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Individual and Combined Effects of Freeze-Thaw and Ferrate(VI) Oxidation for the Treatment and Dewatering of Wastewater Sludges

James Diak · Banu Örmeci

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Abstract The study examined the individual and combined effects of potassium ferrate(VI) additions and freeze-thaw conditioning for the treatment and dewatering of sludge samples. The first part of the experiments, using primary sludge, compared potassium ferrate(VI) additions prior to freeze-thaw treatment (pretreatment) versus potassium ferrate(VI) additions following freeze-thaw treatment (posttreatment). A low dose (LD) of 1.0 g/L and a high dose (HD) of 10.0 g/L of potassium ferrate(VI) were evaluated along with a freezing temperature of −20 °C and freezing periods of 1, 8 and 15 days. Following the designated freezing period, the samples were removed from the freezer and thawed at room temperature for 12 h. The second part of the study, using anaerobically digested sludge, evaluated the effects of potassium ferrate(VI) pretreatment, using LD = 0.5 g/L and HD = 5.0 g/L, and used simulated drainage beds to separate meltwater from the sludge cake during the thawing period. The study demonstrated that stand-alone freeze-thaw can reduce faecal coliform by >3-log after being frozen for only 1 day, and pretreatment with potassium ferrate(VI) can be used to improve the effects of freeze-thaw on faecal coliform inactivation in sludge. Furthermore, the drainability of the sludge following freeze-thaw was not significantly deteriorated when potassium ferrate(VI) was added to the sludge prior to freezing, despite greater than fourfold increases in the concentrations of soluble proteins and soluble carbohydrates. The meltwater collected during the sludge thawing was approximately 85 % of the initial sludge volume. When 5 g/L of potassium ferrate(VI) was added to the sludge prior to freezing, the meltwater collected had <0.28 MPN/mL faecal coliform, the turbidity was <10 NTU and the pH was 9.1. Pretreatment with potassium ferrate(VI) also reduced the concentration of faecal coliform in the sludge cake, suggesting that freeze-thaw coupled with potassium ferrate(VI) additions can be used to stabilise sludge and reduce sludge volume.

Keywords Sludge · Biosolids · Freeze-thaw · Ferrate · Dewatering · Stabilisation

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1 Introduction

Freeze-thaw sludge conditioning can be used to dewater sludge (Hu et al. 2011; Diak et al. 2011; Northcott et al. 2005; Parker and Collins 1999) and reduce pathogens and indicator bacteria (Gao et al. 2009; Gao et al. 2006; Kato et al. 2002; Sanin et al. 1994). When sludge freezes, ice crystals grow which consolidate sludge solids and create a continuous network of ice (Tao et al. 2006; Vesilind and Martel 1990). When the sludge thaws, meltwater drains freely leaving a dewatered cake (Diak et al. 2011; Martel 1993; Martel and Diener 1991a; Martel and Diener 1991b). Despite the obvious attractiveness of using natural freeze-thaw dewatering in

rural cold climates, there are concerns which need to be addressed. A major concern is the potential for reactivation, regrowth and odour generation, particularly during the thawing stage. This is a particular concern since freeze-thaw disrupts sludge flocs and can rupture cell walls, causing the release of soluble substrate to the sludge supernatant, which ultimately increases food availability for surviving bacteria. Another concern is the quantity, quality, management and disposal of the meltwater and remaining sludge cake.

In recent years, there has been considerable interest in the reactivation and regrowth of indicator organisms during the dewatering and storage of anaerobically digested biosolids (Chen et al. 2011; Gardner and Örmeci 2010; Higgins et al. 2007). Reactivation and regrowth of sludge microorganisms is not only a health and safety concern; it will also lead to odour generation. Odorous compounds in sludge generally contain reduced forms of nitrogen, such as ammonia and amines, and reduced forms of sulphur, such as sulphides and mercaptans (Chen et al. 2011; de Luca et al. 1996).

Ferrate(VI) is a very strong oxidant, capable of oxidising reduced sulphur to sulphate and ammonia to nitrate (de Luca et al. 1996), and it is an effective coagulant and a proven disinfectant, which produces no known harmful disinfection by-products (Gombos et al. 2013; Jiang et al. 2007; Jiang et al. 2006; Schuck et al. 2006). It is also capable of oxidising a variety of pharmaceuticals and personal care products (PPCPs) (Jiang and Zhoo 2013; Yang et al. 2012; Li et al. 2008; Jiang 2007; Zhu et al. 2006). Recent developments in the online generation of ferrate have brought down the cost substantially and increased its applicability for wastewater and sludge treatment. Ferrate(VI) oxidation treatments can be used in conjunction with freeze-thaw to potentially reduce the risks of regrowth and odour generation, and improve the quality of the meltwater and sludge cake. In decentralised regions with cold climates, combined treatments using ferrate(VI) oxidation and freeze-thaw have the potential to be used as a 'stand-alone' sludge treatment technique with limited infrastructure requirements. In addition, the co-treatment could be incorporated into a more conventional, large-scale, sludge treatment system with anaerobic digestion.

Oxidation treatments disintegrate sludge flocs resulting in smaller particle sizes and the release of extracellular polymeric substances (EPS) (Wu et al. 2014). Sludge oxidation can also result in cell lysis, and the release of intracellular organic substances (Saktaywin et al. 2005). The solubilisation of EPS and intracellular constituents increases the concentration of proteins and carbohydrates in the supernatant (Örmeci and Vesilind 2001). This alters the sludge surface charge and increases the polymer demand during sludge conditioning (Apul et al. 2010).

A decrease in particle size increases the amount of water bound to the surface of the sludge particles, which typically reduces sludge dewaterability via conventional means. However, during freeze-thaw, the smaller particle sizes improve particle migration during freezing (Corte 1962), which will improve the formation of ice channels and improve sludge drainability.

The meltwater collected during the thawing stage can amount to more than 85 % of the initial sludge volume (Diak et al. 2011). A well-designed sludge drainage bed will result in a meltwater that is free of solids, and easily collected for subsequent treatment and disposal. Land application of the dewatered sludge cake is an economical way to dispose of sludge, and an efficient strategy to recycle nutrients and organic matter.

The purpose of this research was to evaluate the individual and combined effects of potassium ferrate(VI) additions and freeze-thaw conditioning for the treatment and dewatering of wastewater sludges in cold regions. The first part of the experiments compared potassium ferrate(VI) additions prior to and following freeze-thaw. These tests were also compared to stand-alone freeze-thaw. The second part of the study used freeze-thaw treatment with bench-scale simulated drainage beds to separate the meltwater from the sludge cake via gravity during the sludge thawing period to be able to study the cake and meltwater characteristics individually.

2 Materials and Methods

2.1 Sludge Samples

The sludge used for part I (sludge bottle experiments) was primary sludge, obtained from the Robert O. Pickard Environmental Centre (ROPEC) in Ottawa, Ontario, Canada. The sludge used for part II (sludge drainage experiments) was anaerobically digested sludge from ROPEC. The initial characteristics of the sludges are presented in Table 1.

Table 1 Characteristics of the primary and anaerobically digested sludge samples used for part I and part II, respectively

Parameter	Units	Primary sludge Average (±95 % CL)	Anaerobically digested sludge Average (±95 % CL)
Total solids (TS)	%	4.7 (±0.3)	2.0 (±0.0)
Volatile solids (VS)	%	4.0 (±0.3)	1.2 (±0.0)
Faecal coliform	Log (MPN/mL)	4.7 (+0.4, −0.6)	3.9 (+0.4, −0.5)
Faecal coliform	Log (MPN/g DS)	6.0 (+0.4, −0.6)	5.6 (+0.4, −0.5)
Capillary suction time (CST)	s	912 (±11)	–
Ammonia	mg/L NH_3-N	210 (±11)	–
Sulphide	mg/L S^{-2}	39 (±1)	–
pH		–	7.41 (±0.03)
Soluble proteins	mg/L	–	12 (±1)
Soluble carbohydrates	mg/L	–	28 (±4)
Soluble chemical oxygen demand (sCOD)	mg/L	–	568 (±13)

2.2 Part I: Freeze-Thaw Treatment in Bottles

Two hundred fifty millilitre primary sludge samples were dispensed into 500 mL bottles, and placed in a freezer (VWR FORMA® −40 °C Lab Freezer Model 5722, VWR International, Mississauga, ON) set to −20 °C ± 1 °C. The temperature at the centre of a 250 mL test sample and the temperature inside the freezer were monitored using a Traceable® dual-channel thermometer with type K thermocouples and computer output (Model 4137, Control Company, Friendswood, TX, USA). Temperatures were recorded every minute using the data acquisition software (DAS™, Control Company, Friendswood, TX, USA). When the samples were placed in the freezer, the temperature at the centre of the test sample decreased at a steady rate of 1 °C every 10 min until reaching the sludge freezing temperature, which was approximately −0.3 °C. At this point, the temperature of the sample remained constant for approximately 7 h while the sample froze. During this freezing period, it was assumed that the direction of the advancing ice front was radially and vertically inward, since the sample bottles were not insulated. Once the samples were completely frozen, the temperature of the sample began to decrease again, until eventually reaching the freezer temperature of −20 °C. The 7 h elapsed time for the sludge to freeze and the 31 mm depth to the sample centre were used to estimate the freezing rate of approximately 4 mm/h, which is within the optimal range for pathogen reduction and particle migration leading to improved dewaterability (Wang et al. 2001; Hung et al. 1997). After the samples were completely frozen, they were kept frozen at −20 °C for additional 1, 8 or 15 days. After the designated period in the freezer, the samples were removed and thawed at room temperature (22–23 °C).

2.2.1 Pre and Posttreatment with Potassium Ferrate(VI) (K_2FeO_4)

Primary sludge samples that were pretreated with potassium ferrate(VI) were given a low dose (LD = 1.0 g/L) or a high dose (HD = 10.0 g/L) of Ferratec Brand™ >90 % pure potassium ferrate(VI) (Sigma-Aldrich Canada Ltd., Oakville, ON). Following the addition of potassium ferrate(VI), the samples were stirred using a magnetic stirrer for 15 min and subsequently placed into the freezer.

Posttreatment with potassium ferrate(VI) was conducted in a similar fashion. After the designated time in the freezer, the samples were removed and thawed at room temperature (22–23 °C). Once the samples were completely thawed and warmed to room temperature, 250 mg of potassium ferrate(VI) was added to the bottles designated for LD posttreatment (1.0 g/L), and 2.5 g was added to the bottles designated for HD posttreatment (10.0 g/L). After the addition of potassium ferrate(VI), the bottles were stirred using a magnetic stirrer for 15 min.

2.3 Part II: Freeze-Thaw Treatment in Simulated Drainage Beds

Two hundred millilitre samples of anaerobically digested sludge were placed in 500 mL bottles. The bottles were sealed with a wide-mouth lid and inverted as shown in Fig. 1a. The inverted bottles were placed in the freezer set to −20 °C. The freezing rate generated was approximately 6 mm/h (4.5 h to travel 25 mm). Once the samples were completely frozen, they were kept frozen at −20 °C for additional 1, 8 or 15 days. After the designated time in the freezer, the samples were removed; the solid lid was replaced with a perforated lid lined with drainage fabric, and the tape sealing the air hole was removed. The frozen samples were then placed upside down in a funnel, which rested in the opening of a 50 mL graduated cylinder, as shown in Fig. 1b. The samples thawed at room temperature (22–23 °C), and the meltwater was collected via gravity drainage. The experiments using simulated drainage beds did not use ferrate(VI) as a posttreatment to freeze-thaw due to the separation of solids and meltwater. Only ferrate(VI) pretreatment was used for these experiments, along with stand-alone freeze-thaw treatment.

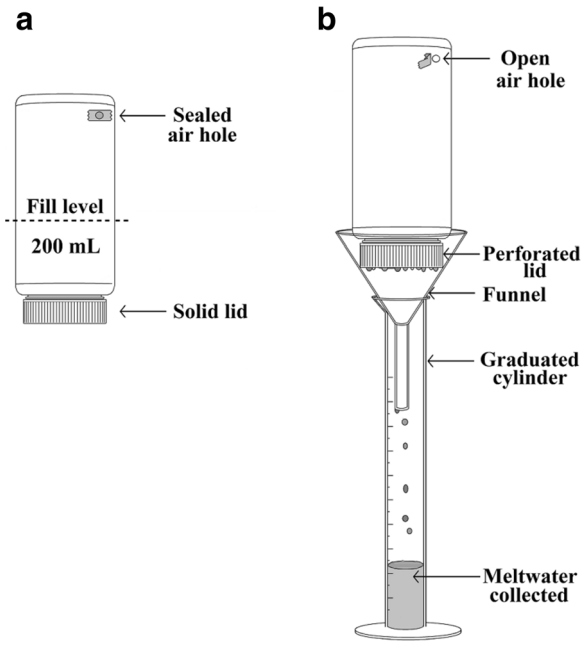

Fig. 1 Schematic of **a** the freezing vessel and **b** the simulated drainage bed with meltwater collection, used for the freeze-thaw experiments with anaerobically digested sludge

2.3.1 Pre-Treatments with Potassium Ferrate(VI) (K_2FeO_4)

Anaerobically digested sludge samples that were pretreated with potassium ferrate(VI) were given LD = 0.5 g/L or HD = 5.0 g/L of potassium ferrate(VI). Following the addition of potassium ferrate(VI), the samples were stirred using a magnetic stirrer for 15 min and subsequently placed into the freezer.

2.4 Sample Analysis

Preliminary tests on the primary sludge evaluated the filterability using capillary suction time (CST), and ammonia and sulphide concentrations before and after the addition of potassium ferrate(VI). Faecal coliform, total solids (TS) and volatile solids (VS) concentrations were measured before and after the addition of potassium ferrate(VI), and before and after freeze-thaw treatment. For the freeze-thaw sludge dewatering experiments, faecal coliform, TS and VS, soluble chemical oxygen demand (sCOD), soluble proteins and soluble carbohydrates concentrations were measured before and after the addition of potassium ferrate(VI). Following freeze-thaw dewatering, faecal coliform, TS and VS concentrations of the sludge cake were measured, and the meltwater was characterised in terms of faecal coliform, sCOD, soluble proteins, soluble carbohydrates, pH and turbidity.

Faecal coliform was measured using multiple tube fermentation (MTF) with A1 medium (EMD Chemicals Inc., Gibbstown, NJ, USA) according to US EPA Method 1681 (U.S. EPA 2005). All MTF tests were carried out in duplicate using a minimum of four dilutions, with five replicates per dilution. All other tests were conducted in triplicate. The TS and VS concentrations were measured according to Standard Method 2540 G (APHA 2005). The CST was measured using a Triton Electronics Type 319 multi-purpose CST apparatus (Triton Electronics Ltd., Great Dunmow, Essex, England) according to Standard Method 2710G (APHA 2005). The turbidity was measured using a HACH Model 2100AN Turbidimeter (Hach Company, Loveland CO, USA).

The sulphide concentration was measured using HACH method 8131 (methylene blue method, 5–800 μg/L S^{-2}). The primary sludge sample was diluted with deionised water by a factor of 100, and the test blank was adjusted for turbidity using a combination of

bromine water and phenol, as outlined in the HACH method. The total ammonia concentration ($NH_3 + NH_4^+$) was measured using HACH method 10031 (high range 0.4–50.0 mg/L NH_3-N) with a dilution factor of 10. The pH was measured using a Thermo Orion 5-star bench-top meter kit and ROSS ultra pH electrode (Thermo Fisher Scientific Inc., Rockford, IL, USA). The sCOD was measured using HACH method 8000 (high range 20–1500 mg/L COD), with a dilution factor of 2. The concentration of soluble proteins was measured using Coomassie brilliant blue G-250 reagent (Pierce Protein Biology Products, Thermo Fisher Scientific Inc., Rockford, IL, USA) with the Bradford method (Bradford 1976), and the concentration of soluble carbohydrates was measured using the anthrone method (Morris 1948). To obtain the soluble component, the samples were centrifuged at 10,000 rpm (relative centrifugal force, RCF = 15,317) for 10 min, then the supernatant was filtered using a 0.45-μm mixed cellulose ester (MCE) syringe filter (Shanghai Derian Instrument Co., Ltd., Shanghai, China).

2.5 Statistical Analysis

Error bars on all figures show the 95 % confidence interval. In cases where the measurements were below the detection limit, a downward arrow was used in place of the error bars. When comparing the data, a two-tailed *t* test was used to determine the *p* values and statistical significance ($p < 0.05$) of the results.

3 Results and Discussion

3.1 Part I: Freeze-Thaw Treatment in Bottles

Experiments in part I evaluated the effects of LD and HD on the CST, ammonia and sulphide concentrations in primary sludge following a 15-min reaction time. Experiments also compared the effects of stand-alone freeze-thaw sludge conditioning using a freezer temperature of −20 °C. Samples were kept frozen for 1, 8 and 15 days and thawed at room temperature. The use of potassium ferrate(VI) as a pre and a posttreatment to freeze-thaw conditioning was also compared. All samples were characterised in terms of faecal coliform, TS and VS concentrations.

3.1.1 Effect of Potassium Ferrate(VI) on the Capillary Suction Time

Chemical oxidation treatments disintegrate sludge flocs and rupture cell walls, causing the release of intra and extracellular biopolymers such as proteins, carbohydrates and colloids (Wu et al. 2014). This may reduce the measured filterability of sludge by clogging the filter papers used in conventional sludge filterability tests such as the CST and the specific resistance to filtration (SRF) (Ye et al. 2014). In this study, LD decreased the CST from 912 to 575 s following a 15-min contact time (Fig. 2a). This may be due to the oxidation of free biopolymers in sludge. However, HD increased the CST from 912 to 2648 s. This suggests that HD led to the solubilisation of sludge flocs and the destruction of cell walls, causing the release of intracellular and extracellular materials to the supernatant. Pretreatment techniques solubilise sludge solids generally reduce sludge dewaterability. However, during freezing, sludge solids are consolidated by the advancing ice front as the free water is drawn away from the particles and added to the growing network of ice crystals (Hoekstra and Miller 1967). Furthermore, Corte (1962) demonstrated that smaller particles are more easily pushed away from the advancing ice front, and less likely to be engulfed by the growing ice crystals. This means that pretreatment with potassium ferrate(VI), prior to freeze-thaw, may improve particle consolidation during freezing and increase the separation of meltwater from the sludge solids during the thawing stage.

According to Vesilind and Örmeci (2000), the escape of water from the sludge following freeze-thaw conditioning is too fast for the CST test, making the movement of water through the filter paper the rate-limiting step, rather than the release of water from the sludge. Therefore, the CST test was not used to characterise samples following freeze-thaw sludge conditioning. In part II of this study, a bench-scale freeze-thaw apparatus, equipped with meltwater collection via gravity drainage, was used to measure the release of water from the sludge following freeze-thaw.

3.1.2 Effect of Potassium Ferrate(VI) on the Concentration of Ammonia and Sulphides

Odorous compounds in sludge generally contain reduced forms of nitrogen and sulphur. These include

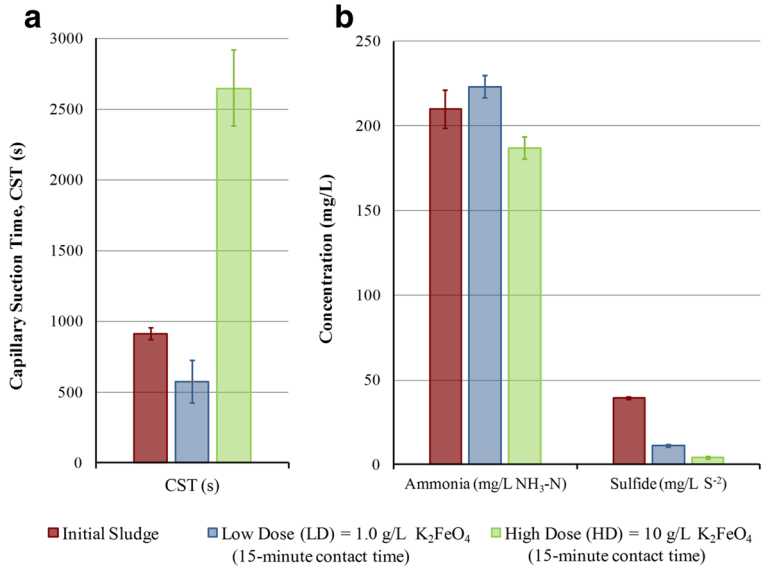

Fig. 2 Effect of LD and HD on the **a** CST and **b** ammonia and sulphide concentrations in the primary sludge, following a 15-min contact time

ammonia and amines, sulphides and mercaptans. Chemical oxidants, such as potassium ferrate(VI), can oxidise reduced nitrogen and sulphur, causing a decrease in the concentration of ammonia, amines, sulphides and mercaptans, and a reduction in sludge odour (de Luca et al. 1996). Following the addition of 10.0 g/L of potassium ferrate(VI) with a 15-min contact time, ammonia decreased by 11 % ($p = 0.0249$), however, 1.0 g/L did not have a significant ($p = 0.1161$), as shown in Fig. 2b. On the other hand, sulphides decreased by approximately 72 % using 1.0 g/L of potassium ferrate(VI), and by 89 % using 10.0 g/L. The authors also noted that following the addition of 1.0 g/L of potassium ferrate(VI), the odour of the primary sludge was considerably less offensive, and following the addition of 10.0 g/L, the odour of the primary sludge resembled an earthy rust water.

3.1.3 Pre and Posttreatment with LD—Faecal Coliform

The initial concentration of faecal coliform in the primary sludge was 1×10^6 MPN/g dry solids (DS), and following a 15-min reaction with LD = 1.0 g/L of potassium ferrate(VI), there faecal coliform inactivation was insignificant ($p = 0.9237$), as shown in Fig. 3. Stand-alone freeze-thaw resulted in a 3.4 to 3.9-log inactivation, with no significant difference among the samples that were frozen for 1, 8 or 15 days (F1 vs. F8: $p = 0.0715$, F1 vs. F15: $p = 0.7173$, F8 vs. F15: $p = 0.1858$). It was expected that samples that were pretreated with potassium ferrate(VI) would have a greater faecal coliform inactivation than stand-alone freeze-thaw; however, LD pretreatment may have reduced the effectiveness of stand-alone freeze-thaw. Samples that were pretreated with LD and subsequently frozen resulted in 1.6 to 2.7-log inactivation, approximately 1.3-log less than stand-alone freeze-thaw. De Luca et al. (1996) suspected that low ferrate(VI) doses may stimulate bacterial growth due to an increase in the nitrate concentration, with little change in the pH. Additionally, potassium ferrate(VI) increased the amount of polymers in the sludge supernatant which may have acted as cryoprotectants, shielding bacteria during freezing (Montusiewicz et al. 2010). Furthermore, sludge solubilisation increased the available substrate (sCOD) for surviving bacteria, which may have contributed to regrowth during the thawing period.

LD posttreatment, following freeze-thaw, did not have a significant effect on faecal coliform. Overall inactivation in LD posttreated samples was similar to stand-alone freeze-thaw treatments. This suggests that 1.0 g/L of potassium ferrate(VI) was insufficient for primary sludge. There are many constituents in sludge which quickly react with the highly reactive ferrate(VI) ions. It is likely that 1.0 g/L of potassium ferrate(VI) was quickly consumed by other components in the sludge, leaving little ferrate(VI) for disinfection.

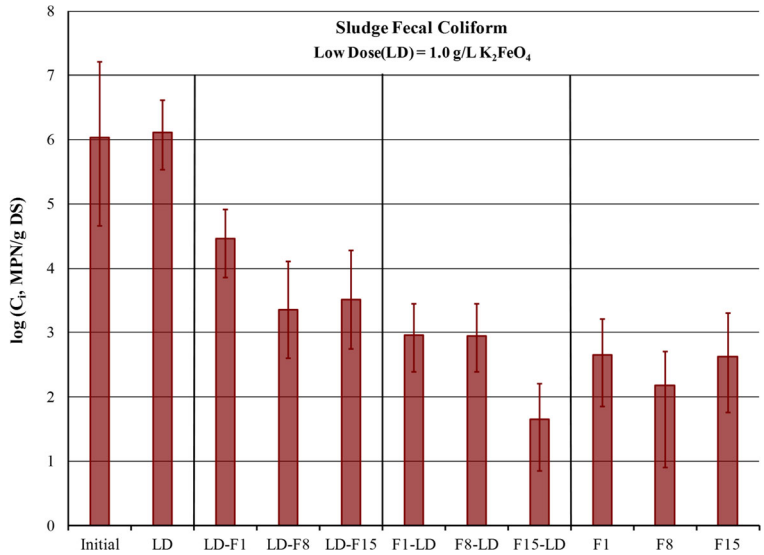

Fig. 3 Effect of LD on the concentration of faecal coliform in primary sludge when used alone, and as a pre and posttreatment with freeze-thaw

3.1.4 Pre and Posttreatment with LD—TS and VS

Following the addition of LD, there was no significant change in TS and VS ($p > 0.05$); however, when LD was used as a pretreatment, the samples that were frozen for 1, 8 and 15 days had TS decreases of 10.6, 16.8 and 16.4 %, and VS decreases of 13.4, 20.1 and 22.2 %, respectively (Fig. 4). Stand-alone freeze-thaw for 1, 8 and 15 days resulted in TS and VS decreases of 12 to 23 %. The decreases in TS and VS may be the result of biodegradation carried out by the surviving microorganisms during the 12-h thaw. In the study by Montusiewicz et al. (2010), the TS and VS of mixed sludge decreased by 16.1 and 16.9 %, respectively, following freeze-thaw. In addition to biodegradation during the thawing stage, the authors also suggested that the decreases in TS and VS may be due to the action of exoenzymes in the system, and endoenzymes released from the cells following intracellular and extracellular ice formation.

3.1.5 Pre and Posttreatment with HD—Faecal Coliform

Following the 15-min reaction period, HD resulted in a 2.5-log inactivation of faecal coliform, and when used as a pretreatment with freeze-thaw, overall inactivation

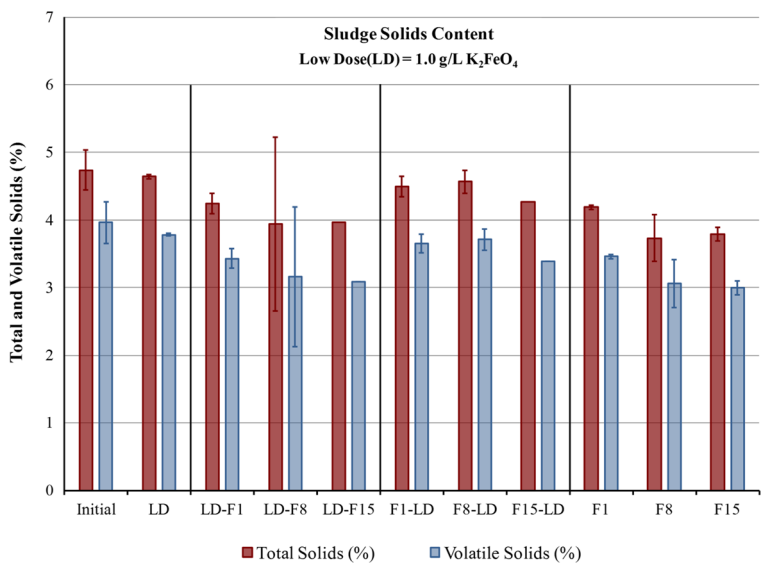

Fig. 4 Effect of LD on the TS and VS when used alone, and as a pre and posttreatment with freeze-thaw

ranged from 4.2 to 4.6-log, with no significant difference among the samples that were frozen for 1, 8 or 15 days (Fig. 5). Similarly, when HD was used as a posttreatment, overall faecal coliform inactivation ranged from 4.4 to 5.0-log, regardless of the time spent frozen, while stand-alone freeze-thaw resulted in a 3.4 to 3.9-log inactivation. These results demonstrate that HD pre or posttreatments increase faecal coliform inactivation by approximately 1-log compared to stand-alone freeze-thaw conditioning.

3.1.6 Pre and Posttreatment with HD—TS and VS

Figure 6 shows the effect of HD on TS and VS of sludge samples. Following the 15-min reaction period, HD increased the TS by 18 % (8.5 g/L) ($p = 0.0052$) with no significant change in VS ($p = 0.4754$). This was likely due to the formation of inorganic solids, such as iron oxides ($Fe_2O_3 \cdot nH_2O$) and iron oxide-hydroxides ($FeO(OH)$, $Fe(OH)_3$), which also gave the sludge a rust colour. In addition, when the sludge samples were diluted in buffered water to enumerate faecal coliform, HD pre and posttreated samples contained readily settleable solids, whereas the stand-alone freeze-thaw samples contained colloidal particles. All samples treated with HD had increases in TS ranging from 5.8 to 19.1 %, while stand-alone freeze-thaw samples had decreases in TS from 11.6 to 21.1 %. As discussed earlier, the decreases in TS and VS following stand-alone freeze-thaw may be the result of biodegradation during the 12-h thawing stage. Samples that were pretreated with HD also had VS reductions following freeze-thaw, ranging from 7 to 24 %. However, samples that were posttreated with HD had insignificant reductions in VS from 4.2 to 8.6 %, which was also the trend when LD was used as a posttreatment to freeze-thaw.

3.1.7 Summary

Potassium ferrate(VI) additions of HD = 10 g/L significantly changed the sludge properties following the 15-min reaction period. The CST increased by threefold, the concentrations of ammonia and sulphide were reduced by 11 and 89 %, respectively, the TS increased from 4.7 to 5.6 % solids, and faecal coliform inactivation was 2.5-log. While ferrate(VI) additions reduced the concentration of sulphide and ammonia, which contribute to sludge odours, the significant increase in sludge CST following the potassium ferrate(VI) additions suggest that sludge dewaterability was reduced. To offset this negative effect on sludge dewaterability, potassium ferrate(VI) additions would be better suited as a pretreatment to freeze-thaw treatment, since freeze-thaw treatment leads to particle agglomeration. In addition, the oxidation of odour-causing compounds, such as ammonia and sulphide, would reduce the potential for putrefaction when the sludge is applied to the freezing bed. Furthermore, sludge mixing following the addition of ferrate(VI) would be facilitated in liquid sludge, prior to freeze-thaw dewatering, as opposed to the dewatered

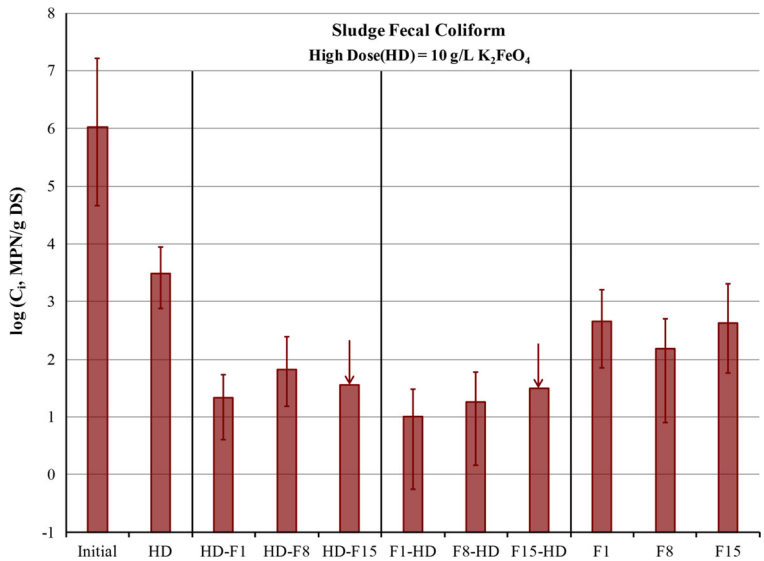

Fig. 5 Effect of HD on the concentration of faecal coliform in primary sludge when used alone, and as a pre and posttreatment with freeze-thaw

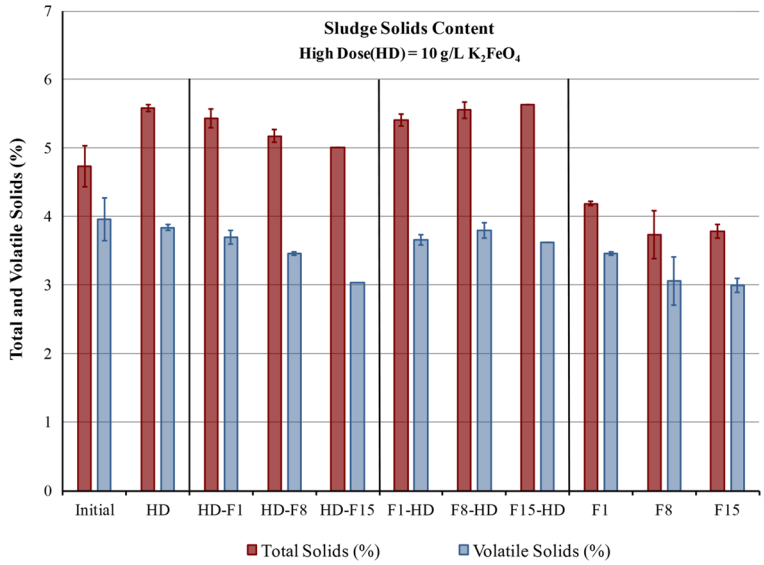

Fig. 6 Effect of HD on the TS and VS when used alone, and as a pre and posttreatment with freeze-thaw

sludge cake, following freeze-thaw. For these reasons, ferrate(VI) pretreatment was selected as the most appropriate and beneficial way to use ferrate(VI) oxidation and freeze-thaw co-treatments.

3.2 Part II: Freeze-Thaw Treatment in Simulated Drainage Beds

The second part of the study evaluated the effects of potassium ferrate(VI) pretreatment, prior to freeze-thaw, using simulated drainage beds to separate the meltwater from the sludge cake during the sludge thawing period (Fig. 1). Ferrate(VI) pretreatment was selected over ferrate(VI) posttreatment due to the solids-liquid phase separation during thawing, which would make ferrate(VI) additions and mixing the dewatered sludge cake more difficult. Furthermore, pretreatment offers several other practical benefits, such as pathogen inactivation and odour suppression, which would alleviate some of the concerns related to the application of sludge to a freezing bed.

Anaerobically digested sludge samples were pretreated with either 0.5 g/L (LD) or 5.0 g/L (HD) of potassium ferrate(VI), frozen at −20 °C for 1, 8 or 15 days, and thawed at room temperature for 12 h. Another set of samples underwent stand-alone freeze-thaw, without potassium ferrate(VI) additions. For these tests, two sample bottles were kept frozen at −20 °C for each period of 1, 8 and 15-days. Following freeze-thaw, all 200 mL sludge samples released approximately 170 mL of meltwater via gravity when thawing, leaving approximately 30 g of sludge cake. When the initial, unfrozen, sludge sample was placed on the drainage setup, only 10 % of the sample was able to drain before the drainage fabric, and perforated lid was completely clogged.

3.2.1 Meltwater

Faecal Coliform The concentrations of faecal coliform in the meltwater samples are presented in Fig. 7. For comparison, the figure also includes the initial (untreated) sludge sample, and the LD and HD sludge samples following a 15-min reaction period with the potassium ferrate(VI). The concentration of faecal coliform in the meltwater following stand-alone freeze-thaw for 1 day was approximately 760 MPN/mL, 1-log lower than the initial sludge. Samples that were frozen for 8 and 15 days had additional inactivations of approximately 0.5 and 1-log, respectively. By grouping the replicates for samples F1 with F1 #2, F8 with F8 #2 and F15 with F15 #2, *t* tests were performed, which suggest that this decreasing trend is statistically significant (F1 vs. F8: $p = 0.0015$, F8 vs. F15: $p = 0.0433$). Results from preliminary experiments suggested that the freezing temperature and the time spent frozen did not influence the level of inactivation of faecal coliforms caused by freeze-thaw. Similar results have also been reported by Gao et al. (2009) and Sanin

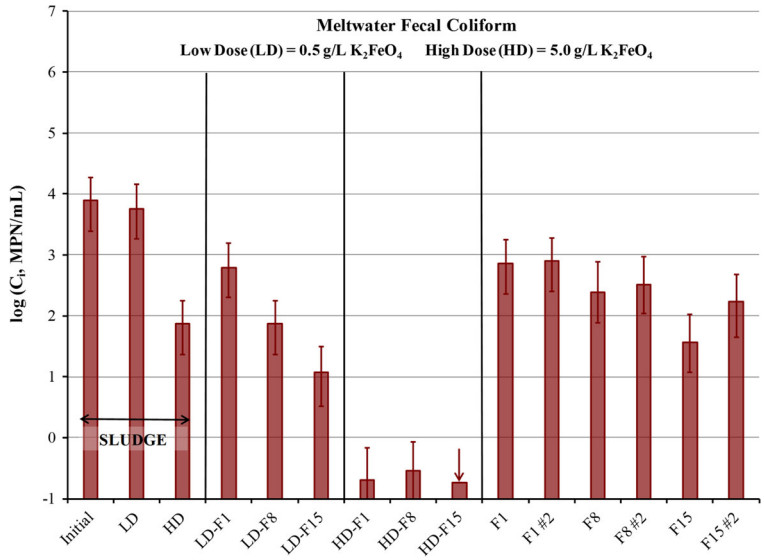

Fig. 7 Effect of LD and HD on the concentration of faecal coliform in the meltwater collected during the thawing stage

et al. (1994). However, these experiments, which incorporate meltwater collection, suggest that the faecal coliform, which was captured by the ice, and drained with the meltwater, was further inactivated when the time spent frozen was increased. This trend was also observed in samples that were pretreated with LD prior to freeze-thaw (LD-F1 vs. LD-F8: $p = 0.0130$, LD-F8 vs. LD-F15: $p = 0.0424$). In addition, LD pretreatment did not improve the inactivation of faecal coliform resulting from stand-alone freeze-thaw, after being frozen for 1 day; however, when the time frozen was increased to 8 days, LD did result in greater faecal coliform inactivation compared to stand-alone freeze-thaw for 8 days ($p = 0.001$). This also seems to be the case when the time frozen was 15 days; however, due to a large amount of variation in the sample replicates, the results were not statistically significant ($p = 0.0694$). HD pretreatment, on the other hand, reduced the concentration of faecal coliform in the meltwater to <0.28 MPN/mL following freeze-thaw, regardless of the time spent frozen.

Soluble proteins, Carbohydrates and COD Figure 8 shows the concentrations of sCOD, soluble carbohydrates and soluble proteins. Following the addition of LD, sCOD increased by 13 %, soluble carbohydrates increased by 44 % and soluble proteins increased by 17 %. When LD was used as a pretreatment with freeze-thaw, there were no significant differences in the degree of solubilisation resulting from stand-alone freeze-thaw treatment.

Stand-alone freeze-thaw increased the degree of sludge solubilisation. The sCOD doubled, soluble carbohydrates doubled and soluble proteins increased by an order of magnitude. These results agree with previous studies which have demonstrated that freeze-thaw disrupts sludge flocs, causing the release of EPS into the sludge supernatant (Hong et al. 1995; Hung et al. 1997). Furthermore, the largest increases were soluble proteins, which were also observed in the study by Hu et al. 2011.

Following the addition of HD, the sCOD increased by a factor of 2.3, soluble carbohydrates increased by a factor of 3.5 and soluble proteins increased by a factor of 7.7. When HD was used as a pretreatment with freeze-thaw, soluble proteins in the meltwater were lower than stand-alone freeze-thaw and LD pretreated samples; however, the sCOD and soluble carbohydrate concentrations were considerably higher. This may be due to direct oxidation of proteins by the ferrate(VI), or perhaps the biodegradation of proteins during thaw, stimulated by the addition of potassium ferrate(VI). However, it is also possible that the sequential transformation of ferrate(VI) ions, which solubilised sludge solids, also resulted in a variety of ferric species and contributed to the coagulation of proteinaceous compounds, which remained in the sludge cake during drainage. Formation of precipitates may have reduced the drainability of the sludge and clogged the drainage

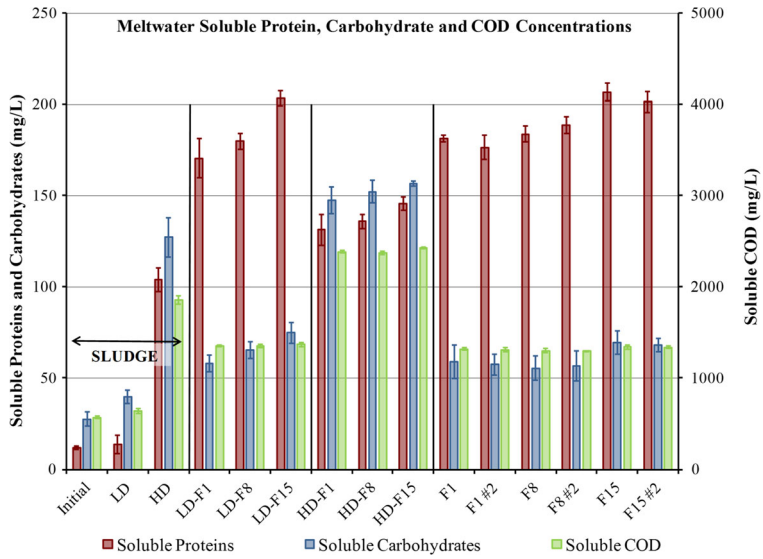

Fig. 8 Effect of LD and HD on the concentrations of soluble proteins, soluble carbohydrates and sCOD in the meltwater collected during the thawing stage

fabric faster than the stand-alone freeze-thaw samples, while reducing the turbidity of the meltwater. More on this point is presented in the discussion below and in the section on total and volatile solids of the sludge cake remaining following freeze-thaw with gravity meltwater drainage.

Turbidity and pH Figure 9 shows the turbidity and pH of the initial sludge and the meltwater samples collected during the thawing stage. The initial turbidity of the sludge was >10,000 NTU (over range). Similarly, the turbidity measurements of LD and HD samples, prior to freeze-thaw, were also over range. When the sludge was frozen, solids were consolidated due to the formation of ice, and during the thawing stage, the meltwater was able to drain freely via gravity drainage, without resuspending the solids. Furthermore, the addition of potassium ferrate(VI), prior to freeze-thaw, improved the precipitation and coagulation of solids, which further reduced the turbidity of the meltwater. This was also observed when sludge cake samples were diluted by a factor of 100 in buffered water to enumerate faecal coliform. The HD pretreated samples were clear and contained readily settleable particles, whereas the untreated sludge samples were cloudy and contained colloids.

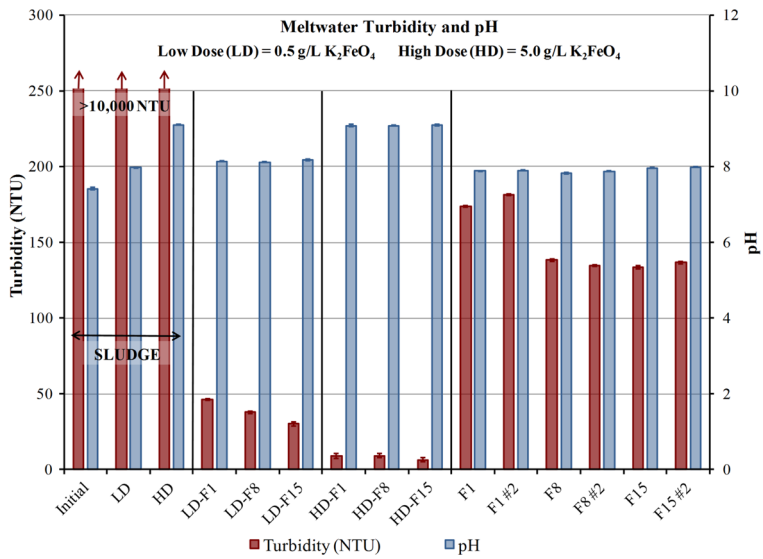

Fig. 9 Effect of LD and HD on the turbidity and pH of the meltwater collected during the thawing stage

Following stand-alone freeze-thaw for 1 day, the meltwater collected had a turbidity of approximately 178 NTU. When the time frozen was increased to 8 and 15 days, turbidity was reduced to 136 NTU, with no significant difference between F8 and F15 samples. When LD pretreatment was used, the turbidity of the meltwater samples were 72–78 % lower than the stand-alone freeze-thaw meltwater samples, and when HD pretreatment was used, the turbidity was approximately 95 % lower. It was also shown that increasing the time spent frozen from 1 to 15 days reduced the turbidity of the meltwater samples. However, the drastic reductions in turbidity occur as a result of the freeze-thaw process, and increasing the time spent frozen only slightly reduces the turbidity further.

The initial pH of the anaerobically digested sludge was 7.4. Following a 15-min reaction with LD and HD, the pH of the sludge increased to 8.0 and 9.1, respectively (Fig. 9). When LD was used as a pretreatment with freeze-thaw, the meltwater had a pH of approximately 8.1, regardless of the time spent frozen. Similarly, when HD was used as a pretreatment, the pH of the meltwater from all three samples was 9.1. This suggests that the increases in pH are due to the ferrate(VI) additions, and very little to do with freeze-thaw. Furthermore, the length of time that the samples were kept frozen did not have an effect on pH. This was also the case with stand-alone freeze-thaw. The meltwater collected had a pH of approximately 7.9, regardless of the number of days that the samples were kept frozen. The increase in pH from 7.4, in the initial sludge, to 7.9 in the meltwater following stand-alone freeze-thaw, may be the result of precipitation of buffering salts during freezing. As the water in sludge freezes, the solute concentration increases. This can lead to salt precipitation depending on the concentrations of the salt components and their relative solubilities (Pikal-Cleland et al. 2000). Furthermore, the increases in soluble proteins, carbohydrates and other sludge constituents following freeze-thaw may also affect the pH of the meltwater.

Ferrate(VI) is a strong oxidant throughout the pH scale; however, under acidic conditions (pH < 6), the protonated forms of ferrate(VI) decompose very rapidly with an oxidation potential of 2.20 V, whereas under basic conditions (pH = 10–11), the non-protonated ferrate(VI) is relatively more stable, with an oxidation potential of 0.72 V (Graham et al. 2004). For wastewater sludges with near neutral pH, non-protonated FeO_4^{-2} and mono-protonated $HFeO_4^{-1}$ are the dominant species (pKa = 7.3), and ferrate(VI) decomposes to Fe(III) species very quickly (Graham et al. 2004). For biological sludges from an activated sludge process, alkalinity is lost during nitrification when nitrifying bacteria consume dissolved oxygen to convert ammonia to nitrate. However, despite the increases in pH caused by ferrate(VI) additions, the oxidation potential remains strongly positive, which suggests that ferrate(VI) oxidation can be used on sewage sludge.

3.2.2 Sludge Cake

Faecal Coliform Figure 10 shows the effect of LD and HD on the concentration of faecal coliform in the sludge when used as a pretreatment, prior freeze-thaw with meltwater separation. The figure also shows the effects of stand-alone freeze-thaw. The initial concentration of faecal coliform in the anaerobically digested sludge was approximately 3.9×10^5 MPN/g DS. Following a 15-min contact time, HD resulted in 2.1-log inactivation of faecal coliform, whereas LD did not have a significant effect ($p = 0.3910$).

When LD was used as a pretreatment to freeze-thaw with meltwater separation, overall faecal coliform inactivation in the sludge cake ranged from 0.9 to 2.0-log. However, stand-alone freeze-thaw resulted in 1.4 to 2.1-log inactivation, suggesting that LD pretreatment did not improve faecal coliform inactivation caused by stand-alone freeze-thaw ($p = 0.1354$). Similar to the experiments with primary sludge, the length of time that the samples were kept frozen (1, 8 or 15 days at −20 °C) did not have a significant effect on faecal coliform inactivation in the sludge cake ($p > 0.05$).

When HD was used as a pretreatment with freeze-thaw, overall faecal coliform inactivation ranged from 3.6 to 3.9-log, which was 1.8 to 2.2-log greater than stand-alone freeze-thaw, indicating that pretreatment using 5 g/L of potassium ferrate(VI) prior to freeze-thaw increases faecal coliform inactivation caused by stand-alone freeze-thaw ($p = 0.0016$).

TS and VS Figure 11 shows the effect of LD and HD on the TS and VS when used alone and as a pretreatment to freeze-thaw with meltwater separation. The initial TS and VS of the anaerobically digested sludge were 2.0 and 1.2 %, respectively. Following the addition of 5 g/L (HD) of potassium ferrate(VI), the TS increased to 2.5 % with no change in VS, and following the addition

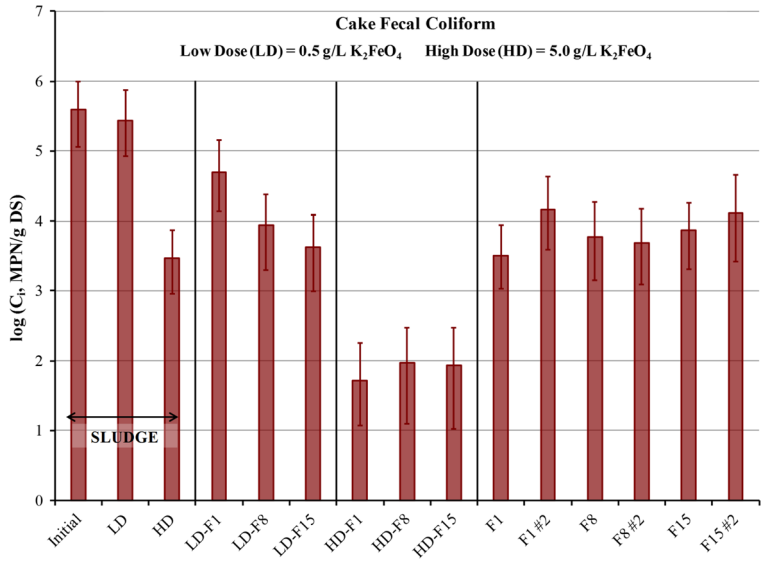

Fig. 10 Effect of LD and HD on the concentration of faecal coliform in the sludge cake when used alone, and as a pretreatment to freeze-thaw with meltwater separation

of 0.5 g/L (LD), there was no significant change in TS or VS. This demonstrates that ferrate(VI) contributed to the formation of inorganic solids, most likely iron oxides and iron oxide-hydroxides.

Freeze-thaw with meltwater collection via gravity drainage reduced the 200 mL sludge samples to approximately 30 g of sludge cake, indicating a reduction of approximately 85 % in the sludge mass. The TS of the sludge cakes ranged from 12 to 14 % solids. However, HD pretreatment may have decreased the drainability of the sludge slightly and/or clogged the drainage fabric more quickly. During the thawing process, up to 5 % less meltwater was collected, up to 7.6 g more sludge remained, and the TS and VS were slightly lower than the non-treated samples. Comparing the group of HD pretreated samples to the group of stand-alone freeze-thaw samples, there is a statistically significant decrease in the TS when HD pretreatment was used ($p = 0.0038$). This was likely due to the sequential action ferrate(VI) additions. First, the ferrate(VI) solubilised sludge solids causing an increase in sCOD, including soluble proteins and carbohydrates. Following ferrate(VI) decomposition, ferric species acted as coagulants and resulted in the formation of settleable solids, which clogged the

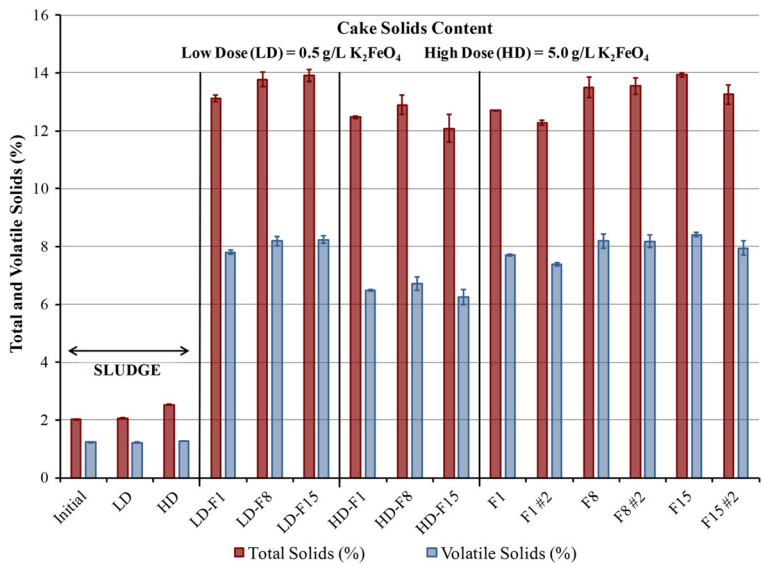

Fig. 11 Effect of LD and HD on the TS and VS of the sludge cake when used alone and as a pretreatment to freeze-thaw with meltwater separation

drainage fabric faster than the untreated samples. Additionally, higher concentrations of EPS in the supernatant also likely reduced the filterability of the sludge (Ye et al. 2014), and clogged the drainage fabric.

Furthermore, samples that were frozen for 8 and 15 days may have drained slightly better than the samples that were frozen for only 1 day. Longer freezing periods of 8 and 15 days generally resulted in greater meltwater volume, and reduced mass of sludge cake remaining. In addition, sludge samples that were frozen for 8 and 15 days consistently had higher TS concentrations than the samples that were kept frozen for only 1 day. This was the case for stand-alone freeze-thaw samples (F1 vs. F8: $p = 0.0000$, F1 vs. F15: $p = 0.0002$), and the samples that were pretreated with LD (LD-F1 vs. LD-F8: $p = 0.0102$, LD-F1 vs. LD-F15: $p = 0.0026$). Vesilind and Martel (1990) believed that prolonged freezing periods at low temperatures allowed time for the ice crystals to extract the surface water surrounding the sludge particles, bringing them into contact to create larger particles. Furthermore, while Hu et al. (2011) recognised that the majority of the freeze-thaw sludge dewatering benefits occurs during the bulk freezing stage, extended 'curing' time allowed biological sludge flocs to be further dehydrated by the surrounding ice.

3.2.3 Summary

Freeze-thaw with gravity meltwater drainage reduced sludge volumes by 85 % and inactivated faecal coliform in both sludge cake and meltwater. When 5.0 g/L of potassium ferrate(VI) was used as a pretreatment with freeze-thaw, sludge solubilisation occurred, which increased sCOD, including soluble proteins and soluble carbohydrates. Furthermore, coagulation and precipitation of solids were observed, which reduced the turbidity of the meltwater samples. In particular, soluble protein concentrations were reduced when 5.0 g/L of potassium ferrate(VI) was used as a pretreatment with freeze-thaw sludge dewatering. This may be due to the coagulation of proteinaceous compounds which ultimately remained in the sludge cake. This may have also contributed to filter clogging and reduced sludge drainability, which would explain why 5 % less meltwater was collected from HD pretreated samples following freeze-thaw sludge dewatering.

4 Conclusion

The study examined the individual and combined effects of potassium ferrate(VI) additions and freeze-thaw conditioning for the treatment and dewatering of sludge samples. The first part of the experiments, using primary sludge, demonstrated that stand-alone freeze-thaw can result in >3-log inactivation of faecal coliform after being frozen for 1 day; however, increasing the time frozen up to 15 days did not result in any significant differences. In addition, 1.0 g/L of potassium ferrate(VI) did not have a significant effect on the primary sludge following a 15-min reaction period, or when used as a pre or posttreatment to freeze-thaw, whereas 10 g/L of potassium ferrate(VI) significantly changed the sludge properties following the 15-min reaction period. The CST increased by threefold, the concentrations of ammonia and sulphides were reduced by 11 and 89 %, respectively, the TS increased from 4.7 to 5.6 % solids and faecal coliform inactivation was 2.5-log. Furthermore, when 10 g/L of potassium ferrate(VI) was used as a pre and posttreatment to freeze-thaw, faecal coliform inactivation caused by stand-alone freeze-thaw was increased by an additional 1-log.

The second part of the study tested freeze-thaw treatment on anaerobically digested sludge using simulated drainage beds to allow meltwater to drain out of the sludge during the thawing stage. Gravity meltwater drainage reduced the mass of sludge by 85 %, and increased the sludge TS to approximately 13 % solids. Freeze-thaw also solubilised sludge solids, resulted in 1.4 to 2.1-log inactivation of faecal coliform in the sludge cake and reduced the concentration of faecal coliform in the meltwater to <1000 MPN/mL. Pretreatment with 5 g/L of potassium ferrate(VI) followed by freeze-thaw with meltwater drainage reduced the concentration of faecal coliform to <100 MPN/g DS in the sludge cake, and <0.28 MPN/mL in the meltwater. The meltwater also had lower turbidity and a higher degree of solubilisation than the meltwater from stand-alone freeze-thaw; however, soluble protein concentrations in the meltwater were reduced when 5.0 g/L of potassium ferrate(VI) was used as a pretreatment with freeze-thaw sludge dewatering. It is possible that ferrate(VI) decomposition, leading to a variety of ferric species, coagulated and precipitated proteinaceous compounds in the supernatant, which ultimately remained in the sludge cake. The

coagulated proteins may have also contributed to filter clogging and reduced sludge drainability during sludge thawing.

This study demonstrated that combined ferrate(VI) and freeze-thaw treatments can achieve sludge dewatering, oxidation of organic and odour causing compounds and faecal coliform inactivation. Ferrate(VI) additions also offer process flexibility when dealing with high concentrations of pathogens and odorous compounds in sludge and colloidal sludge matrices.

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