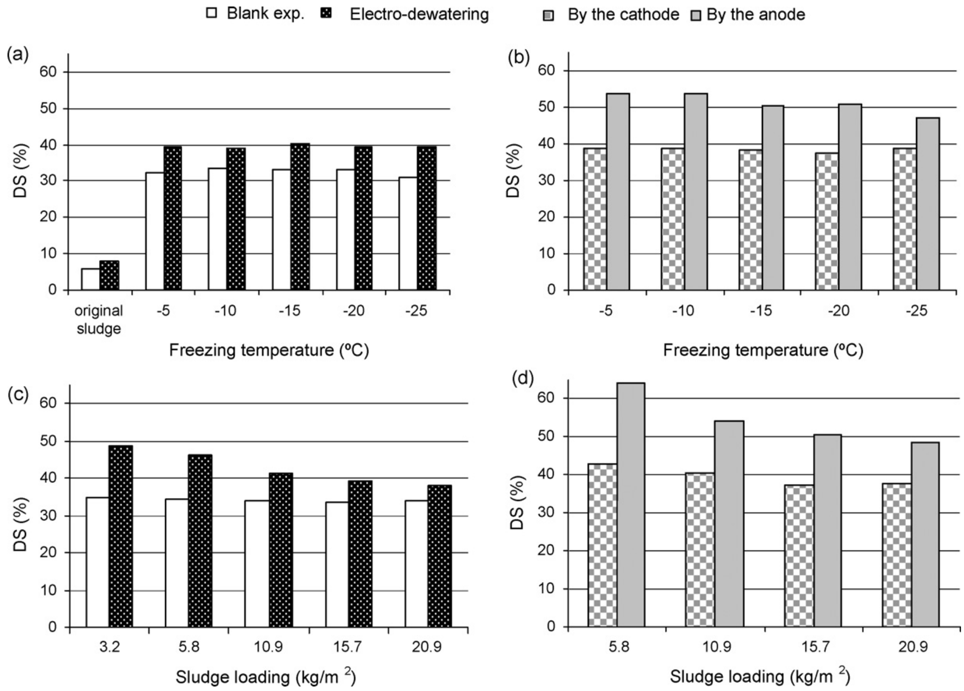


Fig. 3. DS content of the final sludge cake, sludge by the anode and the cathode due to electro-dewatering using freeze/thaw sludge at different temperatures (a and b) and −20 °C freeze/thaw sludge at different sludge loading rate (c and d).

3.2. *Effect of sludge loading rate on water content in the final sludge cake*

Fig. 3c and d shows the DS content in the final sludge cake and the samples at the anode and the cathode, after electro-dewatering with different sludge loading rates using sludge frozen at −20 °C. It was observed that due to electro-dewatering process, a decrease in the sludge loading rate significantly increased the DS content in the final sludge cake. It was contradicted with blank experiments without the applied electric field, when the DS content in the sludge cake was the same regardless sludge loading rate (Fig. 3c). Results from Saveyn et al. [33] showed a clear profile of the sludge cake consisting of different sludge zones with different water contents, gradually increasing from the anode to the cathode during electro-dewatering. At some point during the experiments, the contact between the anode and the sludge matrix was reduced, ceasing the electro-osmotic flow. Therefore, the DS content of the sludge cake may be limited by the dry layer of sludge at the anode. Similar dry layer with high electrical resistance formed at the anode was also observed by Ho and Chen [34]. The thickness of the final sludge cake in experiments with sludge loading rates of 3, 5, 10, 15, and 20 kg DS/m^2 were 3.6, 6.7, 14.6, 20.1, and 29.0 mm, respectively. The thicker sludge cake may contain more wet zones at the cathode. Thus, an increase in sludge loading rate resulted in the reduced water content in the final sludge cake. Besides, electrical gradient plays an important role in reducing water content in the final sludge cake during the electro-dewatering process [14,19,20]. Due to the sludge electro-dewatering with different sludge loading rates, the distance between the anode and the cathode increased especially when higher sludge loading rates were employed. Because of the applied constant voltage, the lower sludge loading rate resulted in the higher electrical gradient, hence higher DS content in the sludge cake was observed (Fig. 3c).

During electro-dewatering process using freeze/thaw sludge samples, water was transported from the anode to the cathode by electro-osmotic flow. Therefore, the water content in sludge cake at the anode was found to be significantly lower than in the sludge at the cathode (Fig. 3b and d). Indeed, it was similar to the observation made earlier while investigating electro-dewatering of anaerobically digested sludge [22].

3.3. *Effect of natural freezing on electro-dewatering efficiency*

The average temperature from January to March, 2008 is shown in Fig. 4. According to the report from the Finnish Meteorological Institute, the period from December 2007 to February 2008 was the warmest in 100 years [35]. The average temperatures were over 0 °C for many days, which allowed sludge to be subjected to multi-freeze/thaw cycles and a long curing time. The advantages of multi-freeze/thaw cycles are the significant reduction in *E. coli* activation [36] and increase in the permeability coefficients of soil and sludge slurries [37]. Curing time was also reported to be beneficial for the sludge dewaterability [27,28]. Due to natural freezing, the average CST of sludge after 1, 2, and 3 months was 69, 54, and 38 s, respectively, which indicated that multi-freeze/thaw cycles and also a long curing time might be facilitated an increase of the sludge dewaterability. However, when natural sludge samples frozen at various durations were used for experiments, the DS content in the final sludge cake was the same (Fig. 5). In comparison with experiments using sludge frozen at different temperatures, the water content in the final sludge cake (Fig. 3a) did not show any significant difference. Also, it was found that electro-dewatering process

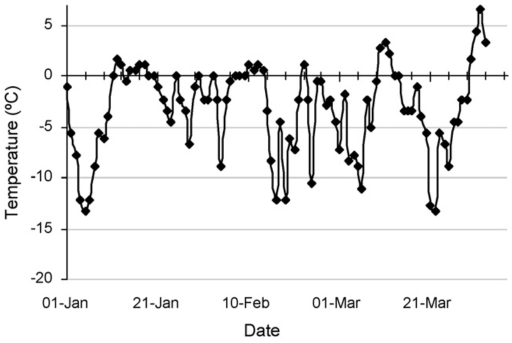


Fig. 4. Average temperatures from January to March in 2006 and 2008.

using 1 month naturally freeze/thaw conditioned sludge lasted 150 min in comparison to 100 min using 2 and 3 months naturally freeze/thaw conditioned sludge under the same experimental conditions. Thus, electro-dewatering using naturally freeze/thaw conditioned sludge could significantly reduce the dewatering time.

3.4. Effect of polyelectrolyte conditioning on electro-dewatering efficiency

An increase in the polymer dosage resulted in a decrease of CST and the improvement of sludge dewaterability. Indeed, the CST of polymer conditioned sludge samples at around 5, 10, 15, and 20 kg/ton DS were 39.7, 12.4, 7.9, and 11.6 s, respectively, when the CST of the original sludge was 439 s. It was similar observations which were made by several authors [38–40]. In experiments using sludge samples with 5, 10, and 15 kg/ton DS of added polymers, electro-dewatering lasted for 10.0, 4.0, and 2.5 h, respectively. This shows that an increase in polymer dose considerably reduces the dewatering time. Moreover, the increase in polymer dose from 5 to 15 kg/ton DS, not only reduced the dewatering time but also significantly decreased water content in the final sludge cake in both, electro-dewatering and blank experiments (Fig. 6a). After 10 min, the amount of water removed at both sides in experiments using sludge samples with 0, 5, 10, and 15 kg/ton DS of added polymers were 2.3, 10.9, 45.8, and 57.2%, respectively. It was assumed that during the initial stage of electro-dewatering process, electro-osmosis and electrophoresis did not significantly contribute to the removal of water. The filtrate flow rate at the anode and the cathode may be expressed by the following equation (1) [41,42]:

$$Q_p = \frac{dV_p}{dt} = \frac{\Delta p_H A}{\eta(r_c L + R_m)} \qquad (1)$$

where Q_p is the pressure-driven filtrate flow rate, V_p is the volume of filtrate, Δp_H is the hydraulic filtration pressure, A is the filter surface area, η is the viscosity of the liquid medium, r_c is the filter cake resistance, L is the cake thickness, R_m is the filter medium resistance. During the process, Δp_H and A were constant, because of the same experimental conditions with applied constant pressure. Due to the short time of experiments (10 min), the filter medium resistance (R_m) was assumed constant. During the dewatering process using original or polymer conditioned (5 kg/ton DS) sludge, the filter cake resistance (r_c) is high due to the applied pressure and the sludge cake thickness (L) subsequently increases, hence, the filter flow rate (Q_p) rapidly reduces, resulting in a small amount of removed water at beginning of experiments. Therefore, in experiments using the original sludge samples, sludge cake was not formed, resulting in the high water content in the final sludge cake (Fig. 6a). On the contrary, in experiments using polymer conditioned sludge (10 and 15 kg/ton DS of added polymers), the viscosity of the liquid medium may have increased and the filter cake resistance decreased. Because of that the filtrate flow rates did not rapidly decrease or even remained constant at the beginning of the experiment due to an increase in the sludge cake thickness, which consequently resulted in the higher initial water removal (Fig. 2d). Moreover, the sludge cake was formed over the shorter period of time in comparison to the blank experiment.

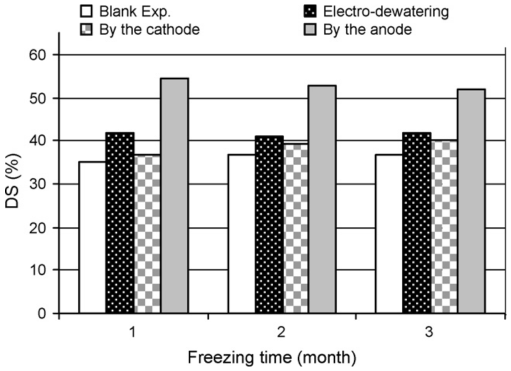


Fig. 5. DS content in the final sludge cake, sludge by the anode and the cathode due to electro-dewatering using natural freeze/thaw conditioned sludge samples.

An increase in polymer dosage from 15 to 20 kg/ton DS and further did not result in the reduction of sludge dewaterability, but the increase in zeta potential as also observed by Lee and Liu [38,43]. During electro-dewatering process, it was found that water content in the final sludge cake in experiments using sludge with 20 kg/ton DS of polymer loading, was higher compared to 15 kg/ton DS sludge. Also, it was found that the water content in sludge by the anode was higher than at the cathode (Fig. 6b).

CST of the sludge samples with 5 and 10 kg/ton DS of polymer addition was 39.3 and 13.0 s, respectively. This was much lower in comparison to the CST of sludge during freeze/thaw at different temperatures. However, due to electro-dewatering, the experiments using polymer added sludge at 5 and 10 kg/ton DS lasted 7 and 1.5 h more, respectively, than the experiments using freeze/thaw conditioned sludge. The DS content in the final sludge cake (Fig. 6a) was also lower than in the same experiments using freeze/thaw conditioned sludge (Fig. 3a).

Fig. 6c shows the DS content in the final sludge after different sludge loading rates with 15 kg/ton DS of added polymer. In comparison to the DS content of the final sludge cake in the same experiments using freeze/thaw conditioned sludge (Fig. 3c), water content in the final sludge cake was similar using the same sludge loading rates. An increase in the sludge loading rate resulted in the reduction of water content in the final sludge cake (Fig. 6c). The potential gradient at the end of experiments with sludge loading rates of about 3, 5, 10, 15, and 20 kg DS/m^2 was 63.4, 36.4, 18.8, 9.5, and 7.1 V/cm, respectively. An increase in the sludge loading rates significantly reduced water content in the final sludge cake and this could be related to the decrease in electrical gradient, which has already been discussed earlier. However, different sludge loading rates using polymer conditioned sludge resulted in the increase in the DS content of the final sludge cake in comparison to blank experiments and were more pronounced than those during the same experiments using freeze/thaw conditioned sludge. During electro-dewatering process, electro-osmosis removes interstitial and some of the vicinal water [44]. Therefore, the same water content was found in the final sludge cake in experiments regardless conditioning method. Conversely, freeze/thaw conditioning also

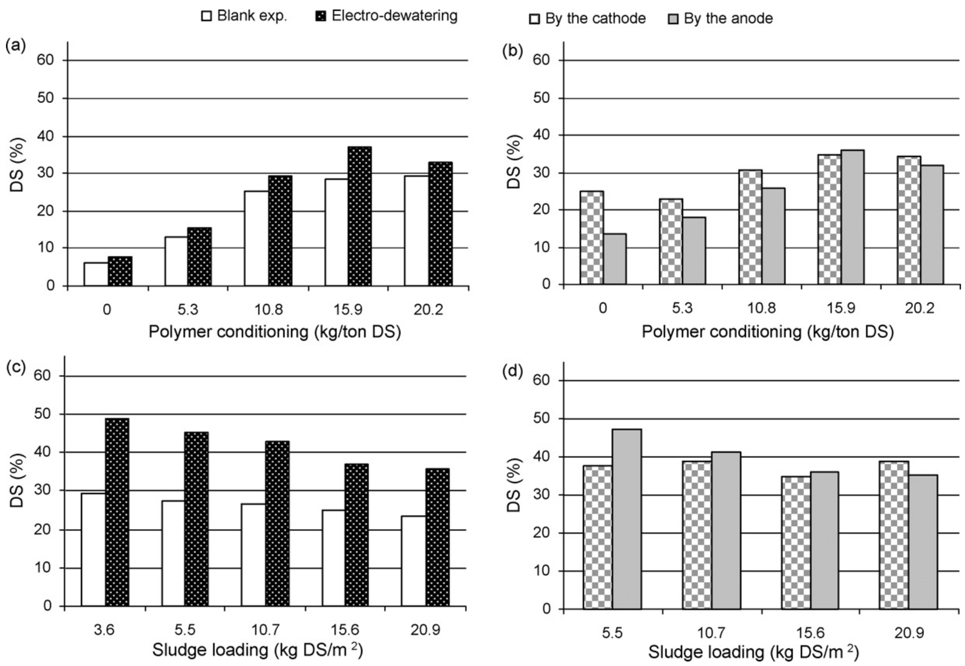


Fig. 6. DS content in the final sludge cake, sludge by the anode and the cathode due to electro-dewatering using different polymer conditioned sludge (a and b) and a sludge sample with 15 kg/ton DS polymer addition at different sludge loading rate (c and d).

reduces sludge bound water content [26,45]. Thus, water content in the final sludge cake during blank experiments using polymer conditioned sludge (Fig. 6c) was higher than in the experiments using freeze/thaw conditioned sludge (Fig. 3c). Therefore, more significant increase in the DS content in the final sludge cake was observed during experiments using polymer added sludge at different sludge loading rates.

During electro-dewatering process, electro-osmotic flow plays an important role in transporting water from the anode to the cathode, and this flow strongly depends on zeta potential. In some cases throughout the current study, an increase in zeta potential caused by the change in pH at the anode, which induced the reverse electro-osmotic flow, resulting in the higher water content at the cathode [22,46]. An increase in zeta potential with increasing polymer dosage was observed by Lee and Liu [38,43]. Indeed, zeta potential value of polymer conditioned sludge sample at 20 kg/ton was −9.6 mV in comparison to −15.2 mV of original sludge. In the current study, the DS content in sludge by the anode and the cathode was significantly different due to different sludge loading rates and using freeze/thaw conditioning (Fig. 3d). Moreover, the distinction between DS in sludge by the anode and the cathode using polymer conditioned sludge was insignificant (Fig. 6d). The DS content in sludge by the anode was lower than the cathode in experiment with sludge loading rate at 20 kg DS/m^2 and electro-dewatering using polyelectrolyte conditioned sludge at 20 kg/ton DS. Fig. 7 shows percentage of water removed from the cathode during electrode-dewatering using freeze/thaw conditioned sludge (−20 °C) and the sludge samples with 15 and 20 kg/ton DS of polyelectrolyte addition. In experiments using freeze/thaw sludge after 40 min of the process, all the removed water was entirely from the cathodic side. In contrast, during electro-dewatering treatment using sludge samples with the same polyelectrolyte loading, there was water removed from the anodic side as well throughout the whole experiment.

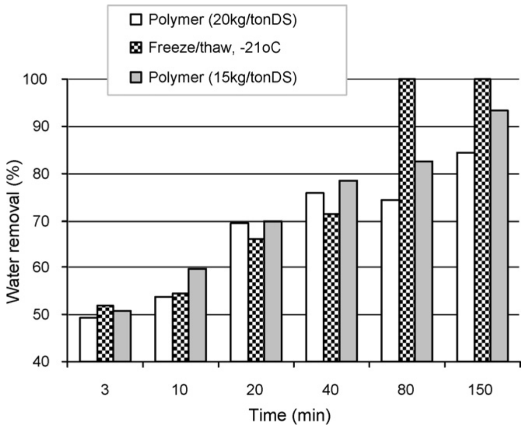


Fig. 7. Percentage of water removal from the cathode as a function of time during electro-dewatering process using sludge samples with 15 and 20 kg/ton DS polymer addition and −20 °C freeze/thaw conditioned sludge.

4. Conclusion

In general, polyelectrolyte and freeze/thaw conditioning of sludge significantly reduced dewatering time and increased the DS content in the final sludge cake during electro-dewatering process. Smooth electro-dewatering occurred in all experiments using freeze/thaw treated sludge samples, but, the smooth electro-dewatering only happened in experiment using polymer conditioned sludge at optimum dosage.

A decrease in freezing temperature resulted in the reduced sludge dewaterability, however, natural freeze/thaw conditioning increased the sludge dewaterability. Due to electro-dewatering using freeze/thaw sludge, electro-osmosis transports water from the anode to the cathode, resulting in a much dryer sludge by the anode than the cathode.

During electro-dewatering process, an increase in sludge loading rates related to the decrease in the DS content in the final sludge cake in experiments using polymer and freeze/thaw conditioned sludge. However, the DS content in the final sludge cake by the anode and the cathode was similar or slightly higher at the cathode than at the anode in experiments using polymer conditioned sludge. This indicates that polymer conditioning had a negative effect on the electro-osmotic flow.

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Paper IV

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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.

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,

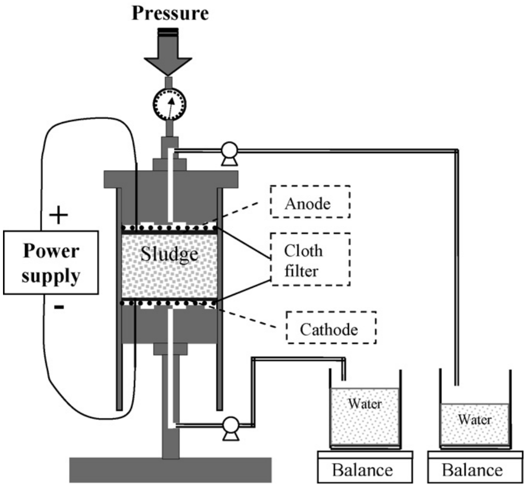

Fig. 1. Schematic representation of the laboratory scale pressure-driven electro-dewatering reactor.

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 determined 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

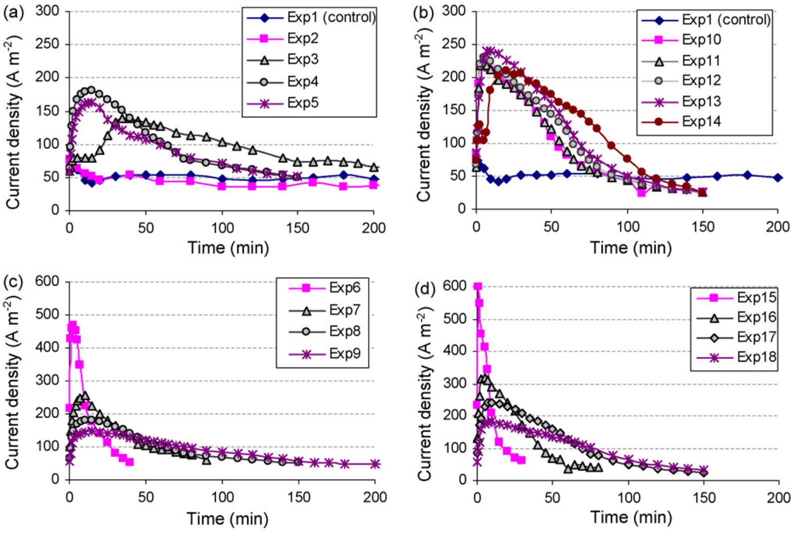

Fig. 2. Current density fluctuation during electro-dewatering process using sludge conditioned at (a) different polymer dosage, (b) freezing temperatures and (c) and (d) electro-dewatering with different sludge loading rates.

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 (PC1and 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).

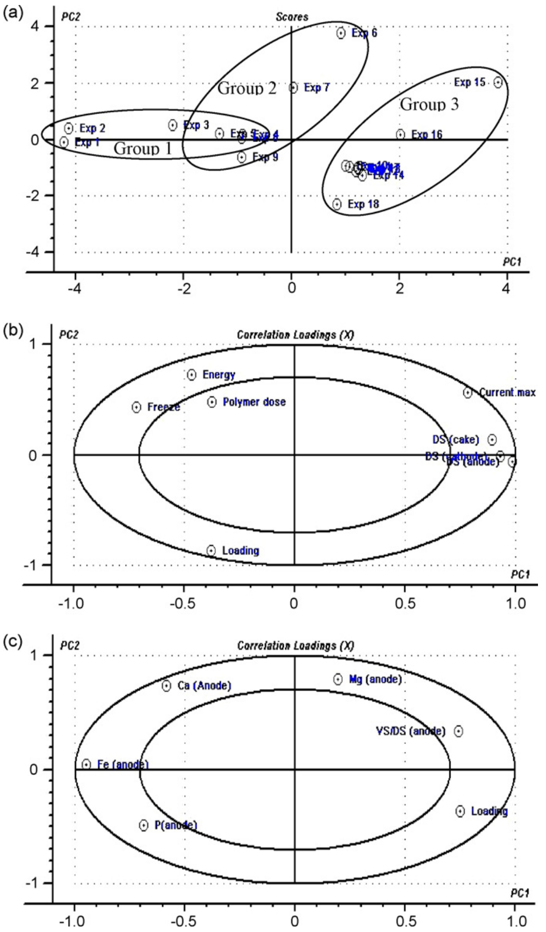

Fig. 3. Principal components analysis within various parameters (a) scores (b) loadings and (c) correlation (loading) of the VS/DS ratio, sludge loading rates and concentrations of macro-elements in sludge at the anode.

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-

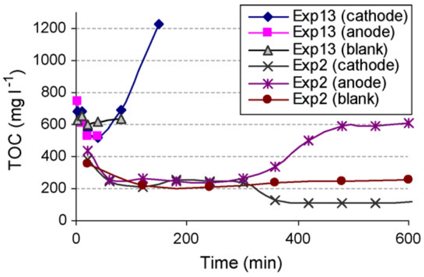

Fig. 4. TOC concentration in the removed water during electro-dewatering process (Exps. 2 and 13).

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

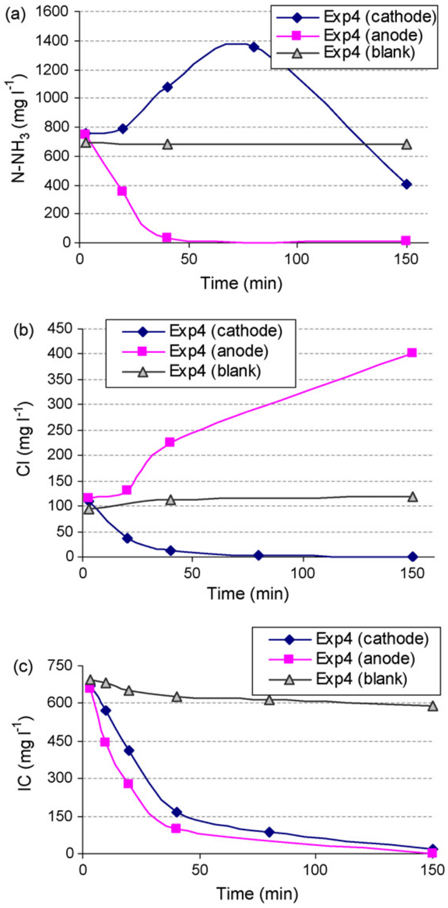

Fig. 6. Concentrations of N-NH_3 (a), Cl (b), and IC (c) in the removed water at the anode and the cathode during electro-dewatering process.

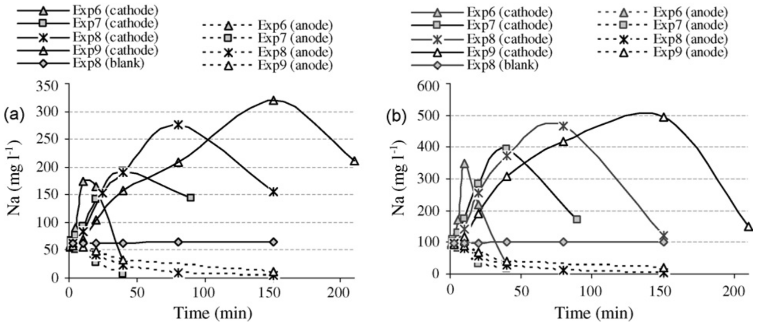

Fig. 5. Concentrations of Na (a) and K (b) in the removed water at the anode and the cathode during electro-dewatering process with different sludge loading rates (Exps. 6–9).

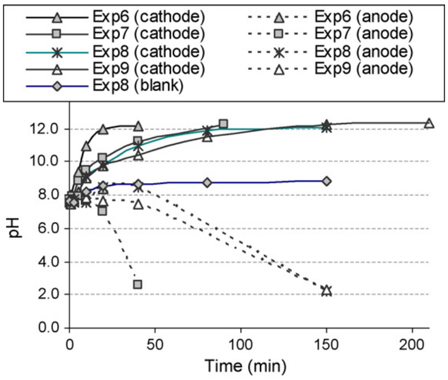

Fig. 7. pH of the removed water at the anode and the cathode during electro-dewatering process with different sludge loading rates (Exps. 6–9).

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

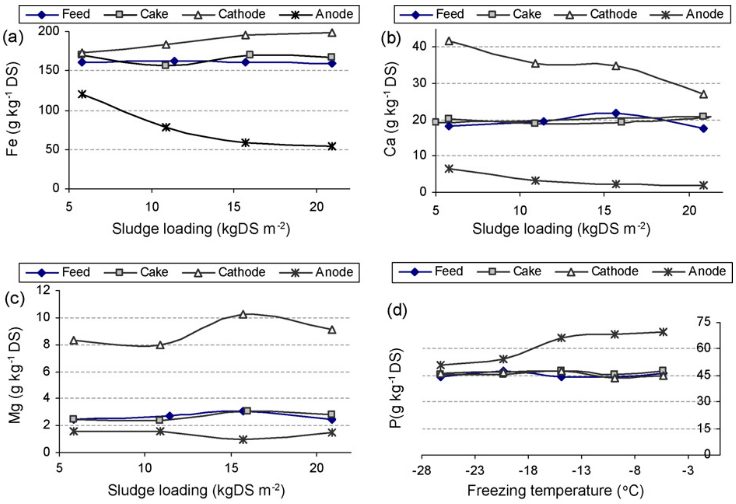

Fig. 8. Concentrations of Fe (a), Ca (b), and Mg (c) in sludge and the final sludge cake, sludge by the cathode and the anode after electro-dewatering process employing different sludge loading rates (Exps. 6–9) and (d) P concentrations in experiments using freeze/thaw conditioned sludge (Exps. 10–14).

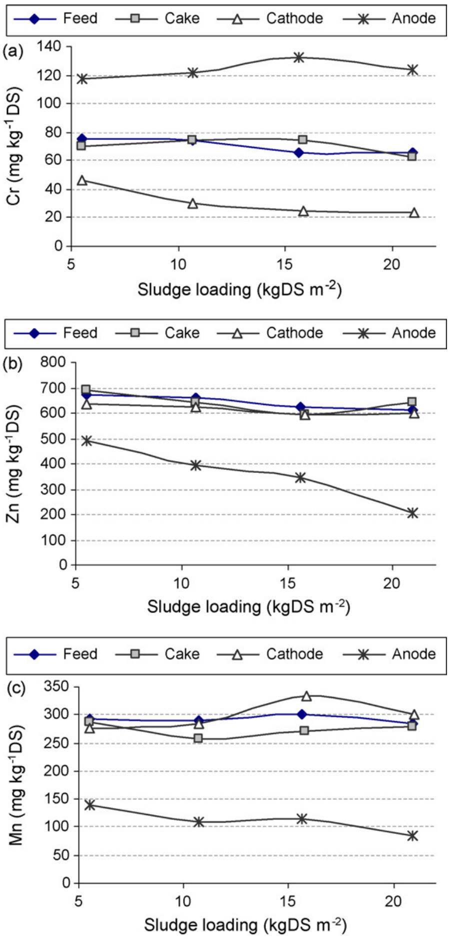

Fig. 9. Concentrations of Cr (a), Zn (b) and Mn (c) in sludge and the final sludge cake, sludge by the cathode and the anode after electro-dewatering process employing different sludge loading rates (Exps. 6–9).

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 ($Cr_2O_7^{2-}$) 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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Fractionation of Macro and Trace Metals Due to Off-Time Interrupted Electrodewatering

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Electrodewatering with interrupted voltage was set up to investigate the effects of long off-time interruption on solid content in the final sludge cake and the fractionation of macro and trace elements in the sludge matrix. In comparison to continuous direct current (DC) electrodewatering, long off-time interruption had a negative effect on water removal, resulting in a high water content in sludge at anode and the final sludge cake. However, long off-time interrupted electrodewatering significantly increased dry solid (DS) content in the final sludge cake in comparison to control experiments. Removal of Na^+ and K^+ from sludge was affected by long off-time interruption. The long off-time interruption also negatively influenced the dissolution and migration of macro (Ca, Mg, and Fe) and trace (Ni, Mn, and Zn) metals in sludge cake matrix. The long off-time interrupted voltage application did not have any effect on the chromium concentrations in sludge at the anode; however, the chromium concentrations in the removed water at the anode significantly depended on off-time interruption.

Keywords Electrodewatering; Electroosmosis; Metal fraction; Off-time interruption; Sludge

INTRODUCTION

Activated sludge is commonly used for municipal and industrial wastewater purification. However, one of the drawbacks of the activated sludge process is the huge amount of waste sludge generated. It is well known that original sludge from wastewater treatment plants usually has poor dewaterability. Mechanical methods such as centrifuge, diaphragm filter presses, and vacuum filter combined with flocculation are usually employed to remove water from waste sludge. However, efficiency of sludge dewatering strongly depends on polymer dosage and characteristics of polymer and sludge. Moreover, mechanical methods cannot reach a sufficiently high potential to drive the interstitial water through the very narrow pore spaces; therefore, dewatering using mechanical means is extremely limited and requires substantial further treatment.[1]

Electric field application through the sludge segment causes electroosmotic phenomenon, which is fluid flow in charged particle matrix. Due to electrodewatering, electroosmosis was reported to reduce the interstitial and some of the vicinal water, thus resulting in a drier sludge cake.[2] Moreover, electrical field application causes electrophoresis, which also contributes to water removal from sludge in the beginning of electrodewatering process.[3] In addition, electrodewatering could lead to significant savings in sludge management process depending on local market prices for investment, operating, and sludge disposal costs.[4] Moreover, electrodewatering is used to remove water from clay,[5–7] tomato paste suspension,[8] food processing,[9] and vegetable sludge and mine tailings.[10]

A sludge electrodewatering process was found to be less sensitive to sludge characteristics[11] and polymer conditioning.[12] According to Yoshida,[11] electrodewatering can easily be combined with mechanical methods to improve the rate and efficiency of water removal. Indeed, bench- and pilot-scale sludge dewatering in a filter press results in a dry sludge cake.[4,13,14] But, electrodewatering combined with a belt press filter did not result in a significant increase of dry solid (DS) content in the sludge cake.[15,16] This could be explained by short contact time during belt press filter dewatering.[4] Application of a higher electrical field was associated with an increase of DS content in final sludge cake.[4,17,18]

Interrupted direct current (DC) electrodewatering was investigated in many studies.[5,7,8,19] During the off-time interrupted electrodewatering of clay and mineral slurries, a short interruption of power application enhanced electroosmotic flow, resulting in 20 to 40% increase in water removal.[20–22] During electroosmotic dewatering under an alternating current (AC) electric field with periodic reversals of electrode polarity, the pH in the sludge profile was not decreased and lower water content in sludge at the anode was significant in comparison to DC dewatering.[22] In addition, during electrodewatering, electromigration, electrolysis, and electroosmosis caused the migration of macro and trace metals in sludge matrix, which resulted in a change of sludge characteristics.[23,24] Moreover, the migration of heavy metals might result in an increase of metal accumulation and mobility, which can cause

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potential risk for the environment, especially when sludge is reused as a fertilizer.

The total metal concentration in sludge usually obtained after microwave digestion in strong acidic solution is useful as an overall pollution indicator. It provides no information on the metal-binding characteristics of the final sludge cake. On the other hand, sequential extraction methods can provide the information about the physicochemical forms of metals in sludge. This information is valuable for evaluating the metals' mobility, bioavailability, ecotoxicity, and environmental impact. In order to evaluate electrokinetic remediation of metals from sludge, several sequential extraction methods have been used. Among various extraction methods, the Community Bureau of Reference (BCR, 1987) is widely used to determine metal fractions in the sludge.[23,25–28]

In this study, pressure-driven electrodewatering experiments under continuous and off-time interrupted direct current were performed to investigate the effects of long off-time interruption on solid content in the final sludge cake and the fractionation of macro and some trace elements in the sludge matrix.

MATERIALS AND METHODS

Sludge Samples

Sludge samples were obtained from the effluent of an anaerobically digested unit (Mikkeli Wastewater Treatment Plant, Mikkeli, Finland). The anaerobic reactor treating primary and secondary sludge was continuously operated with retention times of 17–20 days at 35–38°C. The main characteristics of sludge are presented in Table 1. After sampling, the sludge was pretreated by natural settling to increase the sludge DS content from 3 to 5% and stored in the cold room at 4°C. Prior to the experiments, the sludge was taken out of the cold room to bring it to the room temperature.

TABLE 1
Main characteristics of sludge obtained from Mikkeli Wastewater Treatment Plant

Parameters	Sludge after anaerobic digestion
Temperature (°C)	33.4–34.0
Electric conductivity (μs cm^{-1})	7160–7500
pH	7.16–7.38
Alkalinity (mg kg^{-1} $CaCO_3$)	6862–10,487
Total solid (%)	3.17–2.87
Volatile solid (%)	1.53–1.70
VS/DS (%)	55.1–53.4
Zeta potential (mV)	−15.9 to −14.0
Capillary suction time (s)	307.7–345.8

Sludge Conditioning

Granular polyelectrolyte (Praestol 855BS, 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 use.[12] Sludge samples (500 mL) were filled in a 1000-mL beaker and then polymer dosage was added. A conventional jar test was used to mix an appropriate amount of sludge and the polymer solution at 300 rpm for 1 min, followed by 10 min of slow mixing at 50 rpm. According to the preliminary results of capillary suction time (CST) tests, the optimal polymer dosage was about 15 kg ton^{-1} of DS. Therefore, the optimal dosage was used for sludge conditioning before electrodewatering experiments. After polymer conditioning, sludge samples were fed into the electrodewatering device for the dewatering tests.

Electrodewatering Tests

A laboratory-scale electrodewatering device (Fig. 1) was employed in this study as described by Tuan et al.[29] The device consisted of a polyvinyl chloride (PVC) piston-driven cylindrical filter press (9.8 cm in diameter and 30 cm in length). In the electrodewatering device, the stainless steel mesh (0.5 mm) and a titanium plate electrode (2 mm) were used as the cathode and the anode, respectively.[29] The electrodes were connected to the DC power supply (PSM-6300 GW Instek, Taiwan). The cloth filter (Z104256 PP, Sigma-Aldrich, Finland) was placed near the electrodes. After electrodewatering experiments, the cloth filters in both the cathodic and anodic sides were periodically replaced by the new ones.

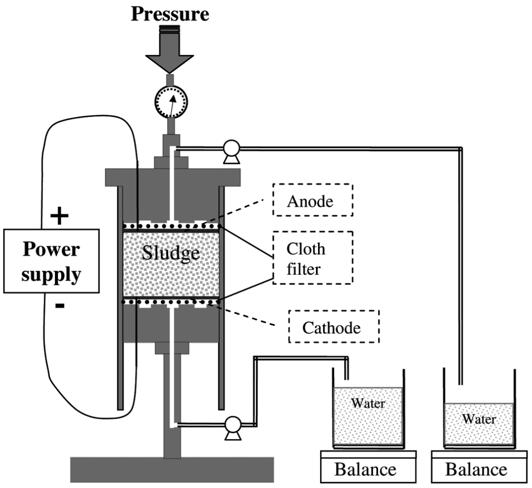


FIG. 1. Schematic representation of the laboratory-scale pressure-driven electrodewatering reactor.

After polymer conditioning, the sludge sample was introduced into the electrodewatering device at a sludge loading rate of 15 kg DS m^{-2}. Then, the sludge segment was subjected to constant voltage and pressure of 5.0 bars. Removed water was collected from both the anodic and the cathodic sides. Electrodewatering was performed for 3 h, and then the final sludge cake was removed from the electrodewatering device. Sludge samples were collected at the anode, the cathode, and the middle of the final sludge cake for quantitative analysis.

Sludge electrodewatering was performed by application of constant DC voltage at 40 V. Two modes of operation were used. The first mode was a continuous DC voltage, which is denoted as *DC electrodewatering*. In the second mode, the power was supplied as an interrupted DC voltage, denoted as *IS*(t_1/t_2) *electrodewatering* where t_1 was the on-time and t_2 was the off-time, both in seconds. In this study, interrupted electrodewatering was performed at IS(45/15), IS(30/30), and IS(15/45). To investigate the effect of electrical treatment, the control experiments were performed without applying voltage. All the experiments were performed in duplicate to ensure the reliability of collected data.

Analyses

Pseudo-Total Metal Digestion

To determine the total amount of metal elements in the sludge, the samples were added with aqua regia solution and then digested using a microwave digester (Perkin Elmer, Anton Paar GmH, Austria).[30] About 0.5 g DS of sludge samples was treated with 10 mL aqua regia (HCl/HNO_3 1:3) in closed pressured 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 room temperature). After cooling, the digested sample was transferred into a 100-mL volumetric flask and diluted to the mark with Milli-Q water. Before chemical analysis, the liquid was centrifuged at 4000 rpm to remove small particles. Then, an ICP spectrometer (ICAP-6000, Thermo, England) was used to determine Na, K, Fe, Ca, Mg, Cr, Mn, Ni, and Zn concentrations in sludge by applying the following wavelengths of 588.995, 766.490, 259.940, 422.673, 285.213, 267.716, 257.610, 221.647, and 213.856 nm, respectively.

Revised BCR Sequential Extraction

Revised BCR sequential extraction protocol was undertaken based on the method described by Mossop and Davidson.[31] The chemicals used for the revised BCR sequential extraction are listed in Table 2. Approximately 1 g DS of sludge samples was used for metal fraction extraction.

Step 1. (Exchangeable fraction) acetic acid extraction: This extraction is related exchangeable/bound to carbonate species. Sludge sample was extracted with 40 mL of 0.11 M acetic acid at pH 7.

Step 2. (Reducible fraction) hydroxylamine hydrochloride extraction: The fraction associated with iron and manganese oxides. In this step, the residual from step 1 was treated with 40 mL of 0.5 M hydroxylamine hydrochloride at pH 1.5.

Step 3. (Oxidation fraction) hydrogen peroxide oxidation and ammonium acetate extraction: The metals species bound to organic and sulfides matter. The residual from step 2 was oxidized by 20 mL of 30% peroxide oxidation at 85°C at pH 2.0 and then extracted with 50 mL of 1 M ammonium acetate at pH 2.0.

Step 4. (Residual fraction) microwave aqua regia extraction: Species associated with mineral matter. The residual from step 3 was treated with 10 mL of aqua regia in microwave digestion as in the pseudo-total metal digestion protocol.

TABLE 2
Chemicals used for the sequential extraction to determine metal fractions in sludge samples

		Extraction conditions	
Fraction	Extracting agents	Shaking time[a]	Temperature (°C)
Step 1. Exchangeable +Carbonates	40 mL CH_3COOH (0.11 M, pH = 7)	16 h	20
Step 2. Iron and manganese oxides	40 mL NH_2OH-HCl (0.5 M, pH = 1.5)	16 h	20
Step 3. Organic matter and sulfides	20 mL H_2O_2 (30%, pH = 2) and then 50 mL CH_3COONH_4 (1 M, pH = 2)	1 h; 2 h; 16 h	20; 85; 20
Step 4. Residual	10 mL demineralized water and 10 mL aqua regia (HCl/HNO_3, 3:1)	26 min	Microwave oven[b]

6 M KOH and HCl solutions were used for pH adjustment.

[a] Shaking was applied at 30 rpm.

[b] Extraction of the residual fraction in the microwave oven was used the same method as the pseudo-total extraction.

TABLE 3
Results obtained (mean ± standard deviation, $n = 5$) from sequential extraction analysis and aqua regia extractable (pseudo-total) metal content of anaerobically digested sludge

	Concentration (mg kg^{-1} DS)						
Metals	Exchangeable fraction	Reducible fraction	Oxidation fraction	Residual fraction	Sum	Pseudo-total	Recovered %
Ca	6662 ± 363.9	10,870 ± 500.1	1868 ± 159.0	189 ± 7.6	19,590 ± 1031	19,800	98.9
Mg	696 ± 31.7	799 ± 31.0	309 ± 11.1	356 ± 10.3	2159 ± 84.2	2217	97.4
Fe	1085 ± 374	101,060 ± 2004	16,774 ± 820.2	23,310 ± 1126	142,230 ± 4324	154,372	92.1
Cr	0.1 ± 0.0	7.9 ± 0.5	25.6 ± 0.6	18.1 ± 0.7	51.6 ± 1.7	49.2	104.9
Mn	25.2 ± 2.4	326.1 ± 7.4	56.4 ± 4.9	24.9 ± 0.7	432.5 ± 15.3	419.7	103.1
Ni	2.3 ± 0.1	21.3 ± 0.5	7.9 ± 0.4	12.4 ± 0.5	44.0 ± 1.5	47.0	93.5
Zn	7.8 ± 0.9	425.5 ± 9.6	28.2 ± 1.7	13.0 ± 0.6	474.4 ± 12.8	461.6	102.8

It is important to note that 6 M potassium hydroxide (KOH) and hydrochloric acid (HCl) solutions were used for pH adjustment. The extraction liquids and residuals were separated by using a centrifuge at 4000 rpm for 20 min. An ICP spectrometer was used to determine concentrations of metals in the extraction liquids. After every step, sludge residual samples were thoroughly washed with Milli-Q water. The analytical performance of metal fraction extraction was evaluated by five replicate analyses of the original sludge. Table 3 shows the data of pseudo-totals and fractionations of metals from triplicates ($n = 5$). The sum of all the fractions was similar to the total metal contents as obtained by pseudo-total metal extraction. The recovery rates were from 80 to 105%.

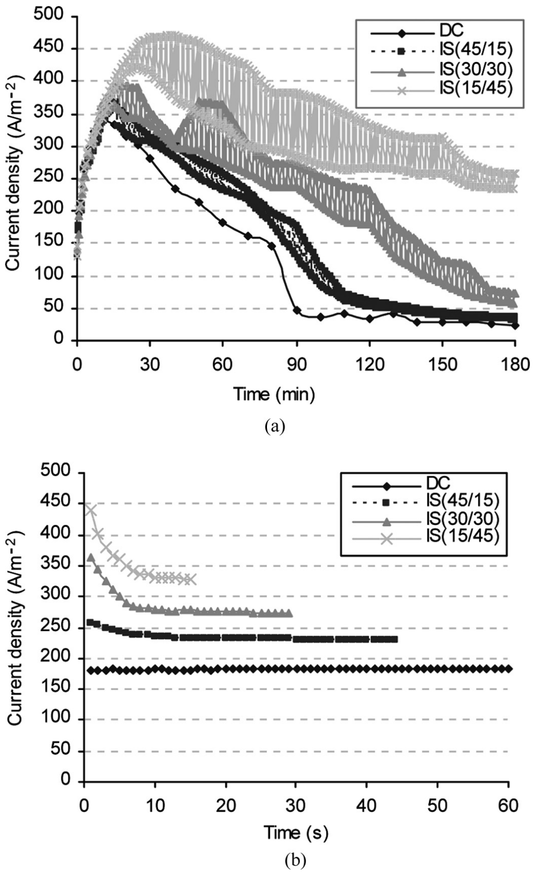
Other Analysis

During electrodewatering, current fluctuations were monitored by a multimeter (Fluke 110, The Netherlands) and electrical balances were employed to measure the amount of removed water from the anode and the cathode. The temperature of the sludge cake was measured by an electronic thermometer (Fluke53 II, The Netherlands). pH of sludge samples, removed water, and BCR sequential extraction steps was measured by a pH meter (WTW pH730, Germany). Other characteristics of sludge, such as alkalinity, DS, volatile solids (VS), and CST were determined by using standard methods.[32] To measure zeta potential, the sludge was centrifuged at 4000 rpm for 10 min, after which the liquid in the upper layer was used to dilute the original sludge sample. Zeta potential was determined by a Malvern zeta sizer (Nano-Series Instruments, England).

RESULTS AND DISCUSSION

Fluctuation of Current Density during Continuous and Off-Time Interrupted Electrodewatering

Figure 2a shows the current density fluctuation during the electrodewatering process under application of



(a)

(b)

FIG. 2. Current density fluctuation during DC and IS electrodewatering processes time (a) and in one cycle (b) at an hour of dewatering.

continuous and interrupted DC voltage. At the beginning, the current density significantly increased in all experiments. After reaching a maximum, the current density decreased until the end of experiment. This could be explained by Ohm's law:

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

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

It can be assumed that the migration of ions and the amount of water in sludge did not have any effect on the conductivity (σ) during initial stages of the electrodewatering process. Polyelectrolyte conditioning reduced CST of sludge samples from 363 to 8.2 s, which resulted in an increase of sludge dewaterability. Thus, 73–76% of water was already removed during the initial 10 min of experiments. The quick removal of water at the beginning of experiments reduced the distance between the electrodes. Because of constant voltage application, the shorter distance between the electrodes resulted in an increase of electrical field (E), which might be directly related to the increase of current density during initial stages of the experiments (Fig. 2a). After increasing to the maximum, the drop in the current density after an initial increase could be due to the increase of electrical resistance of sludge towards the end of the electrodewatering process[33] and the loss of contact between the anode and dry sludge.[34] Furthermore, according to Rabie et al.,[21] during one cycle of interrupted electrodewatering, the current was highest when the power was on. Thereafter, the current decreased until the end of cycle. A similar phenomenon was observed in IS experiments (Fig. 2b). Therefore, the fluctuation in current density was significantly shown in all off-time interrupted experiments (Fig. 2a). In addition, it was found that longer off-time resulted in higher current density and the fluctuation in current also extended over a wider range (Fig. 2a). For example, after an hour of dewatering, in IS(45/15) electrodewatering, the current density fluctuated in the range 258–230 $\mathrm{A\,m^{-2}}$ in comparison to the IS(15/45) experiment in which the fluctuation of current density ranged from 439 to 328 $\mathrm{A\,m^{-2}}$ (Fig. 2b).

Effect of Long Off-Time Interruption on DS Content in the Final Sludge Cake

Figure 3 shows the DS content in final sludge cake after DC and IS electrodewatering. Due to application of a continuous or interrupted electrical field, DS content in the final sludge cake significantly increased in comparison to the control experiments. The sludge samples have negative zeta potential (−10.8 mV). Electroosmotic flow transports water from the anode to the cathode. Therefore, DS content in the sludge cake at the anode was higher than the cathode (Fig. 3).

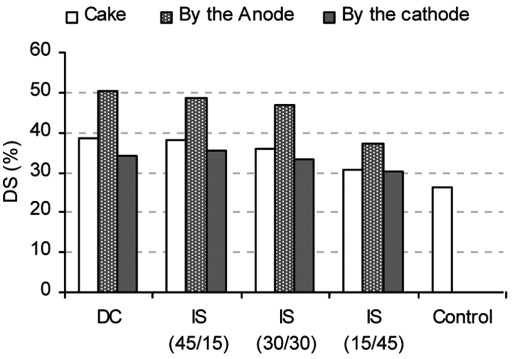


FIG. 3. Solid content of the final sludge cake, sludge by the anode, and the cathode due to DC and IS electro-dewatering.

Rabie et al.[21] documented that interruption with very short off-time application removed more water than DC in IS electrodewatering of clay suspensions. However, if the off-time is too long, water from lower part is drawn upward by capillary force toward the drier part.[20] In addition, longer off-time interrupted electrodewatering had a negative effect on removal of water. Long off-time interruption limited the electrical field strength across the sludge segment and hence reduced electroosmotic flow. Indeed, due to DC electrodewatering, the removed water at the cathode was significantly higher than at the anode and the removed water from the anode was not observed after 80 min (Fig. 4a). On the other hand, in IS(45/15) experiments, the difference in removed water from the anodic and cathodic sites was not significant and removed water from the anode was monitored until the end of experiments (Fig. 4b). Therefore, the low DS content in the final sludge cake and sludge at the anode was observed in IS experiments with longer off-time interruption (Fig. 3).

Effect of Long Off-Time Interrupted Voltage on Migration of Metals During Sludge Electrodewatering

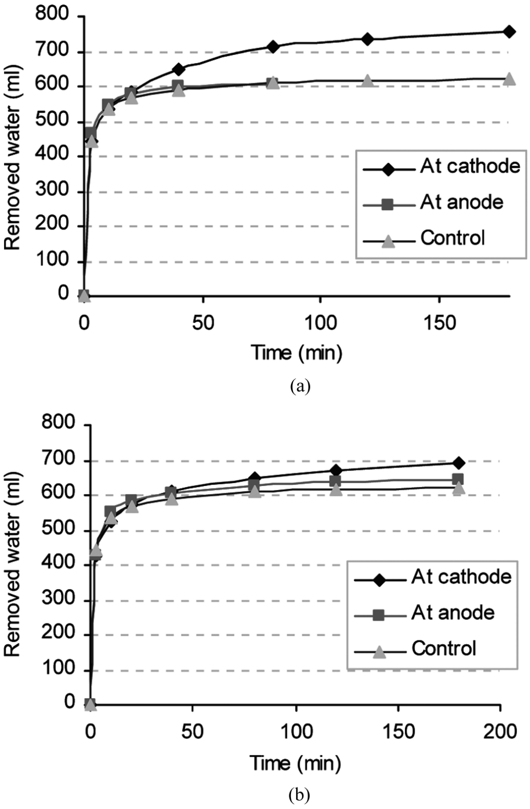
Migration of Soluble Metals

Figure 5 presents Na^+ and K^+ concentrations in the removed water at the anode and the cathode during IS and DC electrodewatering. Under application of electrical field, electromigration of ions can be explained by Eqs. (3) and (4).[35,36]

$$J_j = u_j^* c_j \nabla(-E) \tag{2}$$

$$u_j^* = \frac{D_j z_j F}{RT} \tau n \tag{3}$$

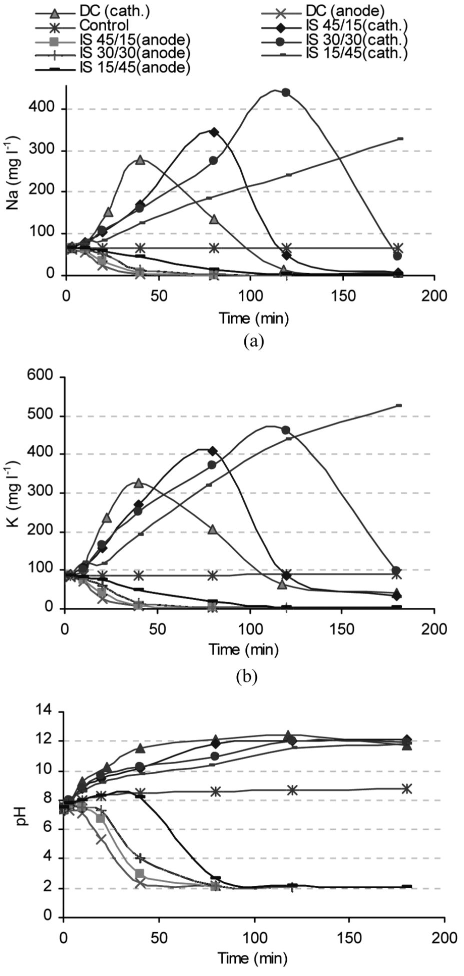
where J_j is electromigration flux of the species j ($\mathrm{mol\,m^{-2}\,s^{-1}}$), u_j^* is an effective ionic mobility, c_j is molar



(a)

(b)

FIG. 4. The amount of removed water during DC (a) and IS(15/45) (b) electrodewatering.



(a)

(b)

(c)

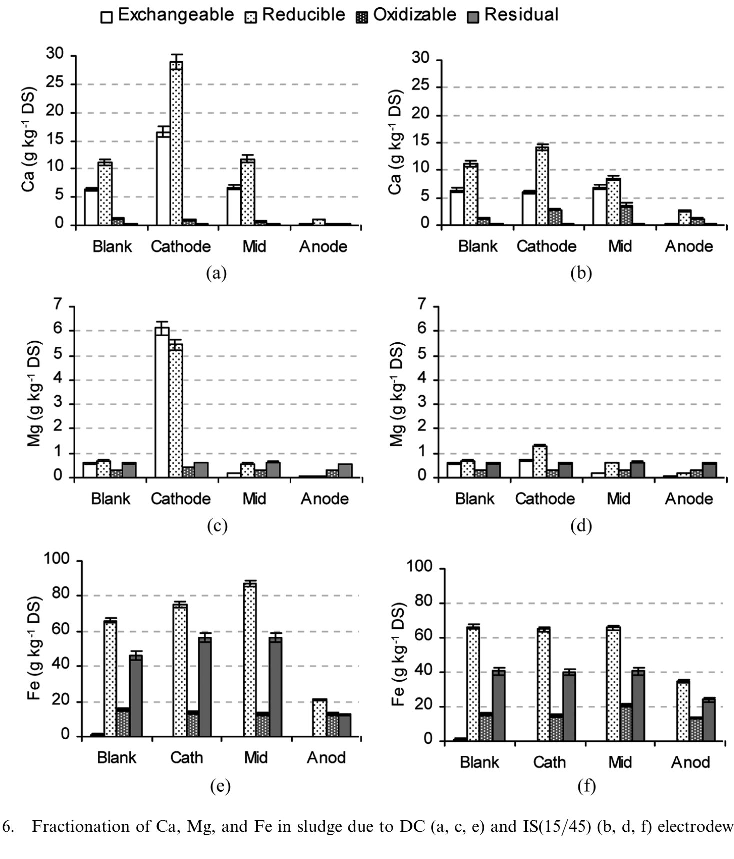
FIG. 5. Concentrations of Na (a) and K (b) and pH (c) in the removed water at the anode and the cathode during DC and IS electrodewatering processes.

concentration of the species j (M), E is electrical potential gradient ($\mathrm{V\,m^{-1}}$), D_j is the diffusion coefficient of species j in the dilute solution ($\mathrm{m^2\,s^{-1}}$), z_j is charge of chemical species (dimensionless), F is Faraday's constant (96,487 C $\mathrm{mol^{-1}}$), R is universal gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$), T is an absolute temperature (K), τ is the porosity of medium, and n is the tortuous factor.

Because Na^+ and K^+ ions have a positive charge, under electrical field application they migrated toward the cathode. Therefore, a decrease of the Na^+ and K^+ concentrations was significantly observed in removed water at the anode (Figs. 5a, 5b). In DC, IS(45/15), and IS(30/30) experiments, the concentrations of Na^+ and K^+ in removed water at the cathode increased at the beginning. After reaching a maximum, the concentrations of Na^+ and K^+ decreased until the end of experiments. A similar fluctuation of Na^+ and K^+ in removed water was discussed earlier.[24,35] However, in IS(45/15) experiments, the concentrations of Na^+ and K^+ in removed water at the cathode increased during the experiment and the maximum concentrations were not observed (Figs. 5a, 5b). The relation between electromigration of ions and the electrical potential gradient (E) is expressed in Eq. (2). During IS electrodewatering, long off-time interruption might reduce the amount of electrical gradient through the sludge segment. Therefore, decrease of Na^+ and K^+ concentrations in removed water at the anode was not significant in comparison to DC experiments. However, due to IS electrodewatering, the maximum concentrations of Na^+ and K^+ in removed water at the cathode were higher in comparison to DC experiments (Figs. 5a, 5b). Longer off-time interrupted electrodewatering also affected the reduction of Na^+ and K^+ in the sludge cake. For example, in DC electrodewatering experiments, concentration of K^+ in the final sludge cake was reduced 74% in comparison to control experiments; on the other hand, the concentration of K^+ was only reduced 23% in IS(45/15) experiments.

Migration of Macrometals

During electrodewatering, electrolysis of water releases an H^+ ion at the anode and electromigration transports the H^+ ion from the anode to the cathode. Thus, a decrease of pH in the sludge profile from the cathode to the anode is well documented.[17,37] At low pH condition, metals associated with the sludge matrix might be dissolved. Under the applied electrical gradient, the metallic cations moved from the anode to the cathode by both electromigration and electroosmosis.[36,38] In conditioning sludge samples, the exchangeable and reducible species were the predominant fractions of Ca (Table 3), which indicated that Ca is highly mobile. Moreover, mineralization of carbonate and bicarbonate ions during electrodewatering was reported to assist in the release of Ca.[24] The exchangeable and reducible fractions of Ca might be dissolved and migrated to the cathode. Therefore, in comparison to the control experiments, a decrease in concentrations of Ca in sludge at the anode and an increase in concentrations of Ca in sludge at the cathode were observed (Fig. 6a). Due to DC and IS electrodewatering, in comparison to the control experiments, the exchangeable and reducible fractions of Ca in the sludge at the anode were decreased 81–96%, respectively. However, an increase of the exchangeable and reducible species of Ca in sludge at the cathode significantly depended on duration of off-time in IS experiments (Fig. 6b). Longer off-time interrupted



(a) (b)

(c) (d)

(e) (f)

FIG. 6. Fractionation of Ca, Mg, and Fe in sludge due to DC (a, c, e) and IS(15/45) (b, d, f) electrodewatering.

electrodewatering resulted in lower concentrations of the exchangeable and reducible fraction of Ca in sludge at the cathode; that is, the reducible fraction of Ca in sludge at the cathode due to DC, IS(45/15), IS(30/30), and IS(15/45) experiments was 29.0, 26.0, 24.2, and 14.1 g kg^{-1} DS, respectively, in comparison to the control experiments, where the concentration of reducible fraction was 11.2 g kg^{-1} DS. A similar effect of longer off-time interrupted electrodewatering on migration of Mg was also observed in Figs. 6c and 6d.

For Fe, the reducible fraction was found to be the highest, about 66.4% (Table 3). During electrodewatering, low pH at the anode facilitated the dissolution of Fe from the sludge particles into sludge porous water, and then Fe ions moved toward the cathode. Therefore, a significant decrease of residual fraction in sludge at the anode was noticed, but an increase in concentrations of the reducible fraction of Fe was not observed in sludge at the cathode (Figs. 6e, 6f). Moreover, the reducible fraction of Fe increased in the middle of the final sludge cake. The increase in reducible fraction of Fe in mid-sludge and the decrease of the reducible fraction in sludge at the anode depended on the duration of off-time in IS experiments. Due to electrical field application, a decrease of the pH in sludge at the anode depended on the amount of current.[39] Longer off-time interrupted electrodewatering might reduce the amount of current through the sludge segment. Consequently, in long off-time IS experiments, pH of removed water at the anode slowly reduced in comparison to short IS or DC experiments (Fig. 5c). In long off-time IS experiments, the dissolution of Fe in the sludge matrix at anode might be limited by a slow decrease of pH. In addition, the reduction of electroosmosis and electromigration due to longer off-time interrupted electrodewatering was discussed above. Therefore, dissolution and migration of Fe were restricted in IS(15/45) experiments, which

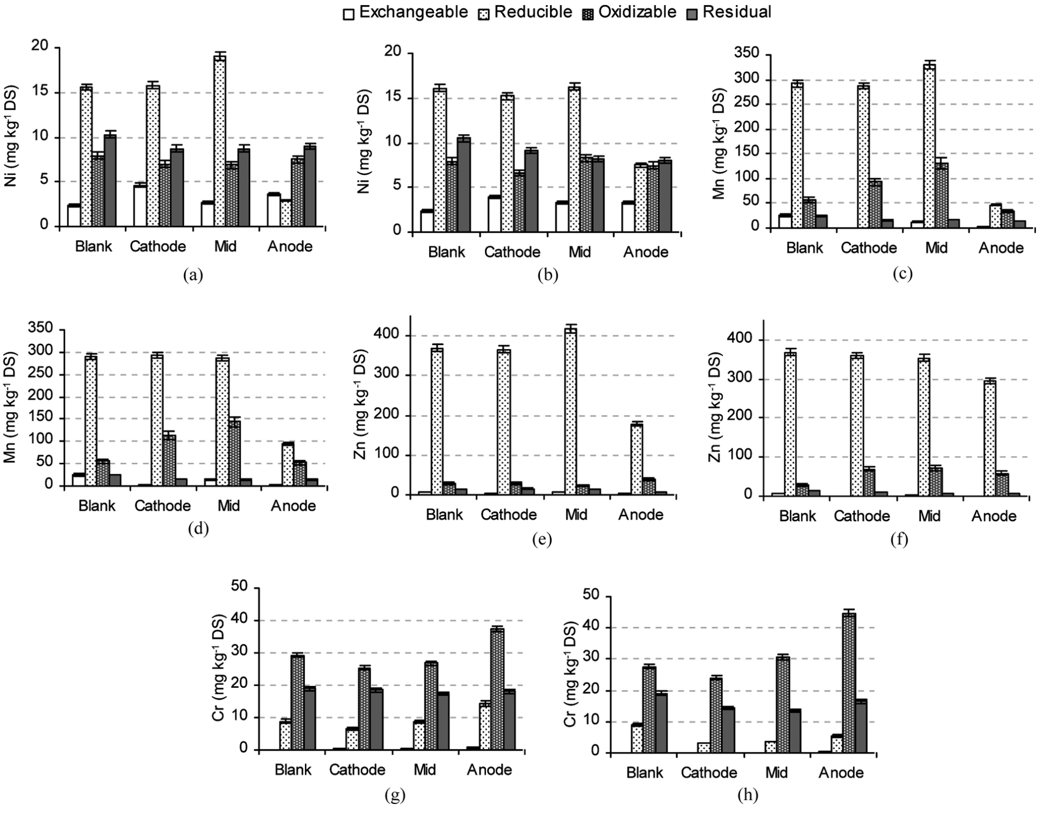


FIG. 7. Fractionation of Ni, Mn, Zn, and Cr in sludge due to DC (a, c, e, g) and IS(15/45) (b, d, f, h) electrodewatering.

resulted in higher reducible fraction of Fe in sludge at the anode than in other experiments (Fig. 6f). During electrodewatering, Fe ions moved toward the cathode. At the boundary between the acid and alkaline fronts in sludge segment, an Fe-rich barrier composed of FeOOH, Fe_2O_3, and Fe_3O_4 was formed.[40] Consequently, a high concentration of reducible fraction of Fe was observed in the middle of the sludge cake. The Fe-rich barrier moved toward the cathodic site depending on current and experimental time.[41] So, in long off-time IS experiments, the increase in reducible species of Fe in the middle of the sludge cake was not significant compared to DC and short off-time IS experiments (Figs. 6e, 6f). Moreover, a decrease in residual fraction of Fe in sludge at the anode was found in all experiments and the reduction of this fraction also depended on duration of off-time interrupted voltage application.

Migration of Heavy Metals

Figure 7 shows the fractions of Ni, Mn, and Zn in sludge cake after DC and IS(15/45) electrodewatering. Due to electrodewatering, the reducible fraction of the Ni, Mn, and Zn reduced in the sludge sample at the anode. Similar observations were also documented by Virkutyte et al.[23] during electrokinetic treatment of methanogenic anaerobic granular sludge. As discussed above, these metals might have been dissolved in the sludge at the anode and migrated toward the cathode. Then, they precipitated at particular points in the sludge segment, where pH changed from acidic to alkaline. This phenomenon is the so-called cathode hindering contaminant migration.[42,43] Therefore, in DC electrodewatering experiments, the reducible fraction of Ni, Mn, and Zn significantly increased in the sludge samples in the middle of the sludge cake (Fig. 7). However, an increase in the reducible fraction of these trace elements in the sludge samples in the middle of the final sludge cake was not significantly observed in IS(15/45) experiments (Fig. 7). This might be the effect of long off-time interrupted voltage application, which resulted in a slowdown in electrolysis, electromigration, and electroosmosis.

The main fraction of Cr was oxidizable species (Table 3). During electrodewatering, instead of migration to the cathode, an increase in oxidizable fraction of Cr was observed in sludge at the anode and long off-time interrupted voltage application did not affect the increase in oxidizable fraction of Cr at the anode (Figs. 7 g, 7 h). In sludge, Cr exists as Cr(III) and Cr(VI) valances. Cr(VI) is an anion species and is usually present as hydrochromate ($HCrO_4^-$), dichromate ($Cr_2O_7^{2-}$), and chromate (CrO_4^{2-}). Under an applied electrical field, the anion species was migrated to the anode.[44,45] and adsorbed by sludge particles at acidic pH regions near the anode.[46] Therefore, a high concentration of Cr in sludge samples at the anode (Figs. 7g, 7 h) might be associated with migration of Cr(VI). However, Cr was not only adsorbed in sludge but also leaked out into the removed water at the anode. The increase of Cr concentration in removed water was more significant in DC and short off-time IS experiments than in long off-time IS experiments (Fig. 8). This phenomenon could be influenced by the limitation of electromigration during long off-time IS experiments. Thus, in DC and short off-time IS experiments, Cr might intensely migrate to the anode. A large amount of Cr was not totally adsorbed in sludge at the anode, which resulted in a high concentration in removed water. On the other hand, in long off-time interrupted experiments, Cr might also migrate to the anode, but at lower rates, the amount of Cr was adsorbed in sludge at anode, hence, a low concentration of Cr was observed in removed water at the anode in comparison to other experiments (Fig. 8).

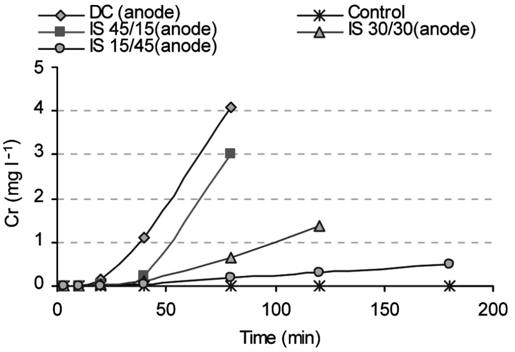


FIG. 8. Concentrations of Cr in the removed water at the anode during DC and IS electrodewatering processes.

CONCLUSIONS

During electrodewatering, long off-time interruption had a negative effect on transportation of water in sludge segment, resulting in high water content in sludge at the anode and the final sludge cake. High current density and intensive fluctuation were observed in long off-time interrupted IS experiments. Long off-time interrupted electrodewatering resulted in a slowdown in the migration of Na^+ and K^+ from the anode to the cathode and affected the removal of these metals in the sludge cake. Application of long off-time interrupted voltage causes a decrease of electrolysis, electromigration, and electroosmosis, which reduced dissolution and migration of macro (Ca, Mg, and Fe) and trace (Ni, Mn, and Zn) metals in sludge cake. However, an increase of Cr in sludge at the anode did not depend on experimental strategy, but an increase in concentration of Cr in the removed water at the anode significantly depended on the off-time interrupted voltage application.

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