Treatment of textile wastewaters using Eutectic Freeze Crystallization

D. G. Randall, C. Zinn and A. E. Lewis

ABSTRACT

A water treatment process needs to recover both water and other useful products if the process is to be viewed as being financially and environmentally sustainable. Eutectic Freeze Crystallization (EFC) is one such sustainable water treatment process that is able to produce both pure ice (water) and pure salt(s) by operating at a specific temperature. The use of EFC for the treatment of water is particularly useful in the textile industry because ice crystallization excludes all impurities from the recovered water, including dyes. Also, EFC can produce various salts with the intention of reusing these salts in the process. This study investigated the feasibility of EFC as a treatment method for textile industry wastewaters. The results showed that EFC can be used to convert 95% of the wastewater stream to pure ice (98% purity) and sodium sulfate.

Key words | Eutectic Freeze Crystallization, freeze desalination, industrial wastewater, sodium sulfate removal, textile wastewater, water treatment

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INTRODUCTION

The conventional approach to wastewater treatment has been to focus on the water recovery and to remove the contaminants as a manageable waste. However, this approach is rapidly becoming outdated. The new approach is to ensure that wastewater treatment recovers both water and useful products in a financially and environmentally sustainable manner. In addition, the advantages of such an approach are far reaching, having benefits to the environment as well as to the general population. For example, a report from the Green Economy Initiative (Corcoran *et al.* 2010) states that the payback (health, societal and environmental benefits) for every dollar invested in water treatment is between US$3 and US$34.

The textile industry is a sector of high water consumption (Lin & Chen 1997) and the ability to treat wastewaters from this industry more effectively than at present would be beneficial in alleviating water shortages since more water will be available for other uses. The wastewaters from the textile industry are a major source of pollution because of the high concentrations of inorganic and organic chemicals, including residual dyestuffs (Badani *et al.* 2005). The specifics of the chemicals in these wastewaters differ from each producer; however, they all consist of salts, dyes and various other chemical compounds that are used to help with dyeing of the textiles.

Many technologies are currently being used (or are under development) to treat textile wastewaters. Technologies from physico-chemical means, oxidation (including the Fenton reaction and ozone oxidation), adsorption and membrane separation processes to biological methods are being used for treating textile wastewaters. The review paper by Robinson *et al.* (2001) describes these processes in detail. However, these processes usually fail to recover the dissolved salt. The textile industry uses various dyes and salts. The salts are dissolved in the wastewater and can damage the ecosystems into which the wastewater stream is released. The dyes in the effluents are often organic and are very difficult to treat (Babu *et al.* 2007).

Eutectic Freeze Crystallization (EFC) is an attractive water treatment technique that is able to treat wastewater and produce pure water and saleable salt products, thus fitting in with the philosophy of recovery of both water and value from wastewaters. The EFC technique is based on the fact that, when a solution is cooled to its eutectic temperature, ice and salt begin to crystallize as two discrete solid phases. These solid phases can then be separated as a result of their density differences (Van der Ham *et al.* 1999) – thus offering a unique water treatment option.

Randall *et al.* (2011) showed that EFC could be used to treat a mining wastewater rich in sodium sulfate, and

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demonstrated that a brine could be decreased by as much as 96% and that pure calcium sulfate (98% purity with no washing), pure sodium sulfate (96% purity with no washing) and ice (of potable quality) could be produced by EFC.

This paper investigated the feasibility of using EFC to treat an industrial textile stream for the recovery of water and salts.

METHODS

All the experiments carried out in the study were conducted using an industrial wastewater from a textile plant in Cape Town, South Africa.

Solution preparation

The textile wastewater was filtered through cellulose filter paper with a pore size of 110 μm before being used in the experiments. This was done to remove all solid particles from the solution, which otherwise would add to the impurities in the samples taken. The wastewater was also analyzed for sodium using atomic absorption spectroscopy (AAS).

Experimental setup

The experiments were conducted in a jacketed 1.5 L crystallizer. The crystallizer was cooled using Kryo 40 which was circulated through the jacket using an MRC BL-30 thermostatic unit. The temperature of the solution in the crystallizer was monitored using a Testo 174/144 temperature logger. The solution was stirred using a six-bladed pitch-blade stirrer set at a stirrer speed of 350 rpm. The apparatus, excluding the thermostatic unit, was placed inside a temperature-controlled room set at 0 °C. The filtration of the solid products obtained from the experiments was conducted inside the temperature-controlled room. A Buchner funnel, connected to a 1 L filtration flask, was used to filter out the crystals from the crystallizer. Filter paper of pore size 110 μm was used to filter out the ice product. A 300 mL Millipore glass funnel with cellulose filter paper of 0.45 μm pore size was used to filter out the salt product from the crystallizer.

Experimental procedure

A cascading concentrating procedure was adopted for this study and is shown in Figure 1. This concentrating

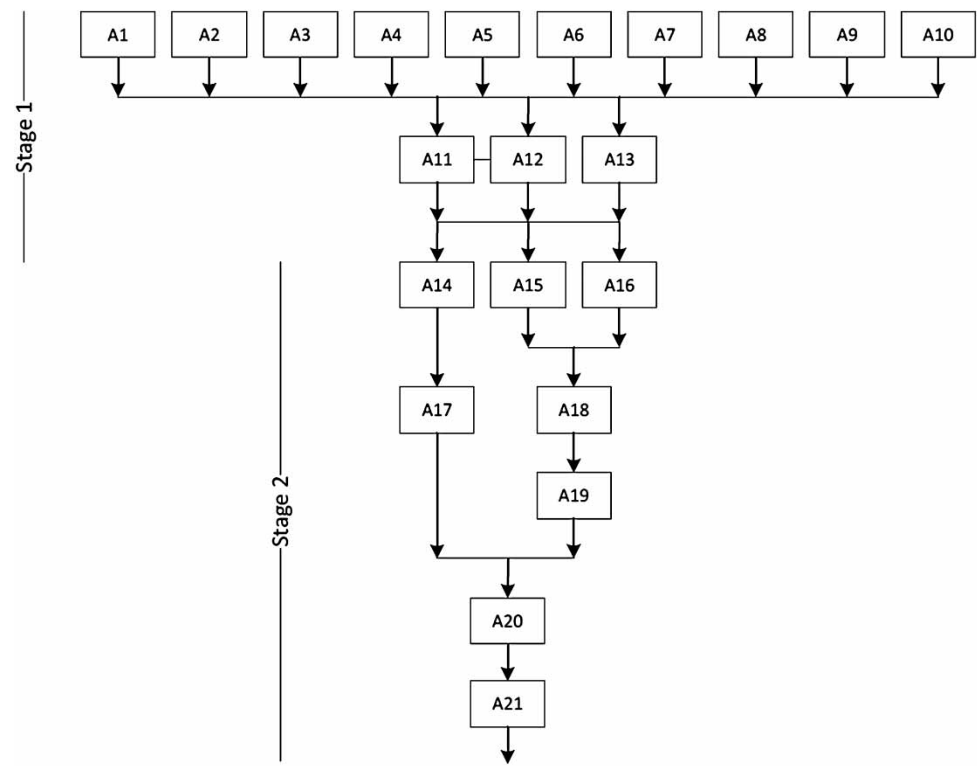

Figure 1 | Cascading concentrating procedure for textile wastewater.

procedure is based on the method outlined by Baker (1967) and utilised for the treatment of mine wastewater by Randall et al. (2011).

For each of the experiments denoted A1–A10 in Stage 1, approximately 1,000 g of solution was added to a crystallizer. This meant that the total feed for the study was 10,000 g. Initially, the crystallizer was maintained at a set temperature of 5 °C below the crystallization temperature of ice. Thus, if ice formed at −1.9 °C, the thermostatic unit was set to −6.9 °C. The temperature of the room was maintained at the same temperature at which the ice formed. The temperature logging started when the solution was added to the crystallizer. The stirrer was turned on after the addition of the solution to the crystallizer. Seed crystals of ice, approximately 1 g, were added to the solution in all experiments once the system was at the temperature at which ice would form. Experiments A1–A10 were run for 30 min after the addition of ice seed crystals, while experiments A11–A21 were run for 20 min. For experiments A14–A21, both ice and salt seeds were added to the crystallizer at the same time.

For experiments in which only ice formed (experiments A1–A13), the contents of the crystallizer were filtered under vacuum for 5 min. When both ice and salt formed (A14–A21), the stirrer was switched off and replaced with a paddle impeller. The impeller was then placed into the solution and set to stirring speed of 85 rpm for 10 min. This promoted the separation of the salt and ice particles. The ice was then collected off the top of the solution, filtered and weighed. The remaining solution, which contained solid salt, was then filtered and the mass noted. Samples of the melted ice and the filtrate were collected from each experiment and their sodium content analyzed using AAS.

For the ice washing, 100 g of deionized water, kept at 1 °C, was added to the ice product and then filtered for 5 min using a Buchner funnel. The ice was weighed again to determine the loss due to washing. After each wash, samples were taken for color hazen analysis using a Merck Nova 60 Spectroquant. The color change from sample to sample was used to determine the relative purity of the solution after each wash. The samples were also analyzed for sodium content by AAS. The ice product was washed four times in total.

RESULTS AND DISCUSSION

The composition of textile wastewater used in the study is given in Table 1. The stream had a high pH of 10.31 and is significantly concentrated (total dissolved solids (TDS) = 50.55 g/L) compared to mining wastewater streams on which EFC has been applied, which typically have a TDS of 30 g/L (Randall et al. 2011). As expected, the major salt in the stream was sodium sulfate at a concentration of 6.13 g/L.

Table 1 | Dye solution analysis

	Value	Units
pH	10.31	–
Conductivity	71.15	mS/cm
Total dissolved solids	50.55	g/L
Na_2SO_4	6.13	g/L
Temperature of measurement	20.15	°C

Figure 2 shows a mass balance for the treatment of the textile wastewater using EFC. The sizes of the stages and arrows indicate the masses for each stream. The first stage of the process was a concentration step, where a significant amount of ice was formed (70% of the feed). No salt was formed during this step, since the stream had not reached a concentration where sodium sulfate could form simultaneously with ice.

In stage 2, sodium sulfate began to form along with ice, indicating eutectic conditions had been reached. A further 951 g of ice formed in stage 2 bringing the total amount of ice formed in the process to 7,983 g. The eutectic temperature (the temperature at which both ice and salt first start to form) for this wastewater was −3.9 °C, which is lower than the binary eutectic temperature for sodium sulfate solution (−1.2 °C) thus indicating that the presence of dye components had a significant effect on the eutectic temperature of a wastewater. The amount of $Na_2SO_4 \cdot 10H_2O$ formed in stage 2 was 43 g (or 19 g Na_2SO_4 anhydrous). Considering the feed had a concentration of 6.13 g/L anhydrous sodium sulfate (see Table 1), the yield of sodium sulfate for these experiments amounted to approximately 30%. The yield of salt could have been significantly higher if the stream had been further concentrated. However, the volume of the crystallizer (1.5 L) limited the amount of solution that could be used in an experiment to approximately 500 mL. Furthermore, the focus of the study was not to improve the yield of salt, but to demonstrate that EFC could be used to treat textile wastewater. Future work will focus on improving the process and investigating continuous EFC.

The application of EFC to the treatment of a textile wastewater resulted in a 95% reduction of the wastewater to ice and salt, with the majority of the products being ice. The ice produced during the EFC process was initially impure because of mother liquid entrainment on the

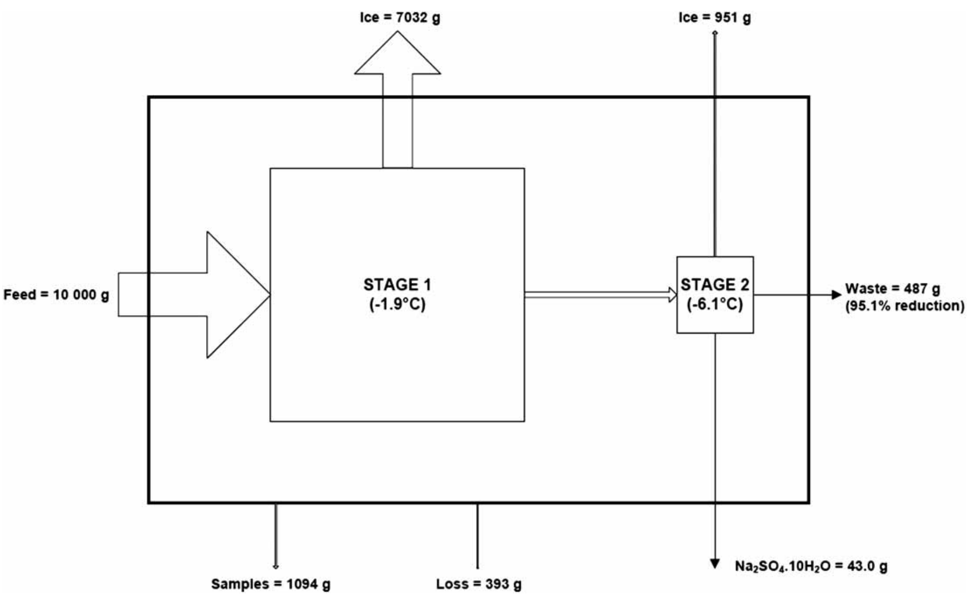

Figure 2 | Mass balance for the treatment of a textile wastewater using EFC.

surfaces of the ice crystals. In order to remove this mother liquid entrainment, the ice crystals had to be washed with water kept at 0 °C in order to also minimise losses during the washing process.

Figure 3 shows the purity of the ice formed during EFC as a function of washing. Initially, the melted ice product was only 54% pure (relative to pure water). However, after one wash with water the relative purity of ice increased to 89 and 99% after four washes, showing that although the purity of the ice product was initially very low, washing can be used to improve the purity to acceptable standards. The loss of ice during each wash was marginal (<4%). This is in line with similar work conducted by Conlon (1992) which showed that pure ice (water) could be produced from a water stream contaminated with food colorant. Halde (1980) also showed that pure water could be produced from a waste stream by crystallizing ice.

Ultrafiltration (UF) has been shown to be an effective pre-treatment method for a textile wastewater (Fersi & Dhahbi 2008). The integration of UF, reverse osmosis (RO) and EFC could offer a hybrid treatment process. RO could be used to concentrate the feed to the EFC unit process, to a point where salt and ice can form. The ice product formed in the EFC section could be recycled to the RO unit for further treatment. This hybrid UF–RO–EFC process could offer a cost-effective, integrated textile wastewater stream and is conceptually shown in Figure 4.

In terms of energy savings, Table 2 shows that EFC offers significant energy savings when compared to multiple-effect evaporative crystallization, thus showing that the proposed process demonstrated in this paper will likely be cheaper than an evaporative crystallization process.

An economic analysis for an EFC process presented by Van der Merwe (2011) estimated that the operating costs are approximately USD1.42/m^3 of recovered water for a full-scale, 100 m^3/h EFC plant (adjusted for inflation and based on March 2012 figures). This cost did not take into account the profit that could be made from the sale of the salt(s) or water.

A detailed economic analysis of EFC, compared to conventional textile wastewater treatment technologies, has not been conducted, as it is beyond the scope of this paper. The cost estimation of USD1.42/m^3 of recovered water could be considered high, but EFC is a new technology and still has room for improvement, while most of the conventional treatment processes have little or no room for improved efficiencies and resultant reductions in operating costs. In addition, EFC can recover both pure salts and pure water, which can be reused in the process, thus reducing the cost of raw material. Most conventional textile wastewater treatment processes do not recover salts.

CONCLUSIONS

This study demonstrated that EFC can be used to treat a textile wastewater. A 95% conversion of the wastewater to ice and sodium sulfate was achieved. The relative purity of the ice

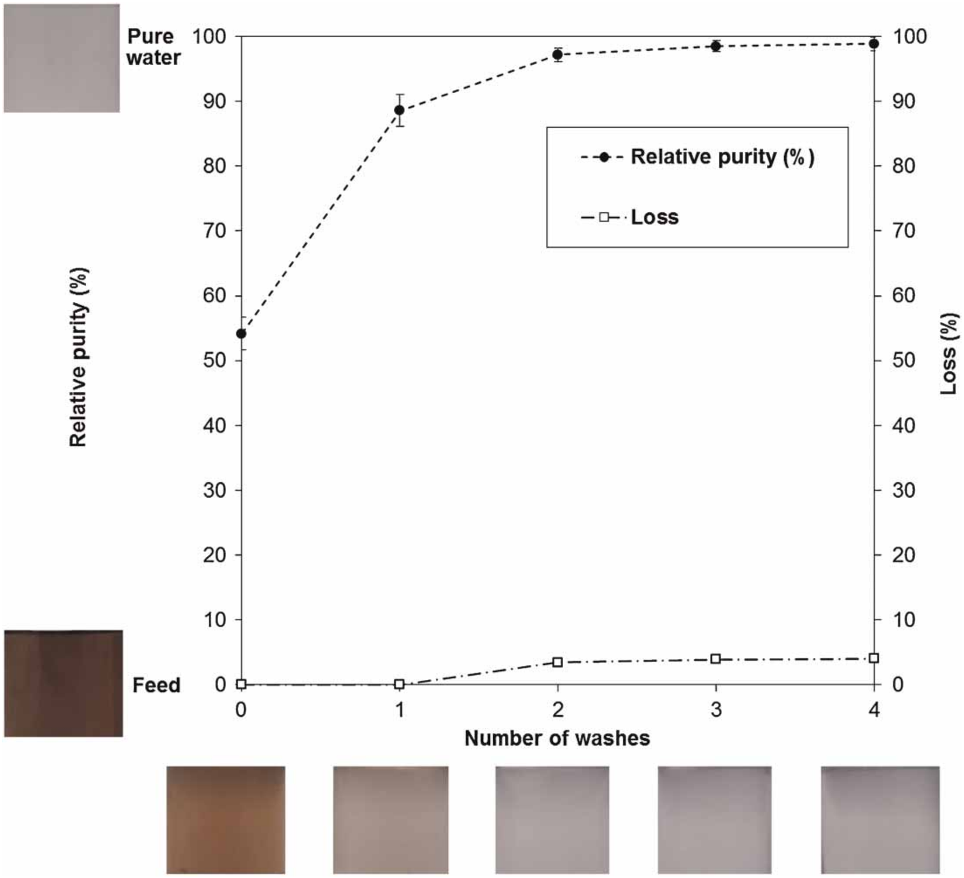

Figure 3 | Purity of ice product as a function of washing.

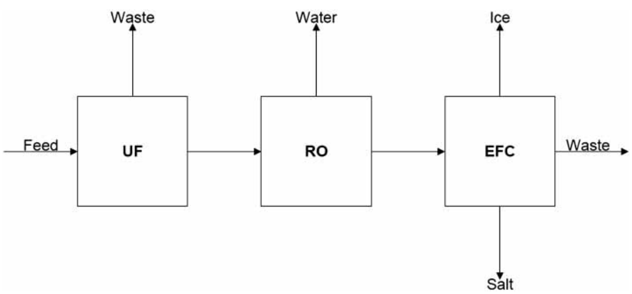

Figure 4 | The hybrid UF–RO–EFC process for the treatment of textile wastewater.

Table 2 | Energy savings for different systems as compared to evaporative crystallization

System	Energy savings (%)	Reference
$CuSO_4 \cdot 5H_2O$	70	Vaessen (2003)
KNO_3–HNO_3	69	Van der Ham (1999)
$MgSO_4 \cdot 11H_2O$	60	Himawan (2005)
Na_2SO_4 brine	80	Nathoo *et al.* (2009)
NaCl brine	85	Nathoo *et al.* (2009)

product was 98% after four washes with deionized water. The yield of sodium sulfate was 30%, but this could be improved by concentrating the wastewater. The results show that EFC offers a new alternative, more sustainable water treatment option for textile wastewater because it can convert the waste to useable products. The integration of EFC with RO might offer even better results. The initial cost estimation indicated that EFC is more expensive than conventional textile wastewater treatment technologies in terms of capital expenditure, but this comparison does not consider the fact that EFC can be used to recover pure salts and pure water which can be reused or sold, thus defraying the operating costs. Finally, it is expected that hybrid processes will be highly competitive for the treatment of textile wastewaters.

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