Freeze concentration for enrichment of nutrients in yellow water from no-mix toilets

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Abstract Separately collected urine ("yellow water") can be utilized as fertilizer. In order to decrease storage volumes and energy consumption for yellow water transport to fields, enrichment of nutrients in yellow water has to be considered. Laboratory-scale batch freeze concentration of yellow water has been tested in ice-front freezing apparatus: a stirred vessel and a falling film freeze concentrator (coolant temperatures: –6 to –16°C). With progressing enrichment of the liquid concentrate, the frozen ice was increasingly contaminated with yellow water constituents (ammonia, total nitrogen, total phosphorus, TOC, and salts determined as conductivity). The higher the initial salinity of the yellow water and the lower the mechanical agitation of the liquid phase contacting the growing ice front, the more the frozen ice was contaminated. The results indicate, that in ice-front freezing devices multistage processes are necessary, i.e. the melted ice phase has to be purified (and the concentrates must be further enriched) in a second or even in a third stage. Energy consumption of this process is very high. However, technical scale suspension freeze concentration is reasonable in centralized ecological sanitation schemes if the population exceeds 0.5 million and distance of yellow water transportation to fields is more than 80 km.

Keywords Ecological sanitation; energy consumption; freeze concentration; nutrients; yellow water

Introduction

Compared to the "flush and discharge system" of conventional sanitation, ecological sanitation (i.e. separated collection and treatment of different flows of domestic wastewater) offers several advantages: besides converting faeces to valuable and nutrient-rich soil conditioner and at the same time preventing faecal pathogens from spreading into the aquatic environment (Gajurel *et al*., 2003), enabling simple treatment of greywater to yield a high quality for reuse (Gulyas *et al*., 2003), one of the main benefits of ecological sanitation is that separately collected urine (yellow water) contains the major part of fertilizer components of the domestic wastewater like nitrogen, phosphorus and potassium. The use of this fertilizer, which is very poor in heavy metals (Jönsson *et al*., 1999), is highly sustainable, because economically minable fossil potassium and phosphorus ressources are limited and synthesis of nitrogenous fertilizers requires high amounts of energy. Moreover, collecting yellow water separately and using it as fertilizer contributes to saving energy and activated sludge tank volume in municipal treatment plants, because yellow water is the predominant source of nitrogen in domestic wastewater.

If yellow water is used as fertilizer, enrichment of its constituents prior to transport to farmlands has to be taken into consideration with respect to saving transportation energy and storage volume in dense settlements (about 500 l of yellow water are generated per capita and year; Otterpohl, 2001). Potential separation processes for yellow water concentration are reverse osmosis, evaporation and freeze concentration. Especially for highly concentrated salt solutions like urine, reverse osmosis is highly energy-consuming due to high osmotic pressures which have to be overcome. Although modern vacuum evaporators

would consume less energy than freeze concentration, there might be some advantages of freeze concentration vs. vacuum evaporation for enrichment of yellow water: after some storage time urea decays yielding ammonia and hydrogen carbonate. As pH is rising during storage of urine, the generated gaseous ammonia, NH_3, is transferred to the gas phase during evaporation and thus lost from the concentrate. Moreover, during freeze concentration, the yellow water concentrates are kept at low temperatures preventing them from odour emissions.

Ban *et al.* (1999) have presented data about freezing and thawing of urine. After freezing the urine to a block, this block has been slowly melted, and the melted yellow water has been collected in fractions. In the first fraction, conductivity as well as total nitrogen and total phosphorus concentrations were highest, decreasing exponentially from fraction to fraction. This refers to increasing inclusion of yellow water constituents into the ice with progressing freezing.

In freeze concentration experiments performed for enrichment of trace organics in wastewaters for analysis, Baker (1970) has demonstrated, that decrease of mechanical agitation of the liquid concentrate as well as increase of salt concentration leads to enhanced trapping of solutes into the ice. This is due to sudden growth of ice dendrites at the ice/liquid interface with inclusions of highly enriched concentrate. A consequence is decreased purity of the frozen ice. As urine is a saline liquid, this study should clarify under which conditions freeze concentration could be a suitable process for concentrating nutrients in yellow water. Experiments have been performed in very simple ice-front freezing concentrators: a stirred vessel and a falling film freeze concentrator.

Materials and methods

Yellow water
Urine of several female and male individuals had been collected and mixed before the experiments. The mixtures have generally been used within one week after collection.

Freeze concentration
Laboratory-scale ice-front freezing batch experiments have been performed in a falling film and in a stirred vessel freeze concentrator (Figure 1, left) with walls cooled by means of a coolant ("Antifrogen N"/water 1:1) with temperatures kept constantly at –6 to –16°C by a cryostat. The falling film freeze concentrator consisted of a tube (height: 30 cm; inner diameter: 7 cm; surrounded by a cooling jacket) with a bottom containing an outlet tube. On the top of the freezing tube, a cylindrical vessel with a short inner Plexiglass tube (height: 6.5 cm) and an outer Plexiglass tube (height 10 cm) has been fixed. The inner Plexiglass tube acted as a weir. Over this weir, initial volumes of 900 to 2,000 ml yellow water were recirculated from the collection vessel under the concentrator by a geared pump (volume flow: 240 l/h) resulting in a falling film over the growing ice layer. The stirred vessel concentrator was a cylindric Plexiglass vessel (height: 26.5 cm; inner diameter: 7.8 cm) with a drain valve at the bottom for concentrate collection and a cooling jacket. Different types of stirrers (Figure 1, right) were tested; rotational speed has been varied between 130 and 500 rpm. Stirrers A to D were of stainless steel while stirrer E was formed from a thin metal foil. Processed volumes in the stirred vessel concentrator were between 530 and 750 ml.

Some stirred vessel experiments (stirrer E, 340 rpm) have been performed with "prefreezing" of deionized water: prior to freeze concentration of yellow water, the concentrator was filled with 700 ml deionized water. When about 100 ml of water have been frozen (after 0.5 h), the remaining liquid water was removed and its volume was determined. Then 600 ml yellow water precooled to 3°C were transferred to the concentrator with the prefrozen ice layer, and the process was continued. Parameters analyzed in the melted ice
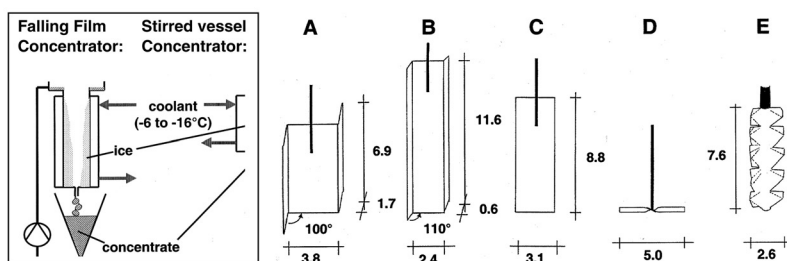
Figure 1 Left: laboratory scale falling film and stirred vessel freeze concentrators; right: types of stirrers investigated in the stirred vessel freeze concentrator; dimensions are given in cm

phases from pre-freezing experiments were corrected for the dilution factor caused by the pre-frozen deionized water. These experiments have not been interrupted by sampling. In the stirred vessel as well as in the falling film concentrator, also multi-stage experiments were run, i.e. several concentrates (as well as melted ice phases) of the prior stage were combined and subjected to another concentration step.

Analytical procedures

Volumes of original urine, concentrates and melted ice phases were determined by means of graduated cylinders (1,000 ml or 250 ml). Conductivity was measured with a conductometer (WTW LF 196) after equilibration of temperature to room temperature. Chemical analyses of yellow water samples were conducted after suitable dilution (up to 1:10,000). Ammonia and total phosphorus were analyzed by flow injection analysis, total nitrogen and TOC analyses in a "multi N/C 3000" TOC analyzer (analytik Jena AG) by incinerating the sample at 850°C (catalyst: CeO_2) according to German standard methods.

Data evaluation

"Theoretic concentration factor" (TCF) is the ratio of initial liquid volume to volume of concentrate, $V_o/V_{conc.}$. Efficiency of the process has been evaluated by analysis of conductivity, ammonia, total nitrogen, TOC, and in some cases of total phosphorus in the original urine, in the remaining liquid concentrates and in the melted ice. Ratio of concentration in concentrate, $c_{conc.}$, to concentration in original yellow water before freeze concentration, c_o, is termed "determined concentration factor" (DCF). Recoveries, R, of the different yellow water constituents were calculated by dividing DCF by TCF. Dependence of recoveries, R, on theoretic concentration factor, TCF, is assumed to be represented by Eq. (1) and was calculated from experimental data by linear regression.

$$R = a - b \cdot e^{-1/\text{TCF}} \qquad (1)$$

From regression lines (R, $e^{-1/\text{TCF}}$), conductivity recoveries for TCF = 1.5, $R_{cond.}$ (TCF = 1.5), were calculated for comparing experiments with different initial yellow water conductivities.

Results and discussion
Falling film concentrator

Due to urine constituents with detergent properties (proteins, bile acids), falling of the concentrate into the collecting vessel and pumping caused foaming of the yellow water. Recoveries of all parameters were exponentially decreasing with increasing TCF (Figure 2), indicating that the frozen ice contained some yellow water constituents.
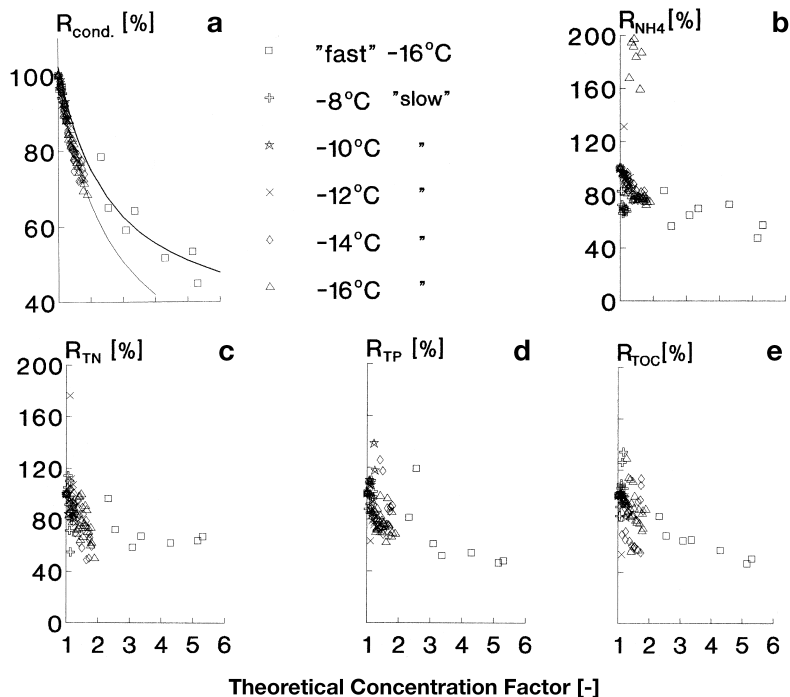
Figure 2 Recoveries R for conductivity (a), ammonia (b), total nitrogen (c), total phosphorus (d) and TOC concentrations (e) during freeze concentration in the falling film freeze concentrator

The most reliable results were obtained with conductivity while the chemical parameters showed high variances obviously due to improper analyses in the saline urine matrix. Especially ammonia data exhibited some extreme outliers, which might be caused by urea decay during the experiment or storage until analysis. Conductivity data in Figure 2 show that recovery was not affected by coolant temperature. The deterioration of recovery by frequent sampling during the falling film freezing concentration process ("slow" in Figure 2; "fast": only one sample has been taken at the end of the experiment for measuring recoveries) as shown with the reliable parameter conductivity, can be explained by interrupting the recirculation of the concentrate for sampling. Thus, the residual concentrate which could not escape from the freezing ice-front has been totally included into the ice. Figure 2 demonstrates that in the falling film concentrator with the chosen recirculation volume flow, a theoretical concentration factor of 5 decreases the recovery to about 50%! Therefore, yellow water freeze concentration in a falling film ice-front freezing device can only be applied as a multistage process without losing fertilizing nutrients to a high extent with the ice phase. These losses occur, because with high salt concentrations, the freezing ice front forms more dendritic structures leading to inclusion of yellow water constituents. In the investigated falling film freeze concentrator, TCF far above 5 could not be realized, because higher TCF would have led to complete blocking of the cooled tube by ice.

Stirred vessel concentrator

In Figure 3, recoveries for the parameter conductivity derived from different stirred vessel experiments performed with a coolant temperature of –16°C are shown. Stirrer C with 500 rpm delivered the most efficient recoveries, while stirrer E (with a smaller diameter) operated at lower speed (340 rpm) led to significantly worse conductivity recoveries. This indicates, that low mechanical agitation leads to decreased recoveries (lacking transport of yellow water constituents from the freezing ice front because of a relatively thick diffusion layer).
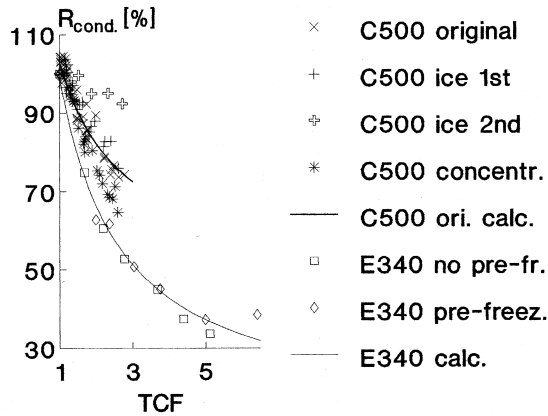
Figure 3 Recoveries for conductivity in stirred vessel freeze concentration experiments with a coolant temperature of –16°C employing stirrer C at 500 rpm (C500) and stirrer E at 340 rpm (E340); original: original yellow water; ice 1st and ice 2nd: melted ice from 1st and from 2nd stage, resp.; concentr.: concentrates of 1st and 2nd stage; pre-freez.: prior to actual freeze concentration of yellow water, about 100 ml of deionized water has been frozen as ice on to the walls

The data "C500" in Figure 3 show another influence: the C500 regression curve has been exclusively calculated for data obtained with original urine (symbols X). These data show some variance. But when the recoveries for original urine are compared with recoveries for concentrates (asterisks in Figure 3), it can be clearly stated that freeze concentration of concentrates leads to significantly lower recoveries (obviously caused by their higher salinity) than enrichment of original yellow water. More explicitly, freeze concentration of melted ice obtained from a second freeze concentration stage led to recoveries above 90% even at TCF = 3 (⊕ in Figure 3). According to results of Baker (1970), Figure 3 indicates that the ice is incorporating more yellow water constituents when the salinity of the source is high.

In the experiments with stirrer E and 340 rpm it was shown, that freezing of an ice layer from deionized water of about 0.3 cm ("E340 pre-freez." in Figure 3) prior to the actual freeze concentration of yellow water did not influence recoveries of conductivity (and also of TOC, ammonia, and total nitrogen; data not shown). This means that a better heat transfer at the start of the concentration process (when no ice layer has been formed yet), which might lead to a higher ice formation rate, did not result in detectable initial increase of dendritic ice growth (with the eventual consequence of enhanced inclusion of yellow water constituents into the ice).

Influence of initial salinity of yellow water on freeze concentration recoveries
In order to clarify the influence of salinity (represented by the parameter conductivity) on recoveries of yellow water freeze concentration, from all obtained curves $R_{cond.}$ = f(TCF) the characteristic recovery for a TCF of 1.5 has been calculated. These characteristic recoveries are given as a function of the initial conductivity of the processed liquid (original yellow water, concentrate, or melted ice) for the experiments with stirrer C at 500 rpm (Figure 4a), for all other stirrers and stirrer speeds (Figure 4b) and for all falling film experiments (Figure 4c). The data show a general decrease of the recoveries at TCF = 1.5 with increasing initial conductivities. Note, that the ordinates are not starting with zero, but with 70%. The data for the stirred vessel concentrator with stirrer C and 500 rpm show the most unambiguous dependence of recovery on initial salinity. An influence of coolant temperature cannot be detected from Figure 4a.

Results in Figure 4 are in accordance with findings of Baker (1970) who found decrease
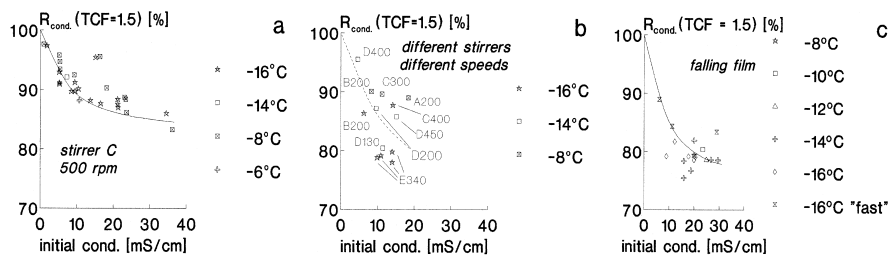
Figure 4 Dependence of conductivity recoveries for TCF = 1.5 on initial conductivity: a) stirred vessel freeze concentrator equipped with stirrer C (500 rpm); b) different stirrers, different stirrer speeds (letter: stirrer type in Figure 1; number: stirrer speed in rpm); c) falling film freeze concentrator

of m-cresol recoveries during freeze concentration of aqueous cresol solutions with increasing concentrations of phosphate buffer (10^{-4} to 10^{-1} mol/l). Figure 4b shows the most varying data, but there is also a decreasing trend of $R_{cond.}$ (TCF = 1.5) with increasing initial conductivity. Influence of initial conductivity is massively superimposed by hydraulic influences: for stirrer A even at a moderate speed of 200 rpm ("A200" in Figure 4b) the highest recovery for yellow waters with initial conductivities above 15 mS/cm was observed. Stirrer C led to a slightly lower recovery although initial conductivity was lower and the stirrer speed was twice as high (400 rpm; "C400" in Figure 4b). This can be explained by the smaller diameter of stirrer C (3.1 cm vs. 3.8 cm for stirrer A; see Figure 1). With a comparable initial conductivity, stirrer D caused an even lower recovery in spite of an even higher speed and a farout larger diameter of 5 cm ("D450" in Figure 4b). This is obviously caused by the lower mechanical energy input of this stirrer, because its height was very low compared to heights of the other tested stirrers. With a very low stirrer speed of 130 rpm, stirrer D led to a very low recovery ("D130"). This recovery was comparable to those obtained with stirrer E and 340 rpm ("E340"). The higher stirrer speed in the "E340" experiments compared to the "D130" experiment was obviously counteracted by the smaller diameter of stirrer E (2.6 cm). The stirrers B and D were probably not very different in terms of mechanical energy input into the liquid, although they had different shapes (compare data "B200" and "D200"). Figures 4a and 4b clearly indicate that in stirred vessel freeze concentrators with ice front freezing on cooled walls the mechanical energy input has to be sufficiently high to reach optimum recoveries of yellow water constituents in the concentrate.

In the falling film concentrator, recoveries for a TCF of 1.5 (Figure 4c) were significantly lower than in the stirred vessel concentrator with stirrer C at 500 rpm. This indicates that mechanical energy input can be increased to a greater extent in the stirred vessel concentrator. The variance of data in Figure 4c might be caused by different sampling frequencies and by slight deviations of pump velocity as well as by eventual differences in flow velocities of different yellow waters (different contents in detergents like bile acids which might lead to different degrees of foaming affecting the flow of the yellow water film upon the freezing ice).

Multi-stage experiments

Three-stage experiments (further concentration of obtained concentrates and further purification of melted ice in two additional stages) e.g. in the stirred vessel freeze concentrator (−16°C) generated relatively pure ice phases (cond.: 0.27 mS/cm; ammonia: 27 mg NH_4-N/l: TN: 72 mg/l; TOC: 35 mg/l) as well as highly enriched concentrates (cond.: 55.9 mS/cm; ammonia: 5,400 mg NH_4-N/l; TN: 16,600 mg/l; TOC: 34,700 mg/l). Compared to original urine, concentrations in three-stage concentrates were about 4 times higher.

Energetic aspects of urine freeze concentration

In this study, energy consumption calculated for an annual yellow water excretion of 500 l per capita for the small-scale freeze concentrators was about 600 kWh/(cap·a) for a one-stage process due to the very small units (falling film, –16°C, TCF ≈ 5). The concentrators were not at all optimized concerning heat transfer and insulation. Technical-scale freeze concentrators consume less energy the higher their dewatering capacity is: for the NIRO freeze concentrator "W33" with a capacity of 250 l/h, the specific energy consumption is given as 244 kWh per m^3 of water removed from the original aqueous solution, whereas a NIRO freeze concentration plant with a dewatering capacity of 25,000 l/h only requires 30 kWh per m^3 (NIRO Process Technology, 1992). A commercial freeze concentration plant with a dewatering capacity of 250 l/h can serve a community of 5,840 inhabitants for concentrating their yellow water fourfold, and the large concentrator type is suitable for a population of 584,000 people. In NIRO freeze concentrators, decrease of recoveries for yellow water constituents with increasing enrichment will not be as drastic as in ice-front freezing concentrators (Klomp, personal communication).

In Table 1, energy consumption for three different scenarios of yellow water handling is compared: conventional sanitation (without urine separation), ecological sanitation (i.e. separation of yellow water and its utilization as fertilizer), and ecological sanitation with centralized freeze concentration of separately collected yellow water in order to reduce transportation energy. These scenarios are calculated for a community of 5,840 inhabitants (to be served by the "W33" freeze concentrator) as well as for a community of 584,000 inhabitants (largest commercially available freeze concentrator is suitable). Table 1 is based on the following rough assumptions: 1st, the municipal treatment plant is equipped with efficient aerators consuming about 12 kWh per capita and year (Dichtl *et al.*, 1991); 2nd, yellow water separation and its use as fertilizer avoids nitrification/denitrification in the municipal treatment plant saving about 50% of the aeration energy; 3rd, modern natural gas based ammonia plants require about 34.5 GJ per ton NH$_3$-N fixed (Kongshaug, 1998) which can be substituted by a certain yellow water equivalent (2.72 kg nitrogen are excreted per capita and year with yellow water; Otterpohl, 2001); 4th, yellow water or its fourfold concentrate, resp., is transported for 20 km with a tank lorry (maximum loading capacity 15.3 t, 100% loaded for one way, no load way back) consuming 28.1 g diesel per ton load and km (Kaltschmitt and Reinhardt, 1997) which is equivalent to 0.307 kWh.

Ecological sanitation without freeze concentration requires less energy (Table 1) than conventional sanitation (with activated sludge treatment), because a high amount of energy is saved in ecological sanitation due to substitution of synthetic nitrogenous fertilizer by yellow water. Freeze concentration does not contribute greatly to compensation of yellow water transportation energy, because under the assumed conditions, freeze concentration in the smallest commercially available unit needs about 30 times more energy than transport of non-concentrated urine (in the largest available freeze concentrator scale about 4 times)! However, in large centralized systems with separate urine collection, the ecological sanitation scenario combined with freeze concentration will consume less energy than the conventional sanitation scheme. If yellow water has to be transported for a distance of more

Table 1 Estimated annual per capita energy consumption related to yellow water management in conventional and ecological sanitation with and without freeze concentration (for details, see text)

Scenario	Annual specific energy consumption [kWh/(cap·a)]	
	5,840 inhabitants	584,000 inhabitants
Conventional sanitation	38.1	38.1
Ecol. sanit. without freeze concn.	9.1	9.1
Ecol. sanit. with freeze concn.	98.3	17.3

than 75 km, large freeze concentration units will lead to a significant saving of transportation energy. Although the energy consumption of around 600 kWh per capita and year by small-scale freeze concentrators investigated in this study was comparably high, a viable option for decentralized freeze concentration in small ice-front freezing devices might be their use for enrichment of separately collected yellow water in arctic regions where cold can be purchased without additional energy consumption.

Conclusions

Freeze concentration is generally suitable for enrichment of nutrients in yellow water, avoiding odour problems and ammonia losses. Concerning energy consumption, commercially available suspension freeze concentrators can be operated in a sustainable way only in centralized yellow water collection systems serving a community of more than half a million inhabitants. However, freeze concentration is only energy-saving in such a scheme, if yellow water has to be transported to fields (where it is used as fertilizer) that are more than 75 km away from the yellow water collection facility. For smaller distances, transportation consumes less energy than freeze concentration. The small ice-front freezing devices investigated in this study are expected to be used in decentralized urine collection scenarios exclusively in arctic regions, where cold is available without additional energy consumption. The stirred vessel concentrator is more advantageous than the falling film concentrator, because it can be equipped with powerful stirrers leading to better recoveries of yellow water constituents than in the falling film apparatus.

Acknowledgements

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