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Purification efficiency of natural freeze crystallization for urban wastewaters

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Abstract

Human population growth and urbanization are aggravating water quality problems in many regions, and wastewater volumes and quantities of pollutants are increasing due to greater industrial and urban activity. Thus, it is necessary to find efficient, sustainable and simple methods to separate miscellaneous impurities from wastewaters. One potential separation methods is freeze crystallization, because of its non-selective nature. However, previous research investigating freeze separation using real wastewaters has been rather marginal.

This study examines natural freeze crystallization in purification of urban origin wastewaters, that is, municipal wastewater and landfill leachate of various organic and inorganic matter concentration. The effect of different freezing conditions on ice growth and separation efficiency in terms of ice impurity relative to initial solution impurity was investigated with a laboratory scale winter simulator. The results showed air flow velocity to have an almost as significant an influence on ice mass growth as air temperature. Although separation efficiencies decreased linearly with increased ice growth rates, no clear correlation was found between the impurity concentration of the wastewater and the ice mass growth rate. This finding notwithstanding, the separation efficiency of freeze crystallization of concentrated wastewater (landfill leachate) was noted to decrease more clearly with increased ice growth rate. Purification efficiencies of 95% to nearly 100%, determined by indicators such as chemical oxygen demand (COD), were achieved in

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treatment of municipal wastewater when using low ice growth rates. These findings indicate that the approach can meet future legislative requirements for treatment plants and that further research of the utilization of freezing techniques for wastewater purification is warranted.

Keywords: Freezing point depression; Ice purity; Impurity removal; Natural freezing; Wastewater treatment

1. Introduction

Increased environmental awareness among urban populations means that there is now little need to restate arguments articulating the importance of water saving and water protection activities. To date, conventional wastewater treatment plants are designed to remove organic matter and nutrients from wastewaters for environmental protection and to minimize pathogenic microorganism populations in effluent for sanitary reasons. However, concerns have recently been raised over the adequacy of the wastewater treatment methods currently used and the quality and characteristics of the effluent discharged (Prasse et al., 2015).

Constantly improving living standards among urban populations together with wastewater treatment plants with very large population equivalent have resulted in increased quantities of so-called emerging contaminants in discharged effluents. Enrichment of effluents with micropollutants like pharmaceuticals, antibiotics, synthetic sweeteners and personal care products used in everyday life affect adversely the aquatic environment, flora and fauna, and, ultimately, human health (Rodriguez-Narvaez et al., 2017). Improved knowledge and a changed socioeconomic context thus mean that new or complementary methods are needed for advanced wastewater treatment to ensure adequate removal of organic and inorganic matter, nutrients and micropollutants. In addition to being effective, the capital, operating and maintenance costs of such innovative wastewater treatment technologies must remain economically acceptable.

Freeze crystallization is one potential alternative wastewater purification method, as ice possesses natural high intolerance towards impurities (Bogdan and Molina, 2017). When impure water freezes, the water molecules tend to crystallize, i.e. arrange into as pure ice as possible, while impurities are disposed to the remaining liquid water. High separation efficiency of impurities is therefore achievable, provided impurities are not entrapped as inclusions inside the bulk ice. Freeze crystallization is recognized as an energy-efficient and simple water treatment process that needs no chemicals, and it can be assumed that operating costs will be modest and total environmental impact relatively minor (Yin et al., 2017). In the freeze separation process, nutrients in the wastewater are concentrated in the residual liquid in their initial form, for the most part, because no significant biological or chemical reactions occur. As a result, efficient and sustainable recovery of nutrients is possible.

Ice and the freezing process have been studied for decades in many different fields of engineering science and there are many applications where freezing is used to separate water from liquid mixtures and solutions. For instance, freeze concentration has been used in the food industry to produce high quality fruit juice and coffee extracts. Similarly, freeze separation has been used as a desalination process in fresh water production, although mainly on a laboratory scale (Chang et al., 2016; Williams et al., 2015). Eutectic freeze crystallization (EFC), a special form of melt crystallization, can be considered a fairly sophisticated application for water and salt separation because at the eutectic point, ice and salt can be crystallized simultaneously from the electrolyte solution. In EFC studies, attention has been directed to recovery of the salt formed as well as the water treatment itself (Hasan et al., 2017). In recent years, freeze crystallization research has principally focused on the development of experimental or pilot-scale equipment and devices for separation of a specific compound, e.g. sodium carbonate or sodium sulphate from specific industrial wastewater streams or brine (Williams et al., 2015; Randall and Nathoo, 2015). For example, Randall et al. (2014) used wastewater from a textile plant in investigation of a cascading EFC procedure in a jacketed crystallizer. In their study, 98% ice purity and 30% yield of sodium sulphate were achieved. Ice produced by suspension freeze crystallization from brines has also been shown to be very pure. For instance, van der Ham et al. (2004) obtained impurity concentrations in ice below 100 ppm of copper in an EFC-based cooled disk column crystallizer with an initial copper sulphate solution concentration of 0.145 $kg_{salt}/kg_{solution}$. Utilization of more efficient washing of ice enabled levels of 5 ppm or less to be achieved.

Freeze purification (or separation) studies have been undertaken mostly using model or synthetic wastewater and few studies have used real wastewaters. Work reporting the purification efficiency of total organic or inorganic matter when using urban origin wastewaters, which are complex multi-component aqueous solutions, is even more limited. In the area of industrial wastewaters, Gao et al. (1999) studied ice nucleation by spray droplets with a pulp mill effluent, piggery wastewater and oil sands tailings pond water. They continued their spray freezing studies in field conditions with the same industrial waters and achieved ≥60% impurity reduction efficiencies for chemical oxygen demand (COD), electrical conductivity and color. Different efficiencies were found for organic and inorganic matter (Gao et al., 2004). A few years later, the same research group compared laboratory-scale spray and unidirectional downward freezing techniques with oil refinery and pulp mill effluents. Layer freezing with mixing of the liquid resulted in the greatest organic contaminants reduction, 90-96% reduction (based on COD and total organic carbon (TOC) analysis). Without mixing, the efficiency was much lower; it was at the same level as spray freezing (Gao et al., 2009).

The separation efficiency of freeze concentration with a rotating evaporator for soluble pollution in urban wastewater, food factory effluents and cutting oil wastewater was studied by Lorain et al. (2001). The study attained close to 100% separation efficiency for TOC (i.e. organic matter). Similar very high purity of the ice layer (measured by COD) was found also by Shirai et al. (1998) in layer freezing studies with food industry (dairy and rice cracker) wastewaters. The spray freezing research carried out in field conditions by Bigger et al. (2005) with mining tailings lake water achieved 87-99% removal of mostly inorganic matter when measured with electric conductivity. Their work also analyzed removal of some ions, elements and toxins such as arsenic and cyanide. It should be noted, however, that mining waters can also contain significant amounts of organic matter in addition to heavy metals, as detected in our previous study of natural freezing in mine wastewater basins (John et al., 2018).

Some freezing studies have investigated compounds that are now classified as micropollutants. Gao and Shao (2009) studied two commonly used pharmaceuticals, namely the anti-inflammatory drug ibuprofen and the antibiotic sulfamethoxazole. Their work used model solutions and analyzed TOC as a gross parameter. They found that pharmaceuticals content reduced by 84-92% in single-stage freeze concentration and about 99% in a two-stage ice layer freezing process. Yin et al. (2017) studied a Grignard reagent wastewater from a pharmaceutical intermediates company that contained the organic solvent tetrahydrofuran. COD removal of >90% was found when using layer freezing and suspension crystallization. Feng et al. (2018) proposed a freezing concept for use with oil recovery from waste cutting fluids. 90% COD removal efficiency was obtained with suspension crystallization.

Previous freezing studies with real wastewaters have implemented freezing techniques at temperatures varying from -2 °C in the laboratory to -33 °C in field conditions. The studies give only little information about the ice production rate at specific conditions, and appraisal of the total potential efficacy of the freeze separation process is hence difficult, even though the separation efficiency for some impurities was shown to be high and sometimes close to 100%.

This study investigates ice layer growth and purification efficiency of natural air-cooled freezing of urban wastewaters originating from a municipal wastewater treatment plant and solid waste landfill. The effect of freezing conditions (i.e. air flow velocity and temperature) on ice mass growth and separation efficiency was examined under controlled conditions using winter simulation apparatus. The freezing point depression temperatures of the studied wastewaters were experimentally determined to initialize the thermodynamic actions and to ensure the comparability of the freezing temperatures of the different wastewaters.

2. Materials and methods

2.1. Wastewaters

In this study, real wastewaters from a municipal wastewater treatment plant and leachate from a solid waste landfill were used as the feed water for the freezing experiments. Both sites, the Toikansuo wastewater treatment plant and the Kukkuroinmäki landfill, are situated in the city of Lappeenranta in southeastern Finland. The municipal wastewater contains mainly domestic wastewater, with some industrial wastewater, from a residential population of 60 000 and average daily wastewater volume is 16 000 m^3. The wastewater for the tests was collected from the open water stream after primary clarification and before the water flows to the biological (activated sludge) reactor tank. The wastewater is chemically pretreated in a primary sedimentation basin with calcium hydroxide $Ca(OH)_2$ and ferric sulphate $Fe_2(SO_4)_3$ (feeds ~150 g per m^3 wastewater) for pH adjustment and suspended solids reduction, respectively. Fully processed effluent from the same plant was also collected to be able to test very dilute wastewater. The landfill is situated next to the regional solid waste management center serving municipalities in the area. The landfill leachate water was collected from the inspection and pumping well that captures infiltration water from the normal (non-hazardous) solid waste fill. Total daily leachate volume of the landfill varies from 80 to 120 m^3.

Urban wastewater is a very complex mixture of compounds and pollutants that have accumulated in water. The quality and composition of the wastewater also varies periodically due to fluctuating flow rates caused by domestic water use and precipitation. Infiltration water of landfills is formed by precipitation and melting snow and contains residues from the waste material as well as solid filling material. Both sites, the wastewater treatment plant and the landfill, have a statutory obligation to monitor water quality frequently. Average analyzed compositions of the studied wastewaters are presented in Table 1. Although the landfill leachate contains almost twice the amount of organic matter found in the municipal pretreated wastewater, the biological activity of the municipal pretreated wastewater can be expected to be higher due to its larger microbial population. The measured conductivity of the leachate is high, indicating a high concentration of ionic inorganic matter. The landfill leachate most likely contains small particles like microplastics and fibers, as bigger pieces were visible in the raw water samples.

Table 1. Composition of tested wastewaters.

Wastewater	**COD** (mg L^{-1})	**Color** (PtCo)	**Turbidity** (FTU)	**Conductivity** (μS cm^{-1})	**pH**	**Total solids** (mg L^{-1})
Municipal effluent	21-29	47-66	9-12	575-602	6.16-6.45	-
Municipal pretreated	127-465	360-816	67-151	719-786	7.56-9.12	470-630
Landfill leachate	447-638	450-975	85-184	1850-5005	7.70-8.42	1300-3200

2.2. Experimental setup

The natural freezing of wastewater was done in a wind tunnel-like laboratory-scale apparatus custom-made of a thermally insulated chest freezer. The arrangement enables simulation of natural freezing conditions because the temperature and velocity of cooling air can be carefully controlled. Fig. 1 shows the experimental setup for natural freeze purification of wastewaters. Winter simulator apparatus with a similar set-up was used in our previous freezing experiments with electrolyte solutions (Hasan et al., 2018).

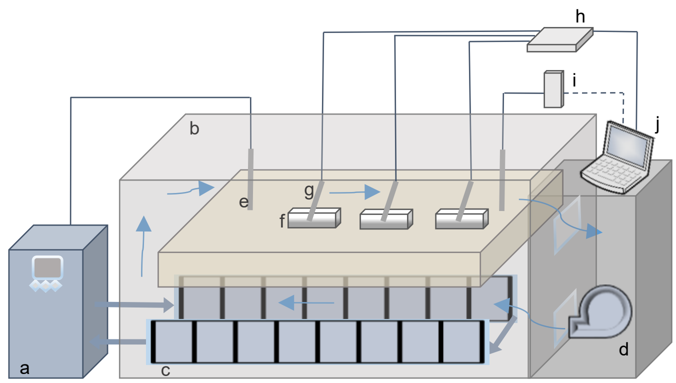


Fig. 1. Experimental setup for natural freeze purification of wastewaters: a) thermostat, b) chest freezer, c) heat exchangers, d) blower, e) temperature sensor, f) crystallizer vessels, g) PT 100 thermometers, h) data logger, i) anemometer and probe, j) computer.

Wastewater samples of 500 mL volume in plastic crystallizer vessels (volume of ~710 mL, edge dimensions ~40 mm · 87 mm · 58 mm) were allowed to freeze so that an ice layer formed on the upper surface of the wastewater. The water surface level was about 15 mm below the upper edge of the vessel and, thus, the freezing area was ~0.013412 m^2. Heat losses through the other sides of the vessels were avoided by thermal insulation when the vessels were installed inside the floor level of the wind tunnel. The designed undercooling temperature degree (ΔT) was obtained by circulating aqueous ethylene glycol coolant in heat exchangers. Air temperature in the wind tunnel was controlled with a Lauda Proline RP 850 thermostat connected to a PT100 sensor measuring air temperature. Cool air flow in the tunnel was produced with a blower. The air production of the blower was adjusted with a frequency converter based on verified operating air flow velocity (v_{air}) measured with a Kimo VT100 (or VT210) anemometer (accuracies ±0.1 ms^{-1} and ±0.3 °C, respectively). The temperatures of the wastewater samples in the vessels were measured with PT100 platinum resistance thermometers. Temperature data was collected by Pico PT-104 Data Logger (resolution 0.001 °C, accuracy ±0.015 °C) and PicoLog software.

2.3. Freezing point depression test

The freezing point depression (FPD) temperatures (T_f) of different types of real wastewaters were determined to enable comparison of the undercooling temperature degree (ΔT) in the freezing experiments. The FPD test was executed with a simple cooling curve method in which measured temperature responses during cooling were plotted as a function of time. A 200 ml wastewater sample was poured into a jacketed class reactor equipped with a magnetic stirrer. The circulation of ethylene glycol coolant in the jacket was controlled by a Lauda Proline RP 850 thermostatic unit. The temperatures of the water were measured with a PT100 sensor connected to the thermostat and the temperature data was logged to a file by a computer and Lauda Wintherm Plus software. The reference junction (calibration) of the thermostatic unit and probe was obtained with a pure ice and water mixture and verified using a mercury thermometer with a certificate of calibration.

2.4. Experimental procedures and methods

500 mL samples of well-stirred wastewater were prepared for the freeze separation tests. Two or three replicates were prepared and frozen at the same time. Although the wastewater contained some visible solids, no pre-filtering or settling were used in order to simulate the process realistically. Before the freezing test, the water samples were allowed to cool to near to freezing temperature in a freezer room at -18 °C to avoid too high undercooling degree and to generate initial seed ice crystals for the freezing test. The precooling time needed varied between 30-50 minutes depending on the wastewater type.

Before and immediately after the freezing test, the masses of the samples in the vessels were measured (balance Precisa BJ2200C, capacity 2200 g, readability 0.01 g) to determine the total mass loss, i.e. evaporated water, during the test. After the test period, the vessels were removed from the winter simulator and the remaining concentrated liquid (residual) and the formed ice layer were separated. The mass of the ice was measured as well as the volume of the concentrated liquid. The average thickness (mm) of the ice layer was determined by multipoint measuring with a caliper. The ice piece was lightly rinsed with pure water cooled to near to 0 °C to avoid adherence of external contaminants on the ice surface during manual sample handling. All ice and residual concentrated liquid were collected and stored in a freezer at -18 °C for further analyses.

The ice layer growth rate is known to decrease during the freezing process as the heat insulating effect of the ice layer increases with increasing layer thickness (Hasan et al., 2017). For this reason, the freezing time was set at a constant 24 hours to be able to study how two controllable variable parameters, i.e. air temperature and air flow velocity, affect ice growth rate and separation efficiency. The basic parameters used were undercooling temperature degrees ΔT 0.5, 1.0, 1.5, 2.0 and/or 3.0 °C (or K), and air flow velocities v_{air} 0.5, 1.0, 1.5, 2.0 and/or 3.0 ms^{-1}. Thus, at least nine different freezing conditions were assessed with each type of wastewater, see the experimental design in Fig. 2.

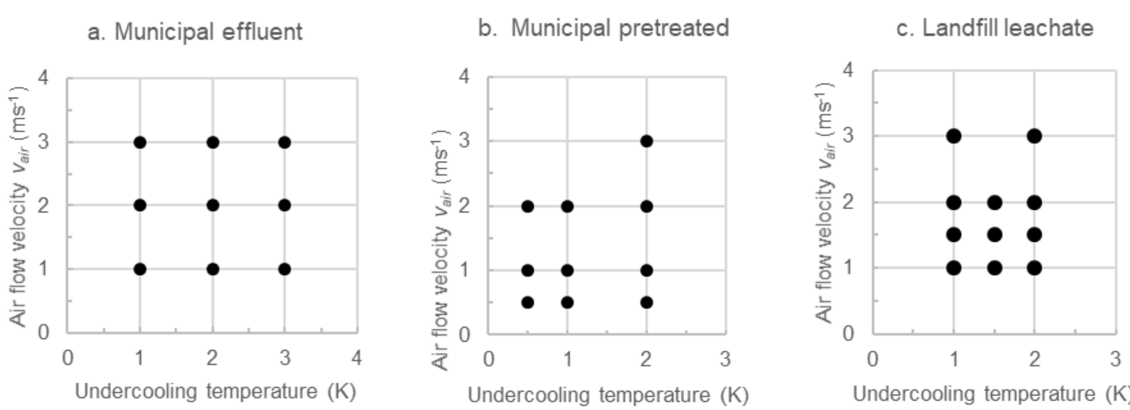


Fig. 2. Design of experiments for different wastewaters with the used combinations of undercooling temperature and air flow velocity with freezing test time of 24 hours.

Similar freezing tests were carried out with ultrapure water produced with an Elga PureLab water purification system (TOC < 5 ppb, resistivity 18.2 MΩ cm) as blank samples for comparison. Additionally, some tests were performed with different times: 5, 48 and 72 hours, and temperatures: ΔT 5 °C and 10 °C, to be able to survey the limitations of the experimental set-up used, for example, regarding the effect of the obtained freezing ratio on the separation efficiency. The assumption was that the separation efficiency will decrease if the freezing ratio is over 50% (i.e. half of the water is frozen) due to enrichment of the solution (Hasan and Louhi-Kultanen, 2016). The obtained freezing ratio (%) was determined and confirmed by calculation of the percentage of the ice mass formed from the initial water mass.

The average linear ice layer growth rate (ms^{-1}) was determined by dividing the average ice layer thickness by the total freezing time. This calculation method enables comparison with previous studies. The average ice mass growth rate, $g\ h^{-1}m^{-2}$, was calculated by dividing the measured totally formed ice mass by the freezing time and surface area. The evaporation (or sublimation) rate, $g\ h^{-1}m^{-2}$, can be determined in the same manner as the ice mass growth rate by dividing the measured total mass loss by the freezing time and the surface area of the vessel.

Differences in the polycrystalline ice structures formed were observed macroscopically by polarized light and microscopically (Olympus BH2-UMA) for visualization of the impurity inclusion, veins and pockets in the ice. In these studies, however, the focus is on determination of purification efficiency, and ice characteristics are not studied in detail. Thus, the primary use of ice samples with limited volume was for chemical analyses.

2.5. Chemical analyses and methods

The analysis methods used were chosen to indicate the general quality of the water and to indicate the feasibility of freezing as an unselective purification method. When analyzing real wastewaters, the indirect measurements used in the present work, i.e. electrical conductivity and chemical oxygen demand (COD), give overall information about inorganic and organic matter content, respectively. Ice and wastewater samples were analyzed using similar methods as used in previous freezing studies to enable comparison of the achieved purification efficiency with prevailing practices.

Before analysis, the melted ice samples and stored wastewater samples were kept at room temperature to attain ambient temperature. A spectrophotometer HACH DR/2000 was used to determine the apparent color (PtCo, 455 nm) and turbidity (±2.0 FTU, 450 nm). The chemical oxygen demand (COD, mg L^{-1}) was analyzed by spectrophotometer and a dichromate oxidation method corresponding to APHA 5220 D (Greenberg et al., 1995) with a Spectroquant COD reaction cell test measuring ranges 0-150 mg L^{-1} (±2.7 mg L^{-1}, 420 nm) and 0-1500 mg L^{-1} (±14 mg L^{-1}, 620 nm). A Consort C3040 multi-parameter analyzer was used to measure pH and electrical conductivity (probe with temperature compensation, cell constant 1.0 cm^{-1}, range 0.001-100 mS cm^{-1}). Dry matter content as total solids (TS, mg L^{-1}) was determined by an evaporation-weighing method corresponding to APHA 2540 B (Greenberg et al., 1995) for initial wastewater samples. Almost all ice samples had to be excluded because of limited liquid volumes. As the quality of raw wastewater changes even during short cool storing, the initial wastewater used was analyzed for every experiment. Purification efficiency *E(%)* was calculated with Equation 1:

$$E(\%) = 100 \cdot \left(\frac{C_{ww} - C_{ice}}{C_{ww}}\right), \qquad (1)$$

where C_{ww} is the concentration or other measured value in the initial wastewater and C_{ice} the concentration or other measured value in the ice.

3. Results and discussion

3.1. Freezing point depression

The determined freezing point depression (FPD) temperatures and obtained supercooling temperatures of the studied wastewaters are presented in Table 2. It is important to define these temperatures as temperature difference is the driving force for the ice crystallization process. Freezing temperature and the degree of supercooling used affect the ice nucleation and ice crystal growth. The FPD temperatures of the municipal wastewaters, effluent and pretreated wastewater were quite similar. The FDP temperature was slightly lower with pretreated wastewater and the supercooling degree quite moderate, 2 to 3 °C. As expected, landfill leachate showed approximately four times lower FPD temperatures than municipal wastewaters, -0.220 °C at their lowest, because landfill leachate contains more ionic matter. An example of a cooling curve recorded in an FPD test for landfill leachate is presented in Fig. 3. It was of importance to determine the FPD temperature, as FPD of wastewaters is rarely studied. The FPD seemed to indicate the total impurity of wastewater rather sensitively, especially inorganic matter.

Table 2. Determined freezing point depression temperatures and supercooling temperatures of the studied wastewaters.

	Municipal effluent	Municipal pretreated	Landfill leachate
FPD temperature (°C)	-0.035…-0.048	-0.040…-0.060	-0.185…-0.220
Supercooling temperature (°C)	n/a	-1.860…-3.010	-2.880…-3.350

With the studied wastewaters, the freezing point depression was not very significant compared to common dilute salt solutions. More important was the variation in FPD temperatures with the same type of wastewater. The FPD temperature of the wastewaters varies because of the differing composition of the sampled raw wastewater batches. The FPD temperature was also found to change during storage of the wastewater, presumably due to decomposition of impurities in the water. Although the FPD temperature differences between the different wastewaters seemed insignificant, it should be noted that even small temperature difference (0.1 or 0.2 °C) in used freezing temperature may have a significant effect on the heat transfer and hence on total energy consumption of the utilized freezing process.

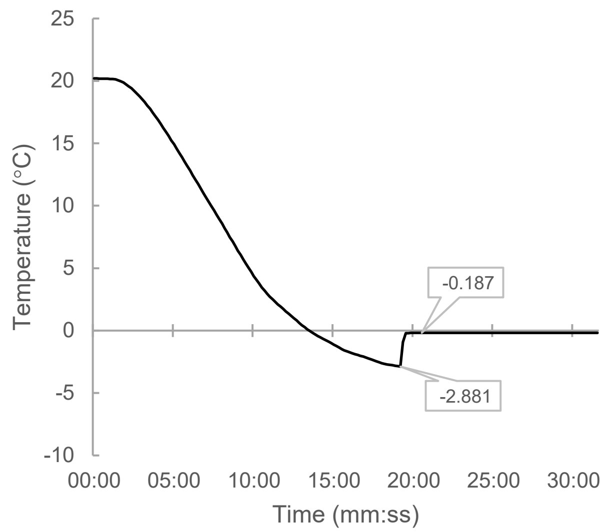


Fig. 3. Cooling curve from a freezing point depression test of landfill leachate at a cooling rate of 1.5 °C min^{-1}. The freezing point and subcooling temperatures are marked within the curve.

3.2. Freezing process

The ice layers formed in a quite similar manner in the different wastewaters in the winter simulator. Usually, the crystal growth began from ice crystal seeds that had formed during the precooling in a freezer. Ice crystal growth continued, forming needle-, dendrite- and/or platelet-like ice on the surface of the water, until the surface was totally covered with a very thin ice layer. The initial dendritic tree-like growth on the liquid surface is presumably due to simultaneous evaporation of water and freezing, and the needle-like ice forms due to seeding and quick cooling (Mullin, 2001). Thin ice formations were sometimes difficult to observe visually (and by a camera) because of their transparency, see Fig. 5a and 5d. After surface ice growth, the ice layer continued growing towards the liquid water.

The measured temperatures of the water under the ice were seen to plateau near the determined freezing temperatures or at lower temperatures with minor supercooling, as can be seen in the freezing temperature profiles of the different waters under the same cooling conditions (ΔT 2 K and v_{air} 2 ms^{-1}) in Fig. 4. With lower air temperatures (<-3°C) and higher air velocities (>3 ms^{-1}) the temperature of the water began to decrease with freezing time due to more intense forced convection. It was noticed, however, that the surface started to freeze before attaining equilibrium freezing temperature, and sometimes even at 0 °C, as the temperature probe measured the average bulk temperature of the water but not the temperature at the ice-water interface. Controlled precooling of the water samples proved to be difficult and the temperature of the replica samples varied at the beginning of the freezing test despite similar preparation for the same time. As a consequence, the starting temperature of the freezing tests varied from 0.75 to 2.25 °C.

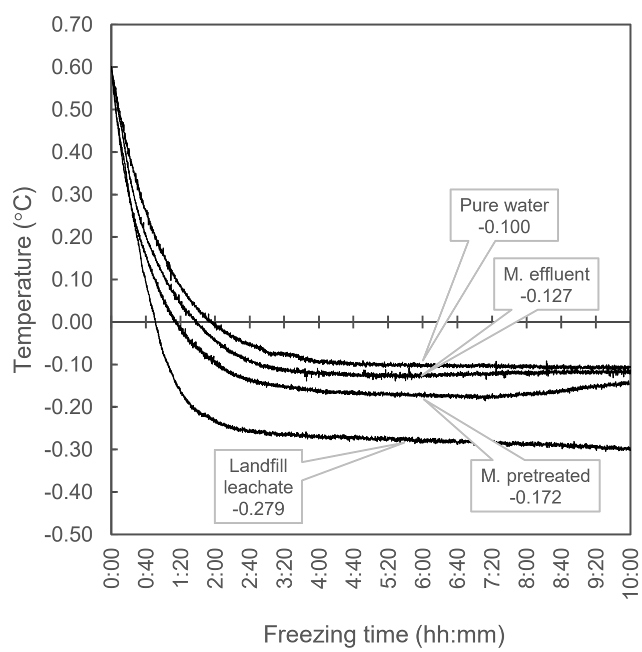


Fig. 4. Temperature profiles of purified water, effluent wastewater, pretreated wastewater and landfill leachate in the crystallization vessel in the wind tunnel during 10 hours' freezing, conditions of ΔT 2 K and v_{air} 2 ms^{-1}. Temperatures (°C) within 6 hours freezing marked in the curves.

Freezing time of approximately two hours was required to form an ice layer fully covering the upper liquid surface. With lower temperatures, development of the ice layer happened a little faster. An exception here was that in some cases, mostly with low air velocity of 0.5 ms^{-1} or undercooling temperature of 0.5 K, no uniform ice layer was formed. In other cases, only two thirds or half of the upper surface was frozen after 24 h freezing time and the temperature of the water in the vessel remained higher than the freezing temperature and sometimes even above 0 °C. Many of the ice pieces were wedge-shaped with a quite planar upper surface and the thinner end edge facing towards the air flow: ice under the air inlet was thinner than the ice layer under the air outlet. This exceptional shape was most likely due to the experimental setup, i.e. local turbulent air flow conditions. Therefore, ice growth rates were primarily assessed by measured ice mass and ice layer thickness was calculated as the average thickness of multiple measurement points. Some suspended solids settled on the bottom of the vessel during freezing of more concentrated wastewater, as can be seen in the municipal pretreated wastewater in Fig. 5b.

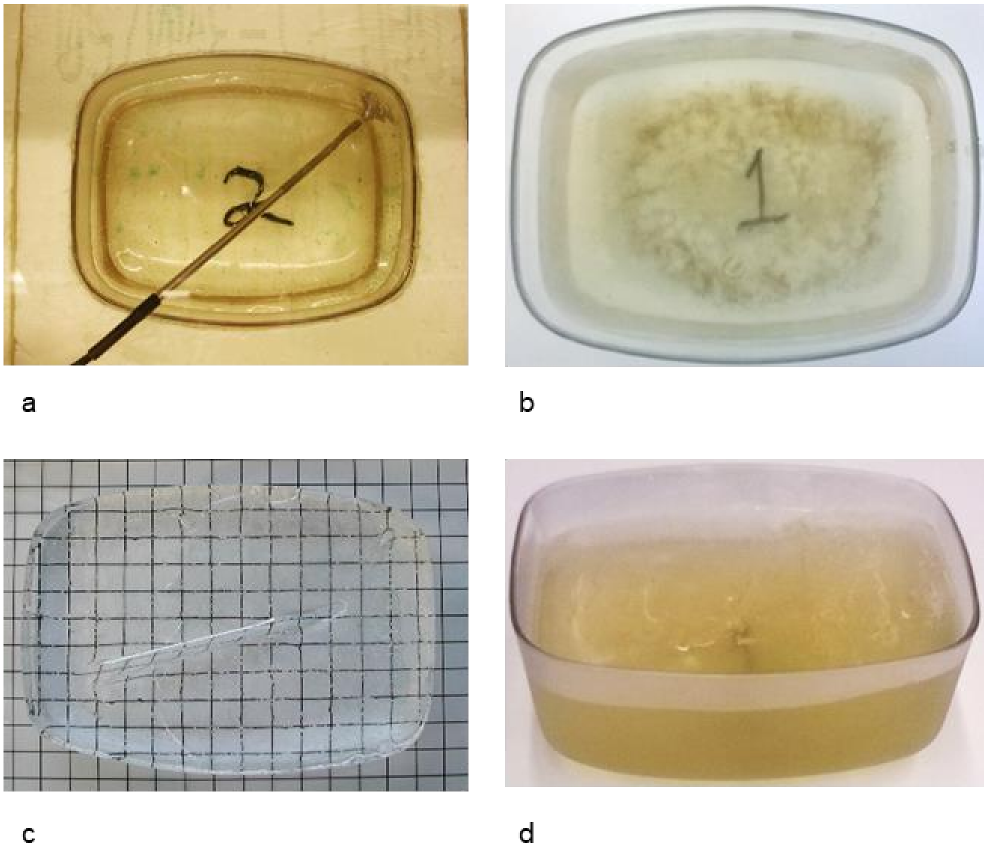
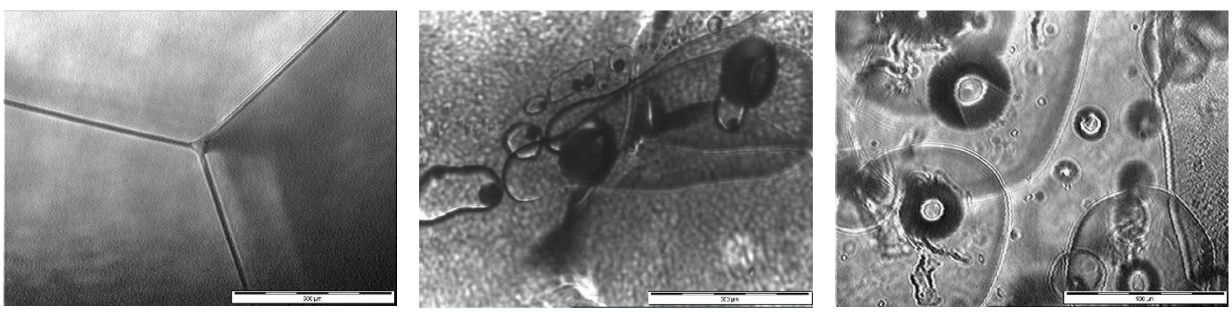


Fig. 5 a) Ice and municipal effluent in the crystallizer vessel with the temperature probe: b) some suspended solids of municipal pretreated wastewater settled on the bottom of the vessel during freezing – notice the pattern; c) an ice piece formed from municipal effluent, measure grid 1 cm x 1cm; and d) ice and landfill leachate in the crystallizer vessel.

3.3. Formed ice

All the ice layer samples seemed to have relatively high mechanical strength compared, for example, with the fairly soft ice formed from salt solutions in previous studies. Thicker ice pieces could not be broken without tools. Some small bubbles or thin veins inside the ice were noticed (see Fig. 5c) but no regular patterns. The upper surface of the ice was mostly planar (with some mild humps and bumps) and clear, and no accumulated solid matter could be seen. The bottom of the ice was also mostly planar, although in some cases the bottom had spiky (small needles) ice formed by higher growth rates. However, no regular patterns, e.g. dendritic platelets, were observed.

The visual color of the ice varied from very transparent ice for municipal effluent to shades of a yellow brownish color for landfill leachate ice. The values of apparent color and turbidity measured in the melt ice did not always match visual observations; ice with high measured values could look misleadingly clear and transparent. Generally, no explanatory correlation could be found between the visual characteristics of the ice and the purification efficiency. In most cases, the purified wastewater water (melt ice) smelled like dilute wastewater, i.e., it was not odorless, even though it looked like clear ice. Microscopic observation revealed clear differences in ice characteristics (Fig. 6). Whereas fairly clean ice showed as blank spaces with clear ice crystal boundaries (Fig. 6a), the municipal effluent ice clearly contained impurity inclusions (Fig. 6b). In addition, landfill leachate ice incorporated small solid grains (Fig. 6c). It was difficult to observe the ice crystal boundaries of impure polycrystalline ice and identify any impurities (fibers, micro-organisms, microplastics etc.) due to overlaps in the structure.



a b c

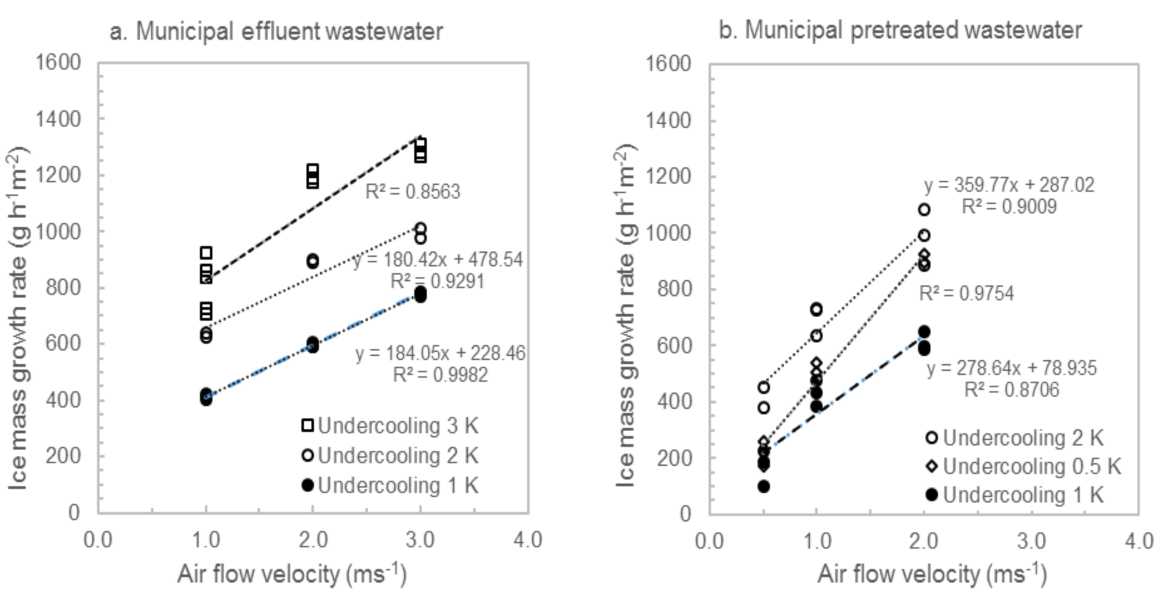
Fig. 6. Microscopic characteristics of ice formed with different waters and under different freezing conditions (undercooling degree temperature and air flow velocity): a) pure water (1 K, 3 ms^{-1}) b) municipal effluent ice (1 K, 1 ms^{-1}) and c) landfill leachate ice (1 K, 2 ms^{-1}), bar scale 500 μm, magnification 5x.

3.4. Ice growth rate

Some correlation was found between the wastewater freezing results and the freezing conditions in the winter simulator. An almost linear function for ice mass growth rate (g $h^{-1}m^{-2}$) as a function of air flow velocity (ms^{-1}) with different undercooling temperatures (K) was obtained based on simple linear regression model fitting results, see Fig. 7. Linear fitting with all experiments gave

R^2 (the coefficient of determination) varying from 0.856 to 0.998. As expected, freezing conditions, i.e. air flow velocity and temperature, directly affected the ice growth rate, as can be seen in Fig. 7a, b and c, for different wastewaters, whereas the effect of wastewater quality can be considered to be more moderate or minor. When all the mass growth rates of the different wastewaters and air velocities with undercooling temperatures 1 K and 2 K were fitted in the same linear model (Fig. 7d) the R^2 values were still at a good level: 0.898 with ΔT 1 K and 0.783 with ΔT 2 K. The lines are very parallel with almost equal slopes (236 and 237).

Deviations and lower R^2 values are more likely due to the experimental setup and measurement conditions, that is, vibration of the chest freezer, humidity differences or minor human errors etc., than the wastewater composition. As was previously noticed for ice pieces formed with low undercooling temperature of 0.5 K, the air-cooled freezing process is very easily influenced by factors that are difficult to measure. This issue can be seen in Fig. 7b, where the line for 0.5 K undercooling indicates higher ice mass growth rates than 1 K undercooling. A part of the water surface was open to air and the increased air flow intensified the ice growth, both as regards mass and ice layer thickness (ms^{-1}).



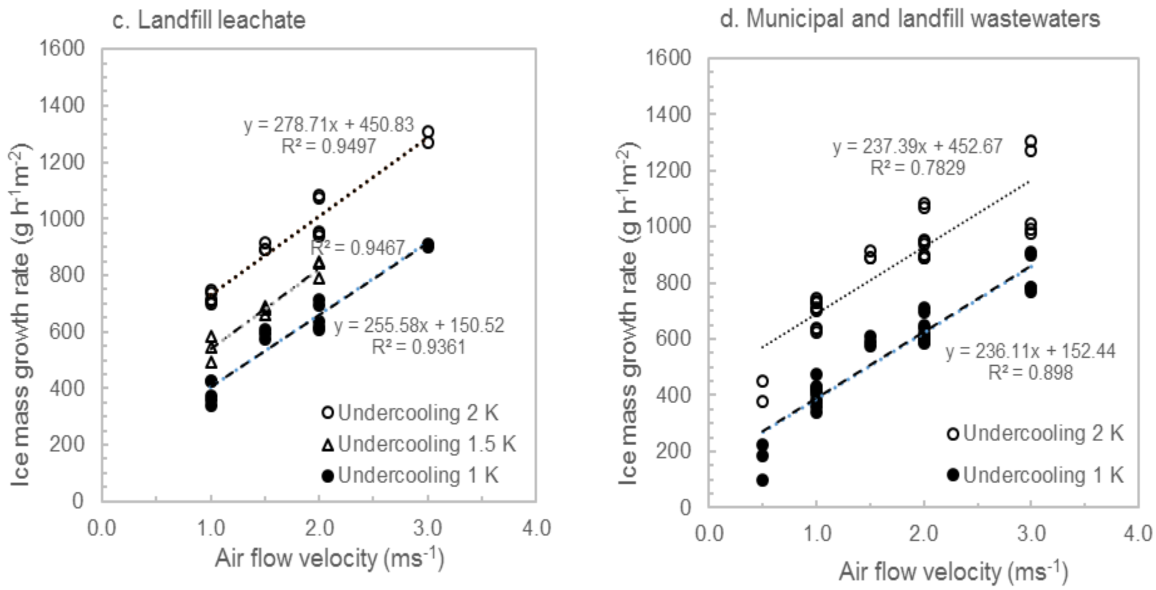


Fig. 7. Ice mass growth rates as a function of air flow velocity with different undercooling degree temperatures: a) effluent, b) pretreated wastewater, c) landfill leachate and d) the combined results of all municipal and landfill wastewaters with undercooling temperatures 1 and 2 K. Linear fittings, N = 6 - 28.

Based on the results of these freezing experiments and the simple model used for the freezing conditions, it can be seen that the undercooling temperature defines the base level of the ice growth rate on the intersection of the y-axis and the air velocity gives the coefficient or impact factor for the intensity of the growth rate by the slope of the linear line (Fig. 7d). For example, with conditions ΔT = 1 K and v_{air} = 1 ms^{-1}, the average mass growth rate (i.e. the ice mass production) was 389 g $h^{-1}m^{-2}$. When air velocity was increased from 1 ms^{-1} to 2 ms^{-1}, the ice mass growth rate increased by 236 g $h^{-1}m^{-2}$ to 625 g $h^{-1}m^{-2}$. With undercooling temperature of 2 K, the growth rate behaved in the same way. The same linearity can be found with ice layer growth rates (ms^{-1}). Verification of the presumption of linearity with lower freezing temperatures vs. growth rates as a function of air flow velocity could not be examined due to limitations in the experimental setup used.

Comparison of the ice growth rate results of the present work and previous studies reported in literature is problematic because most research has been carried out in very different conditions, i.e. with much colder temperatures and lower air flow velocities. However, the ice layer growth rates obtained in our previous study with electrolyte solutions (nickel sulphate) correspond somewhat with the growth rates in freezing of wastewater found in this work. For similar conditions (ΔT = 1 K, v_{air} = 2 ms^{-1}, 24 h), the salt solutions had an average ice layer growth rate of ~2.5 $\cdot 10^{-7}$ ms^{-1} (Hasan et al., 2018) and in this study the average rate was 2.05 $\cdot 10^{-7}$ ms^{-1}.

3.5. Purification efficiency

As previously described in section 3.4., the ice growth rate results from factors determining the freezing conditions, i.e. air temperature and velocity, and similar growth rate can be obtained with various combinations of these parameters. Therefore, when considering the purification efficiency of different wastewaters, it is more meaningful to compare the ice growth rate than the freezing conditions directly.

The calculated results showed that the greater the ice growth rate, the lower the purification efficiency. The effect is clearly seen in more concentrated wastewaters with inorganics, like landfill leachate, see Fig. 8. With a lower ice mass growth rate of 400 g $h^{-1}m^{-2}$, the average purification efficiency was near to 90%. The efficiency decreased to 60-70% when the ice mass growth rate increased to 800 g $h^{-1}m^{-2}$. With the effluent, no obvious correlation between ice growth and purification could be found, partly due to limitations in the analysis methods when used for very dilute wastewaters. However, the average purification efficiency was mainly in the range 75-90% for all water quality indicators and the effect of higher ice mass growth rate on purification can thus be considered to be less significant with dilute effluent.

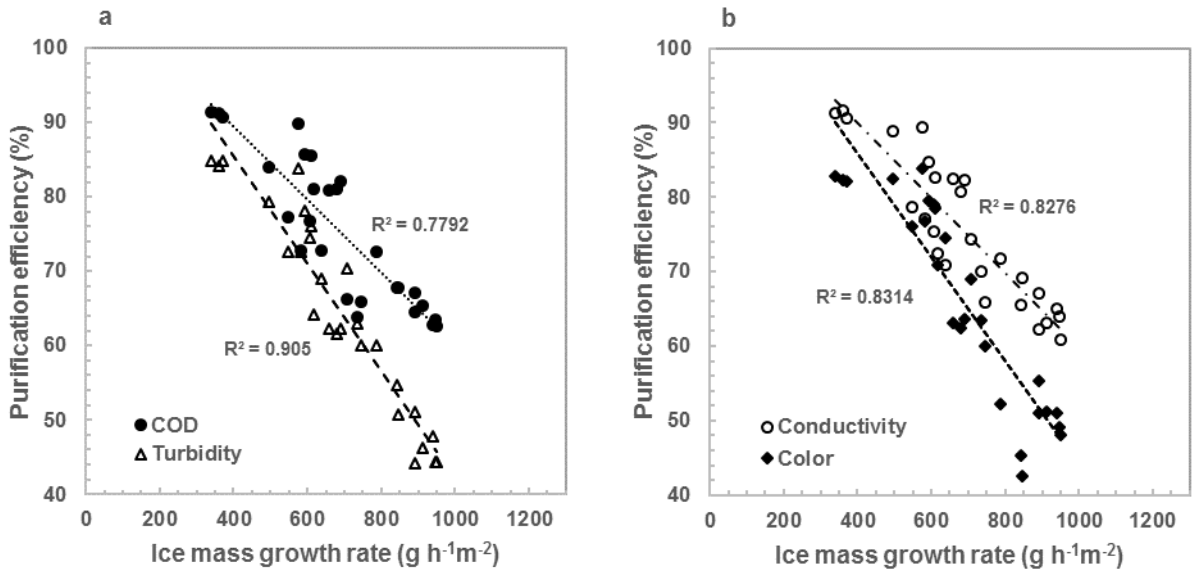


Fig. 8. Purification efficiencies of a) COD and turbidity and b) conductivity and color with different ice mass growth rates in freezing tests of landfill leachate. Linear fittings, N = 27.

With pretreated wastewater, the effect of ice mass growth rate was not as evident as with landfill leachate since the decrease in purification efficiency related to an increase in ice mass growth is much lower and R^2 values are somewhat lower, see the trend lines in Fig. 9. For instance, lower ice mass growth rates of 200 and 400 g $h^{-1}m^{-2}$ showed average purification efficiencies of around 90% and a higher growth rate of 800 g $h^{-1}m^{-2}$ resulted in efficiencies slightly under 80%. Unexpectedly, very fast freezing of municipal pretreated wastewater over 5 hours' freezing time, ΔT = 10 K , v_{air} = 0.5 ms^{-1} and growth rate of ~800 g $h^{-1}m^{-2}$ also resulted in 90% COD reduction. The difference between the test result with the same undercooling degree and a higher air flow velocity of 1 ms^{-1} and growth rate of ~1800 g $h^{-1}m^{-2}$ is noteworthy, as it resulted in 76% COD reduction. The more extreme freezing conditions should be investigated further, as ice mass production over time might be a significant factor in utilization of natural freezing processes.

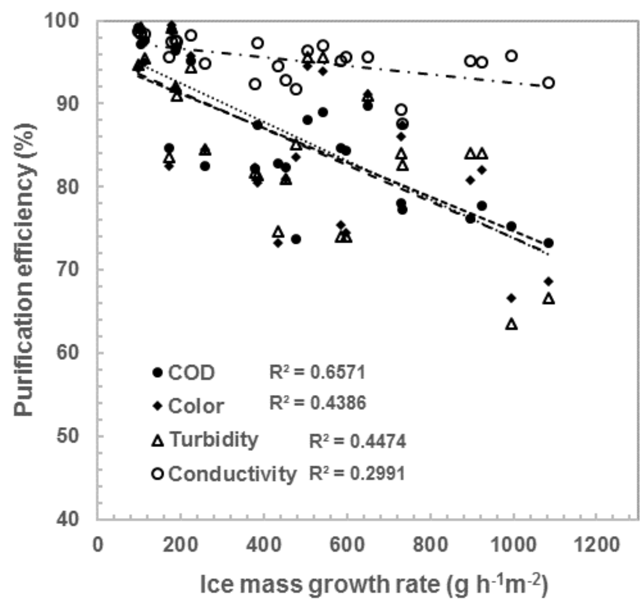


Fig. 9. Purification efficiencies of COD, color, turbidity and conductivity with different ice mass growth rates in freezing tests of municipal pretreated wastewater. Linear fittings, N = 25. Trend lines of COD, color and turbidity are almost parallel.

When municipal pretreated wastewater was frozen under conditions of ΔT = 1 K and v_{air} = 0.5 ms^{-1}, the highest purification efficiencies, >95%, were obtained for all water quality indicators with very low ice growth rates. Longer freezing time of 72 or 48 h did not show any effect on purification efficiency, i.e. the efficiency was at the same level as in 24 h freezing. These conditions were not tested with landfill leachate, since using a velocity of 0.5 ms^{-1} (or a 0.5 K undercooling degree) was earlier seen to cause unexpected deformations in the ice pieces. Very low ice growth rates should be tested with an improved experimental set-up. However, based on these results, it can be concluded that very high purification efficiencies can be achieved with very slow freezing.

The tendency of wastewaters of different concentrations to form more impure ice with an increasing ice growth rate can be seen in Figs. 7, 8 and 9. When comparing municipal pretreated wastewater with more concentrated landfill leachate, it is noticed that the effect of higher ice mass growth rate on purification efficiency is much stronger with landfill leachate, i.e. the direction of the trend line is decreasing and the incline is steeper (Fig. 8). The same trend was seen also in previous studies for freezing salt solutions of different concentrations when plotting the purification efficiency in terms of the effective distribution coefficient as a function of the ice layer growth rate (Hasan and Louhi-Kultanen, 2015, 2016; Hasan et al., 2018). Based on this observation, it can be deduced that the type of wastewater (i.e. impurity concentration) can affect the ice crystallization process and the impurity rejection efficiency.

Despite the very different wastewaters and freezing conditions, the purification efficiencies obtained in the present work are rather similar to previous natural freeze crystallization studies reported in literature. In the present study, COD concentrations in the initial wastewaters were 21–638 mg L^{-1} for freezing temperatures of ~-0.5 to -3.2 °C with a freezing ratio <50%. Yin et al. (2017) studied highly concentrated effluent (20 000–30 000 mg L^{-1} COD) containing organic pharmaceutical intermediates. Their study obtained a COD removal efficiency of 70-90% with an ice formation ratio of 20% at temperatures of -4 to -12 °C. Gao et al. (2009) reported 90-96% COD and TOC reduction in freezing of petroleum refiner effluent with initial COD concentration of 767 mg L^{-1}(freezing ratio 70% at -10 and -25 °C). Soluble pollutants of urban wastewaters were studied by Lorain et al. (2001) using a non-air-cooled freezing setup. Near 90% efficiency was attained (freezing ratio 64%, -7 °C) for freeze crystallization of the wastewater after primary settling. In our previous study (John et al., 2018), comparable separation efficiencies of 65-90% were attained for naturally frozen ice in wastewater basins of a mining site.

When the results obtained in this study are compared with current regulations for municipal wastewater treatment plants, the best purification efficiencies achieved can be considered to be at a good level. For instance, the environmental permit of the Toikansuo wastewater treatment plant, which is the source of the wastewater samples, limits the COD concentration (average of quarterly sampled results) of the effluent to 70 mg L^{-1}, i.e. the minimal acceptable purification efficiency of the plant is 80%. In this study, this requirement was met in freeze crystallization of municipal pretreated wastewater at lower ice growth rates, where COD concentration varied from <3 to 41 mg L^{-1}. It is known that regulations are going to become more stringent in the near future and many wastewater treatment plants are already exceeding minimal requirements. Indeed, the old Toikansuo treatment plant has attained COD concentration in effluent of 30-40 mg L^{-1}, giving a purification efficiency of 95%.

3.6. Further remarks

The effect of the acidity or alkalinity of aqueous solutions is rarely studied in freeze crystallization as pH is assumed to have very minor or negligible effect on the freezing process, although Gao et al. (1999) suggested that pH has an effect on freezing temperature and nucleus concentrations of wastewaters. However, pH is a relevant factor when evaluating the quality of the effluent to be discharged into the environment.

In the freezing experiments in this work, it was noticed that the pH values of the melted ice or concentrated residual may be significantly different from the pH of the initial wastewater (Supplementary material, Fig. A.1). The pH value of the ice can be either higher or lower than that of the initial wastewater depending on the source of the wastewater. Generally, an increase of 0.5 – 1.0 pH (e.g. increase from pH 7.7 to 8.7) was noticed with landfill leachate freezing. Then the highest pH values of ice were still allowable. The largest decrease, from pH 8.8 to 6.5, was detected with pretreated municipal wastewater, although the pH of the ice remained at a rather neutral level as the initial pH of the wastewater was quite high. The most remarkable decrease in pH was found with effluent. The lowest final pH value of effluent melt ice was 4.2 pH (for effluent with a quite low initial pH of <6.5 pH).

Low alkalinity of the effluent because of earlier bio-chemical water treatment could explain the decrease in pH. However, if chemicals are not added to the water in the freeze crystallization, the changes in hydrogen-ion concentration must occur internally. As the pH value changes during the freezing processes were rather chaotic, it is speculated that the changes in pH might be related to decomposition of organic matter in the wastewater resulting in carbon dioxide release to the water. Based on the present study, no direct relationship between pH and purification efficiency could be found. Changes in pH and the factors causing such changes during the freezing process should be studied more comprehensively, because effluent whose pH deviates significantly from the recommended pH of 6.5 - 8.5 (Tchobanoglous et al., 2003) can not be discharged or recycled without neutralization.

The undercooling temperature and air flow velocity affected the rate of evaporation (or sublimation), g $h^{-1}m^{-2}$. The effect on evaporation of temperature alone was minor, but combined with air flow velocity, lower temperature increased the evaporation, as shown for instance in Fig. 10 with landfill leachate freezing tests. The determined amount of water evaporation/sublimation mass during the freezing tests varied from 7-15% of the formed ice mass. Hence, evaporation proved to be a significant factor in mass balance of the freeze purification process design and greater attention should be paid to evaporation in future natural freezing experiments.

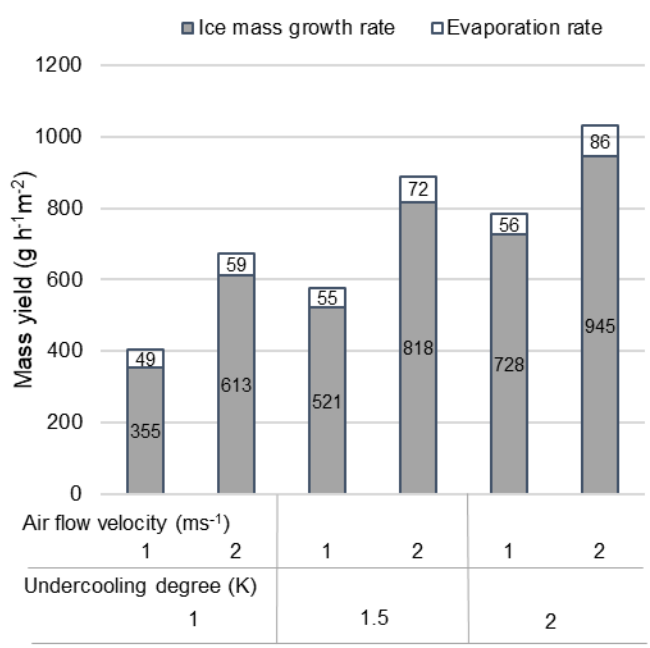


Fig. 10. Average evaporation rates (determined by mass loss measurements) and ice mass growth rates in landfill leachate freezing at undercooling temperatures 1, 1.5 and 2 K and air flow velocities 1 and 2 ms^{-1}.

Based on this study, natural freeze crystallization of wastewaters was found to be a rather complex process. Many parameters affect the system, which made precise control of process conditions challenging and led to unpredictability in the purification efficiency attained. The required effluent quality can be achieved by one-time natural freezing if the wastewater is frozen very slowly. However, low ice growth rates generally require a low temperature gradient, i.e. rather high freezing temperatures, and consequently, a very large freezing surface as well as long freezing time are needed to maintain sufficient ice mass production. Thus, considerable challenges could be faced in optimization of process design, i.e. when resolving the optimal freezing ratio and recycling of concentrated wastewater in the process. Consequently, multiple sequenced freezing processes are likely to be more efficient than simple one-time freezing. The results of ice mass production and purification efficiencies gained in this study are of importance in future studies when realistically evaluating the possible utilization of freeze separation techniques in wastewater purification. Freeze purification could be seen more as an alternative method to be used in conjunction with conventional treatment in purification of a very specific wastewater fraction or when reduction of the volume of wastewater is needed. Due to the (theoretically) non-selective nature of ice crystallization as regards the rejection of impurities, further research is still required on separation of specific fractions like microplastics and fibers.

4. Conclusions

In the present study, the ice growth rates and purification efficiencies of urban wastewaters subject to various freezing conditions (different temperature and air flow velocity) were determined. The research approach used enabled simple evaluation of the purity and mass production rate of ice in freeze purification of wastewaters. The ice growth rate was found to be clearly temperature-dependent, but air flow velocity also had a significant direct effect on ice growth. Temperature change of +1 °C caused the ice mass growth rate to increase by 300 g $h^{-1}m^{-2}$. 1 ms^{-1} increase in air flow velocity (at the same temperature) caused the ice mass growth rate to increase by 230 g $h^{-1}m^{-2}$. The influence of wastewater concentration on ice growth was found to be minor compared to the effect of temperature and air flow.

The hypothesis of the inverse effect of increased ice growth rate on water purification was shown to be valid also with wastewaters (as studied previously with salt solutions): higher purification efficiencies were obtained with lower ice growth rates. The highest purification efficiencies >95% (COD concentrations in ice <10 mg L^{-1}) were obtained with pretreated municipal wastewater and ice mass growth rate of <200 g $h^{-1}m^{-2}$ (at ~-1 °C and 0.5 ms^{-1}). With landfill leachate the highest COD separation efficiency 90% (~50 mg L^{-1}) was obtained with an ice mass growth rate of <400 g $h^{-1}m^{-2}$ (at ~-1 °C and 1 ms^{-1}) but the efficiency began to decrease as the growth rate increased. Nevertheless, natural freezing can be considered as a potential treatment method for wastewaters containing significant amounts of organic and inorganic matter. This outcome together with the findings for ice growth provide a good basis for further studies in the area of the freeze purification application design.

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Appendix A. Supplementary data

Supplementary data produced during this research can be found at https://...

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