University of Alberta

Wastewater Toxicity Reduction by the Spraying with Partial Freezing Technique

by

Mohammad Rashedeen Habib ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of

Master of Science

in

Environmental Engineering

Department of Civil and Environmental Engineering

Edmonton, Alberta

Spring 2005

0-494-08070-1

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN:
Our file Notre reterence
ISBN:

NOTICE:
The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:
L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ABSTRACT

The objective of this research was to investigate the toxicity reduction efficiency of industrial wastewater by spraying with partial freezing technique. Before conducting the spray freezing experiments, wastewaters were partially frozen in beakers to observe the effects of freezing temperatures, dilutions and stirring. Full strength and diluted (1:10) pulp mill effluent and refinery wastewater were partially frozen (70%) at two different temperatures, with or without stirring. Ice and liquid samples were analysed for impurity and toxicity reduction. A range of 45% to 95% of the impurities (TOC, COD and color) were removed from the wastewaters, which produced ice samples with no toxicity. Freezing temperatures, dilutions and stirring had significant effect on impurity separation. Partial freezing in beakers showed higher separation efficiency for diluted wastewater with stirring at warmer freezing temperatures.

Spraying with partial freezing was conducted inside a freezer where pre-cooled pulp mill effluent, refinery wastewater, linoleic acid and abietic acid solutions were pumped and sprayed through a nozzle at two different temperatures which produced approximately 70% ice and 30% runoff. The ice samples were relatively pure and the runoffs contained more impurities. The ice samples were stored at the spray temperatures for two different periods of time, and later melted. Meltwaters were sequentially collected and analysed to see the toxicity reduction and the variations of impurity concentrations. Initial meltwaters were found to be more concentrated with impurities and the longer storage time showed a positive impact on impurity removal by the meltwater. A range of 55% to 90% of the impurity concentrations was removed from the final 50% of the meltwaters which were toxic to a lesser extent or non-toxic. From the correlations of

toxicity with impurity concentrations it was found that the toxicity reduced with the reduction of impurity concentrations. It was also observed that the warmer spray freezing temperature and longer ice storage time improved the impurity separation efficiency.

Scanning electron microscopy images of the ice samples were taken to observe the ice crystal structure and the impurity distributions on the surface of the ice. Differences were observed in the impurity distributions of the ice samples for different spray temperatures and storage times. Impurities on the ice surfaces seemed to be more concentrated for longer storage time. For the ice samples produced at the colder temperatures, impurity layers looked more fragile and dendritic effects of ice crystals were observed.

ACKNOWLEDGEMENTS

I would like to thank my supervisors, Dr. Daniel W. Smith and Dr. Wa Gao for their valuable guidance, encouragement, patience, time and support throughout the course of the research.

I also would like to extend my great appreciations and thanks to Maria Demeter and Nick Chernuka for their total support and assistance for the experimental setup and the laboratory work. I am indebted to their help and cooperation. I also express my gratitude to Mr. George Braybrook for helping out with SEM images.

Finally, I would like to thank my wife Shurovi and my parents for their endless love and support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

For the industries in cold regions, it is important to find an effective wastewater treatment method that is as economic as possible. The technical and economical efficiency of conventional methods of wastewater treatment in cold regions are restricted due to cold weather. It could be the best to make use of the cold weather for the treatment of wastewater.

For years, scientists tried to separate dissolved impurities from the water by freezing and to improve the efficiency of the separation. The use of freezing is based on the fact that, when an ice crystal grows during freezing of an aqueous solution, it is built up by pure water, leaving the solutes concentrated in the remaining liquid phase. So if an aqueous solution is partially frozen, a greater part of the impurities concentrate in liquid phase and a relatively pure ice is found. This process is advantageous as it is a physical separation process, suitable to remove any kind of soluble impurities with a large range of concentration and it is energetically competitive with evaporation processes because of the latent heats ($E_{freezing} = 330$ kJ/kg, $E_{evaporation} = 2200$ kJ/kg). Also, toxic compounds that are difficult to treat can be separated from the water by the freezing technique.

Large scale application of the mechanical freezing process for treatment facilities was never implemented because it is difficult to handle large amount of ice and the freezing of large amount of wastewater may take a long time. On the other hand, the spray freezing technique, making use of natural conditions, to treat wastewater is a potential technique in the cold regions, since it is advantageous over other freezing techniques due to the accelerated freezing process, simple operation and low capital and operating cost.

When water is sprayed at cold temperatures, it breaks up into a large number of very small drops with a large surface area per volume. It enhances the heat transfer and ice formation rate. This process takes advantage of the air's low temperature to freeze pure water and concentrate the impurities. The unfrozen water during the spray freezing process can be used to carry the impurities away. When the temperature rises in spring, most of the impurities that are in the ice mound are discharged with the initial melt water from the ice, leaving a relatively clearer ice behind.

This research project used the partial freezing and spray freezing technique to investigate the effectiveness of wastewater impurity and toxicity reduction. Both industrial wastewaters (pulp mill effluent and refinery wastewater) and synthetic wastewaters (linoleic acid and abietic acid) were used for the study. The purpose of this project was to find out the efficiency of toxicity reduction, along with other impurities such as of total organic carbon (TOC), chemical oxygen demand (COD) and color, by partial and spray freezing and to find the correlation of toxicity with other impurity concentrations. The factors affecting the impurity reduction efficiency of partial freezing and spray freezing technique were investigated. For partial freezing in beakers, the effects of freezing temperatures, stirring and dilutions of wastewaters were investigated and for spray freezing and melting, the effects of spray freezing temperatures, ice storage time and the dilutions of wastewaters were investigated. The differences in impurity separation efficiency due to the nature of the wastewaters were also investigated.

The impurity distribution within the ice columns, produced from the pulp mill effluent by spray freezing, was examined by scanning electron microscopy for a better understanding of impurity removal from the ice column by melt water. The effects of the temperatures and duration of ice storage on the impurity distributions within the ice columns produced from the pulp mill effluent were also investigated.

2. LITERATURE REVIEW

2.1. Partial Freezing Experiment:

During the process of ice formation in an aqueous solution, ice crystals grow with the pure water and reject the impurities dissolved in the water and concentrate the impurities in the unfrozen liquid part of the solution. This process of separation of the dissolved impurities is called the freeze concentration (Rodriguez *et. al.*, 2000).

Impurities are physically rejected from the ice crystal structures and concentrated in the liquid portion during the freezing process. If the solubility of the impurities are concerned, it is higher in the liquid phase than in the solid phase. So when the freezing occurs, the freezing of solutions which contain dissolved impurities causes the enrichment of the liquid phase with impurities and purification of the solid phase which is the ice (Burton *et al.*, 1953). During the freezing of a liquid, the impurities can be repelled and swept along by the solid-liquid interface (Azauni *et al.*, 1997).

Chalmers (1959) described the formation of ice as the ice crystals growing from the addition of water molecules to its structure, as the bricks are added to the construction of walls. The structure of ice crystals was found to have great regularity and symmetry. Because of this highly organized structure of ice structure when the impurities in water come in contact with the growing ice crystal, the impurity molecules are rejected and water molecules were favoured. So the ice crystals normally grow of pure water molecules unless any severe internal strain occurs.

The initial use of freeze concentration technique was in analytical chemistry to concentrate organic compounds. In 1961, as a laboratory method, Shapiro (1961) first applied freeze concentration technique to concentrate organic compounds.

Baker (1967a, b, 1969, 1970) carried out some important works in freeze concentration. The author used the freeze concentration technique as a pre-analytical method to concentrate trace organic compounds (alcohol, phenol and acid) in order to increase analytic device efficiency. The author showed that all compounds remained in the liquid phase, whether single compound or mixture of compounds were involved.

Rodriguez *et. al.* (2000) conducted an experimental study to compare freeze concentration with reverse osmosis for the removal of valeric acid from wastewaters. They determined the conditions for the optimum performance for freeze concentration to be -10 °C of subcooling temperature and 1012 kg/h of feed flow. Refrigerant temperature actually did not affect the amount of acid entrapped in the ice, but it influenced the ice formation rate and their experimental setup was limited to the minimum attainable temperature of -10 °C. Their economic analysis revealed that the high energy consumption by freeze concentration could be compensated by the high costs of membrane replacement in reverse osmosis.

Lorain *et. al.* (2001), from their laboratory experiments with synthetic and industrial wastewater, achieved separation efficiency, in most cases, close to 100%. They defined freezing ratio as the ratio of the volume of the solid phase after melting and the initial volume of the sample. Regardless of the nature of the pollutants, separation efficiency was close to 100% for the freezing ratio up to 80%. They found that higher concentration of wastewater induced pollution of the solid ice.

Chou and Tsren (2000) conducted an in-situ freezing and melting process as a wastewater treatment method, which utilized the ice formation of a falling film on a vertical wall of an ice former. Three experimental conditions on the outer wall surface, which included pre-existing and no pre-existing nucleus of crystallization and the affixed fiber grid, were tested to investigate their effect on the amount of ice formation, the degree of purification, and the overall heat-transfer coefficient. They found that the maximum values of both the amount of ice formation and the degree of purification could be achieved by varying the Reynolds number of wastewater. The lower inlet temperature of wastewater or coolant increased the amount of ice formation but decreased the degree of purification, whereas, pre-existing nucleus of crystallization showed positive effect for both cases. When the wastewater is able to wet the outer surface of the wall thoroughly, affixing fiber grids to the surface will cause unfavourable effects on the degree of purification.

A moving solid-liquid interface appears when freezing of an aqueous solution takes place. For a slow ice growth velocity, particles of nearly all materials are rejected by a moving solid liquid interface (Hoekstra and Miller, 1967). Ice growth velocity is dependent of the freezing rate which can be slowed down by increasing the freezing temperature.

As the ice crystals grow they repel the impurities from the ice crystal structures and the repulsion rate can be improved by stirring the liquid phase in order to avoid the accumulation of impurities at the solid-liquid interface (Gay *et. al.*, 2003).

Production of low-purity ice crystals is one of the reasons that restrict the industrial application of freeze concentration process for wastewater treatment (Shirai *et.*

al., 1998). Low-purity ice crystals reduce the separation efficiency of freeze concentration process, resulting in poor wastewater treatment. Shirai *et. al.* (1998) investigated the conditions of producing an ice layer with high purity. They used water with polypepton concentration of 2000 mg/L to 10,000 mg/L, corresponding to 670 mg/L to 3800 mg/L in chemical oxygen demand (COD), to produce an ice layer on an aluminium plate heat exchanger. Higher purity of ice was observed at higher flow rate, resulting in 10 to 30 mg/L in COD at the superficial flow rate of 0.3 m/s regardless of initial COD levels. The coolant temperature had little effect in producing an ice layer with high purity. They also found that the lower the initial temperature of the wastewater, the lower the purity of melted ice.

Studies showed that with the application of stirring, purification rates can be improved up to 99.97% (Gay *et. al.*, 2003). Gay *et. al's* studies were conducted with samples of dilute Na-montmorillonite suspensions charged with zinc or lead which was placed inside a cylindrical annulus and was cooled at a controlled temperature around -7 °C at its inner wall. The inner wall rotated around a vertical axis. The freezing front propagated toward the still outer wall which was maintained at a constant temperature around +1 °C. The studies also demonstrated that the combination of radial freezing and stirring produced a residual concentration of drinking water standards.

Another study by Iwai *et. al.* (1999) showed that an applied electric field can enhance the reduction of the impurity concentration in solid phase during freezing. They applied a D.C. electric field parallel to the solid-liquid interface during normal freezing solidification of 3, 5-xylenol and naphthalene system. The concentration of naphthalene in solid 3, 5-xylenol was less with an applied voltage of 1800 V and electric field strength of 6000 V/cm, than that without any applied electric filed. They concluded that the enhancement in reduction might be due to the turbulence induced by the electric field in the liquid phase during freezing.

Inorganic impurities can affect the separation efficiency for organic impurities. Some previous studies showed that the separation efficiency of freeze concentration process for organic impurities decreased if the inorganic compounds were present in the sample. The study of Workman and Reynold (1949) concluded that the plane ice front became dendritic because of the ice surface polarization by the inorganic compounds and it increased the probability of the inclusion of liquid slugs in the ice crystals. Same conclusion can be drawn from the work of Islam and Hemond (1991), where they tried to concentrate soluble compounds in tap waters. But their recovery rate was not as high as Baker's (1970), probably due to the presence of inorganic compounds in the tap water.

Extensive work on freeze concentration to understand the mechanism of impurity rejection of ice crystals during freezing and the factors which can improve the impurity separation efficiency of partial freezing has been found in the literature. But little or no work has been found regarding the toxicity reduction of wastewaters, specially pulp mill effluent or refinery wastewater, by freeze concentration.

Freezing technology became of interest in the late fifties for the application in water purification (Ham *et al.*, 1998), as it has some advantages over the other separation process. The process is advantageous as it is a very simple physical separation process as no chemicals are added and freeze concentration is suitable for all soluble pollutant, even the most toxic compounds and the process can be applied to a large range of concentrations (Oliver *et al.* 2001). Wastewater which is difficult to treat biologically due to the presence of toxic compounds can be treated by partial freezing (Ruemekorf, 1994).

De Bruyn and Rasmussen (2001) reported to develop a toxicity testing method by concentrating aqueous samples by partial freezing, using the concept of freeze concentration. They observed excellent recoveries of inorganic and organic analytes, phenol and $ZnSO_4$ by tenfold freeze concentration. A hundredfold freeze concentration permitted the quantification of low levels of ambient toxicity in a wide variety of natural waters using a rapid, inexpensive microbioassay. They also found that freeze concentration approach well suited to ambient toxicity testing, because it was non-specific and had low potential for solvent contamination and the involved low temperatures minimized volatilization and degradation of organic contaminants.

McMinn *et al.* (2003) conducted experiments to determine the processing conditions which would provide the most water removal from the precipitate after freezing and thawing. They examined the effect of variables such as freezing time, freezing temperature, and pre-treatment steps (agitation or concentration), on the freeze-thaw process of ferric precipitates. They found that the pre-treatment steps produced a more concentrated residual. They conclude that the freezing and thawing was a very simple and effective method of dewatering precipitates and did not require the use of additional additives.

Although the potential uses of freeze concentration were investigated thoroughly, its actual application for sea water desalination was never implemented in large scale (Wiegandt and Berg, 1980). But in other fields of applications such as the food industry, the freeze concentration is commonly used (Chowdhury, 1988). NIRO (formerly Grenco) has developed a freeze concentration system that is commonly used in the food industries and also in wastewater management (Ruemekorf, 1994).

The first attempt to remove impurities from industrial wastewater by freeze concentration was taken by Avco Systems Division (ASV) in the beginning of 1970s (James and Johnson, 1972). The system was called "Crystalex" and consisted of establishing close contact between the wastewater and refrigerant in a treatment unit. The evaporation of the refrigerant caused the wastewater to freeze and a mixture of ice and impurity concentrated water was produced. The mixture was separated in a wash column.

NIRO Ltd. named its freeze concentration process as NIRO Freeze Concentration (NFC). They claimed that the freeze concentration can reduce the cost of hazardous wastewater disposal by 70% (Murphy, 2000). NFC has been tested on waste solutions containing sodium hydroxide, sodium benzoate, magnesium sulphate and other organic and inorganic salts. The process reduces the water content of waste streams that must be incinerated, hence, cuts energy demand and reduces costs. The company has already installed the process at two wastewater treatment plants, one for Seraya Chemicals in Singapore and other for Basell in the Netherlands.

2.2. Spray Freezing and Melting Experiment:

Though some research work has been found on freeze concentration in the literature, little has been found about the impurity and toxicity removal from wastewater by spray freezing process. Spray freezing is a freezing process where the aqueous solution is sprayed through a nozzle at a cold temperature below 0 °C. The liquid droplets travel through the air to the ground at cold temperature and partially or totally freeze, producing an ice-water mixture or only the ice, respectively. If a mixture of ice and water was produce, it was observed that the impurity concentrations in the water (runoff) increases significantly (Gao, 1998 and Gao *et. al.*, 2003 and 2004b) and when the water is drained off from the ice-water mixture, it leaves relatively a purer ice behind. This separation of the impurities is based on the same fact as partial freezing that the impurities are rejected from the growing ice crystals and concentrated in the liquid phase. Here the separation of the impurities occurred due to partial freezing of the water droplets. The second step of purification of ice occurs in melting process of ice. The initial meltwater carried away a significant portion of impurities from the ice when it percolated from top to bottom of the ice mound (Wuite *et al.*, 1997b; Gao, 1998; Wuite *et al.*, 1999). After the initial melting of ice, the impurities of the ice are gradually reduced as the continuing meltwater of the ice washes away the rest of the impurities in the ice (Johannessen and Hendriksen, 1978; Gao, 1998; Wuite *et al.*, 1999). So after a certain portion of meltwater generation, the remaining ice samples are purer.

Some practical uses of spray freezing have been reported. Delta Engineering of Ottawa, Ontario, Canada which is a manufacturer of snowmaking equipment named their spraying system the *Snowfluent*™ process (White and Frere, 1994). The *Snowfluent*™ process has been used in the treatment of municipal wastes since 1985 (Huber and Palmateer, 1985). This technology offers a solution to the problem of winter storage of wastewaters. Using the *Snowfluent*™ process wastewater effluent can be turned into snow and stored during winter, so that there is no need to build additional lagoons (Martel, 1998). Martel (1998) mentioned some other benefits of the *Snowfluent*™ process like, low cost of operation and maintenance, lower manpower requirement as the process can be fully automated, no use of chemicals and less odour than conventional treatment.

This process has been used in Maine, USA and Ontario and Saskatchewan, Canada. Martel (1998) found that, depending on the atmospheric condition, up to 40% of the effluent evaporates or is lost through sublimation, reducing the volume of effluent stored as snow. Treatment also occurs as the snow mounds age and melt. The soluble constituents are removed from the snow by a leaching process described by Johannessen and Hendriksen (1978) for natural snow-packs. The snow-pack melts from the top. The resulting meltwater percolates down through the snow-pack and collects soluble constituents. With aging, more leaching occurs and the soluble constituents are carried deeper into the snow pile leaving a purer snow-pack on top. Some volatile impurities (like NH_3) continue to volatilize during the aging of snow. Some insoluble impurities and precipitates also gravitate to the bottom of the snow-pack during the aging process.

Although some practical uses of spray freezing technique has been mentioned above, not much research work has been found in the literature on its application to wastewater impurity and toxicity reduction. Desalination of sea water by spray freezing was achieved by Krepchin (1985). A spray freezing experiment was carried out in the winter of 1984-1985 at a Long Island pilot desalination plant in New York. It was reported that the saline water salt concentration was reduced from 30,000 mg/L to 10 mg/L.

Impurity removal efficiency starting with oil sand tailing pond water, produced from the extraction of bitumen from the oil sands in Northern Alberta, Canada, using spray freezing technique was investigated by Gao *et al.* (1996, 2003). High removal efficiency for TOC and Cl^- concentration was achieved. TOC removal was in the range of

89.3% to 98.9% and the Cl^- concentration removal was in the range of 90.8% to 98.7% in the ice core and meltwater samples.

Gao (1998) and Gao *et al.* (2004a) conducted spray freezing experiments using pulp mill effluent and oil sands tailing pond water to investigate the impurity concentration separation efficiency by runoff and meltwater. During the freezing operation, 30% runoff was generated at a spray temperature of -10^0 C and it was found that a considerable amount of impurities were removed by the runoff. The impurity concentration of the ice core samples were only about 30% to 60% of the source water when the runoff was generated. It was also found that the age of ice influenced the impurity removal efficiency during the ice melting. For the ice samples produced by spraying pulp mill effluent at -10^0 C and stored at the spray temperature for 20 days, the impurity removal with the first 30% of the meltwater of the ice was 55% for COD, 53% for color, 57% for TOC and 54% for conductivity. But the impurity removal was increased by 7% for COD and 5% for color when the ice sample was stored for 40 days. Some work also has been done for toxicity removal by spray freezing from Microtox™ toxicity analysis was used to evaluate the toxicity. The author found that the samples which achieved greater than 80% impurity removal were not toxic. But no extensive toxicity data were found.

Gao *et al.* (2004b) studied the contaminant release from melting spray ice produced from pulp mill effluent and the oil sands tailing pond water. They concluded that the contaminant separation efficiency was not significantly influenced by the characteristics of wastewater.

Wuite *et al.* (1999) applied spray freezing method, which was called *Snowfluent*^{TM} technology, to the liquid manure. It was found that the most of the soluble load of the snow pack, produced from the spray freezing, was flushed out with the initial meltwater volume, leaving a purer snow behind and it was calculated that over 80% of the soluble constituents were contained in the first 20% of the meltwater. The results were similar to that found by Seip *et al.*, (1980), where the fractionation and runoff of the important ions found the natural acid snow meltwater were investigated. It was found that the initial 30% of the meltwater carried about 80% of the sulfate and nitrate and 60% of the sodium and chloride. From the study conducted by Johannessen and Henriksen (1978), it was suggested that the high impurity concentrations in the initial meltwater during the melting process of the ice might be caused by a freeze-concentration process during re-crystallization and melting in which impurities accumulate preferentially at the surface of ice particles.

In some research works, it was found that some ions are preferentially eluted. Bales *et. al.* (1989) applied acid and salt tracer to homogeneous snow in order to investigate the effect of initial distribution of chemical species within the snow pack to the relative concentrations of melt water released from the pack. It was found that the species deposited near the top of the pack eluted out considerably before those more uniformly distributed with the depth. About 80% of the salts dosed at the top of the pack and 70% of the salts dosed at the middle of the pack came out in the first 20% of the melt water.

Brimblecombe *et. al.* (1987) did a set of field-laboratory experiments and also experiments on the controlled melting of ices of known composition. They found that sulphate and nitrate ions are preferentially removed from the ices with respect to chloride ion during melting. For the cations, sodium appeared to be removed least readily. It was found that the differences in the efficiency of removal of ions were more evident by the end of the melt than in the first stages of melting.

2.3. Linoleic Acid and Abietic Acid:

Linoleic acid and abietic acid represent fatty acid and resin acids, respectively. They are toxic and found in many pulp mill effluents. According to Poole *et. al.* (1978), the toxicity causing compounds in pulp mill effluent are resin acids, chlorinated lignins, chlorinated resin acids, chlorinated phenolic and other acidic groups, fatty acids and lignin degradation products.

In Canada, it has been estimated that 50 percent of all the wastewater released in the nations waters are from pulp industries (Sinclair, 1990). It was found that resin acids alone caused 60 to 90 percent of the toxicity in pulp mill effluent and the presence of fatty acids adds to the toxicity (Ali and Sreekrishnan, 2001). Yu and Mohn (2002) also mentioned that the resin acids are the major cause of toxicity of pulp mill effluents to aquatic life. Resin and fatty acid levels in pulp mill effluent may vary from a few µg/L to 10,000 mg/L depending on the type of wood used, pulping process and the nature of the wastewater treatment applied (Fahraeus-Van Ree and Payne, 1999; Liss *et. al.*, 1997). They have been found to be toxic to fish in the range of 0.2 to 8 mg/L (Peng and Roberts, 2000).

Extensive research on pulp mill effluent treatment processes was done to reduce the suspended solids, dissolved oxygen demand, toxicity causing materials and color.

Biological treatment for the reduction of biochemical oxygen demand and toxicity is a common treatment process for pulp mill effluent. But the acidic pH and the fluctuations in contaminant loading of the biological reactor can severely reduce the treatment efficiency (Werker and Hall, 1999). It was also found that both resin and fatty acids inhibit the methanogenic bacteria in biological treatment systems (Ali and Sreekrishnan, 2001). It makes biological treatment systems less effective for the treatment of toxic compounds like resin and fatty acids.

Other treatments for pulp mill effluent include ozone and advanced oxidation processes. The problems associated with ozone treatment are the high demand of ozone, sizing of ozone generation system due to the fluctuations in ozone demand with the variation of effluent impurity content and high cost (Gamal El-Din and Smith, 2002). Advanced oxidation processes are thought to be ideal for degradation of large organic molecules, because the hydroxyl radical is considered one of the strongest oxidizers (Sapach and ViraraGhavan, 1997). But the application of advanced oxidation process produces by-products which sometimes can be more toxic than the original wastewater. Wright *et. al.* (2002) found that the toxicity of the treated solution increased after the advanced oxidation of abietic acid solution. The author concluded that the increase in toxicity was caused by the production of more toxic by-products.

3. MATERIALS AND METHODS

3.1. Synthetic Wastewater: Linoleic Acid and Abietic Acid

Linoleic acid and abietic acid represent fatty acids and resin acids, respectively. Both of the acids were selected due to their high toxicity. Their physical and chemical properties are given in Table 3.1.

Table 3.1: Physical and chemical properties of linoleic acid and abietic acid

Properties	**Linoleic Acid**	**Abietic Acid**
Formula	$C_{18}H_{32}O_2$	$C_{20}H_{30}O_2$
Physical state	Liquid	Solid crystals
Color	Faintly yellow-green	Yellow-orange
Molecular weight	280.46 AMU	302.46 AMU
Boiling point	230 °C at 16 mm Hg	250 °C at 9 mm Hg
Melting point	-5 °C	175 °C
Density	0.92 g/mL	-
Solubility in water	Insoluble	Insoluble

3.1.1. Sample Preparation

Stock solutions of linoleic acid and abietic acid were prepared according to the procedure followed by Wright *et. al.* (2002). A total of 5 g of linoleic acid was purchased from Sigma. (lot no. 072K1173). A total of 2 litres of stock solution of linoleic acid with a concentration of 625 mg/L was prepared by dissolving 1.36 mL of 0.92 g/mL linoleic acid (1.25 g of linoleic acid) to 2 litres of pH 11 phosphate buffer. Linoleic acid does not dissolve in water directly and as the concentration of linoleic acid was high, pH 11 buffer was used.

Abietic acid was purchased from Sigma, which was approximately 75 wt% abietic acid. A 500 mg/L abietic acid stock solution was prepared by dissolving 666.66 mg of abietic acid (75 wt %) to 10 mL of 95% ethanol and applying heat. The volume of the solution was then raised to 1 L with a buffer solution of pH 11.

Buffer solution was prepared with sodium phosphate monobasic, potassium phosphate, de-ionized water and sodium hydroxide solution. First, pH 8 buffer was prepared by dissolving 14.196 g of $Na_2HPO_4.7H_2O$ and 0.852 g of KH_2PO_4 to de-ionized water and making its volume 2 L with de-ionized water. Then 10N NaOH was used to bring the pH to 11. Stock solutions were stored at 4 °C and the working samples were prepared immediately before the freezing experiment. Working samples were prepared from the stock solution by making necessary dilutions using phosphate buffer of pH 11.

3.2. Industrial Wastewater: Pulp Mill Effluent and Refinery Wastewater

Secondary pulp mill effluent was collected from Weyerhaeuser, Grand Prairie, Alberta and the refinery wastewater was collected from the final effluent of Strathcona Refinery, Edmonton, Alberta. A total of 40 L of pulp mill effluent and 20 L of refinery wastewaters were supplied and were transported in 10 L pails. Samples were stored at in a cold room (Room no.538 A) in the Civil Engineering building, where temperature ranged from 0.5 to 4 °C. The characteristics of pulp mill effluent and refinery wastewater are summarized in Table 3.2 (average of three measurements).

Table 3.2: Characteristics of pulp mill effluent and refinery wastewater

Parameters	Pulp mill effluent	Refinery waste
TOC (mg/L)	241	14.2
COD (mg/L)	767	69.6
Color (CU)	889	-
Toxicity (TU = $100/EC_{20}$)	1.04	1.81
pH	6.84	7.26

3.3 Experimental Methods

3.3.1. Beaker Freezing Experiment

Beaker freezing experiments were carried out in a freezer at -25 °C and -10 °C, which were the coldest and warmest temperatures of the freezer. The dimensions of the freezer were 1370 mm (L), 680 mm (W) and 800 mm (H). The freezer was placed inside the cold room (mentioned in section 3.2.) so that the temperature fluctuation inside the freezer was low. The top cover of the freezer was replaced with a cover of Styrofoam. A temperature sensor was placed inside the freezer penetrating the Styrofoam cover and it was connected to a data logger (Data Dolphin, Model 400). The data were transferred to a computer connected with the data logger. The temperatures inside the freezer were recorded every minute and the average temperatures for the duration of the runs were obtained. The temperature fluctuation for the warmer setting (-10 °C) was approximately from -8.5 °C to -11.5 °C and for the coldest setting (-25 °C) was from -22.8 °C to -26.9 °C. Plastic beakers (250 mL) were used for the freezing, because glass beakers might break down at low temperatures. Beakers were insulated except the top so that the freezing would proceed unidirectional from top to bottom (Figure 3.1).

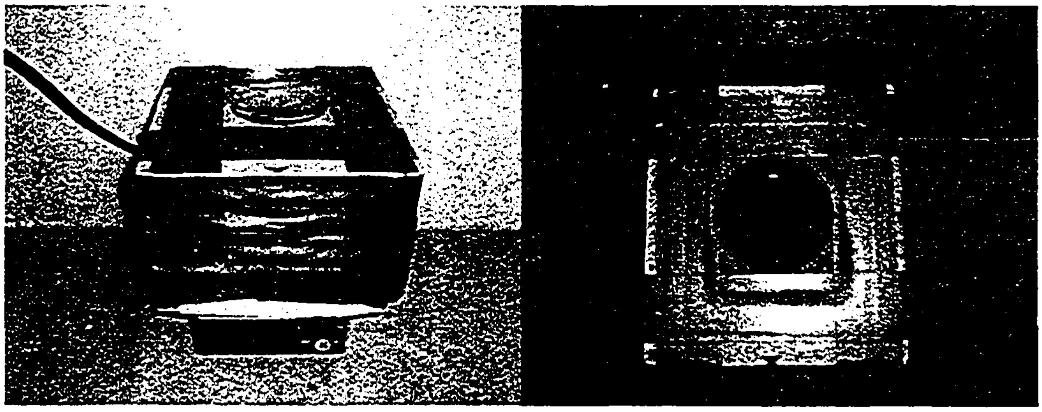


Figure3.1: Insulation of the 250 mL beaker in beaker freezing experiment

Sample volumes of 250 mL were used for 70% partial freezing. Samples were pre-cooled to near 0 °C in the cold room before starting the beaker freezing test. Time required for 70% partial freezing at -25 °C and -10 °C were around 7.5 hours and 24 hours, respectively. The upper portion of the beaker was the frozen portion (ice) and the lower portion of the beaker was the unfrozen portion (unfrozen water) which is pictorially described in Figure 3.2 and Figure 3.3, where the separation of impurities can be observed visually.

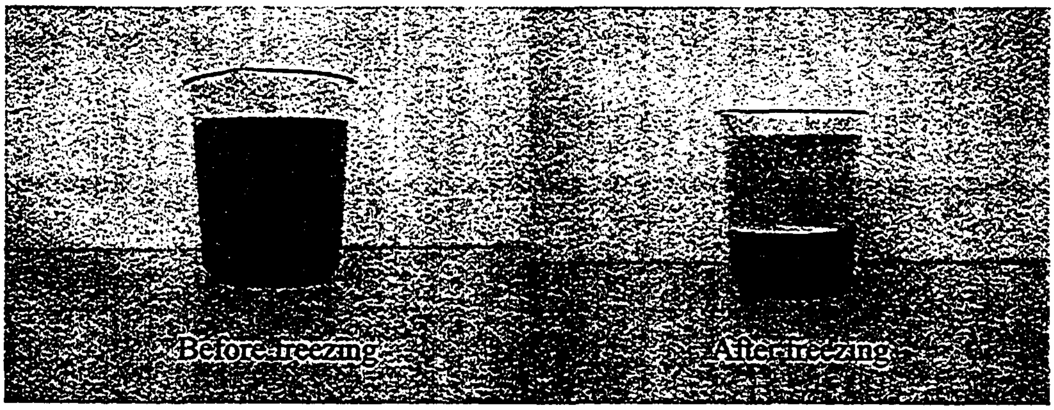


Figure 3.2: Pulp mill effluent in the beaker, before and after partial freezing

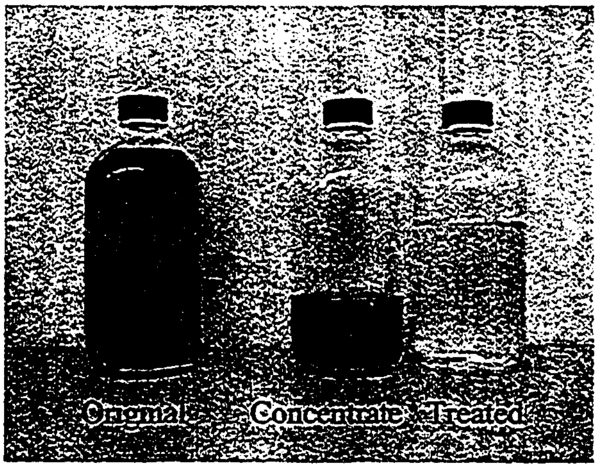


Figure 3.3: Original, concentrate and treated pulp mill effluent in sample bottles

The partial freezing of the samples was carried out in the beakers with and without stirring. A magnetic Fisher Thermix® Stirrer (Model 120 M) was used for the stirring operations. The stirrer was placed inside the freezer. To obtain the same extent of stirring for all the runs, the speed (rpm) dial was fixed at 3 and a same magnetic bar of 24 mm length was used. After 70% freezing was done, the ice samples were separated from the unfrozen water by squeezing the ice samples out of the beaker. The ice was melted at room temperature in plastic beakers. Volumes of ice melt and the unfrozen water samples were measured by using gradated cylinders and were stored in sample bottles (Figure 3.3) inside a refrigerator for TOC, COD, color and toxicity analysis.

3.3.2. Spray Freezing and Melting Experiment

The spray freezing experimental set up is shown in Figure 3.4. Spray freezing experiments were carried out inside the freezer mentioned in section 3.3.1, where samples were pumped and sprayed through a spray nozzle at a certain flow rate on a plastic tray at -10 °C and -25 °C. The brand name of the nozzle was Evenmist™, manufactured by Field Controls, Kinston, NC 28504, USA. The size of the nozzle was 0.65 mm in diameter and it could spray at an angle of 60°. The pump was a diaphragm pump (Model no. 8000-813-238, Garden Grove Company, California) and its flow rate could be adjusted. The freezer was kept inside the cold room, mentioned in section 3.3.1, so that the temperature fluctuation inside the freezer was low. The actual cover of the freezer was removed and a structure of Styrofoam was placed on top of the freezer. Another Styrofoam structure of 600 mm×4000 mm×400 mm was built on top of the Styrofoam cover to allow more height for spraying. The structure was built in such a way so that the height of the spray nozzle from the bottom of the plastic tray can be adjusted

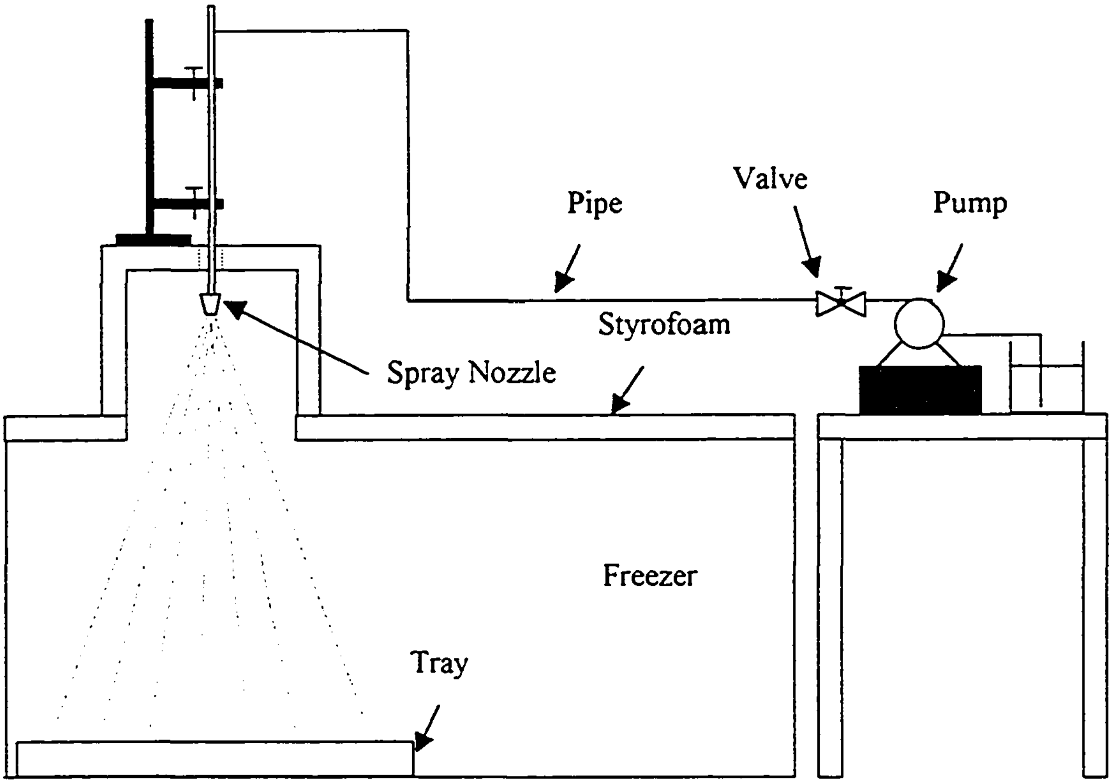


Figure 3.4: Diagram of the spray freezing experimental setup

as needed. The size of the plastic tray was 460 mm×360 mm×130 mm. A temperature sensor was placed inside the freezer and the sensor was connected to a computer via a data logger (Data Dolphin, Model-400). Continuous temperature inside the freezer was obtained every minute during spray freezing operation, which gave the average temperature of the spray freezing experiment. Figure 3.5 shows the picture of the Styrofoam structure on top of the freezer.

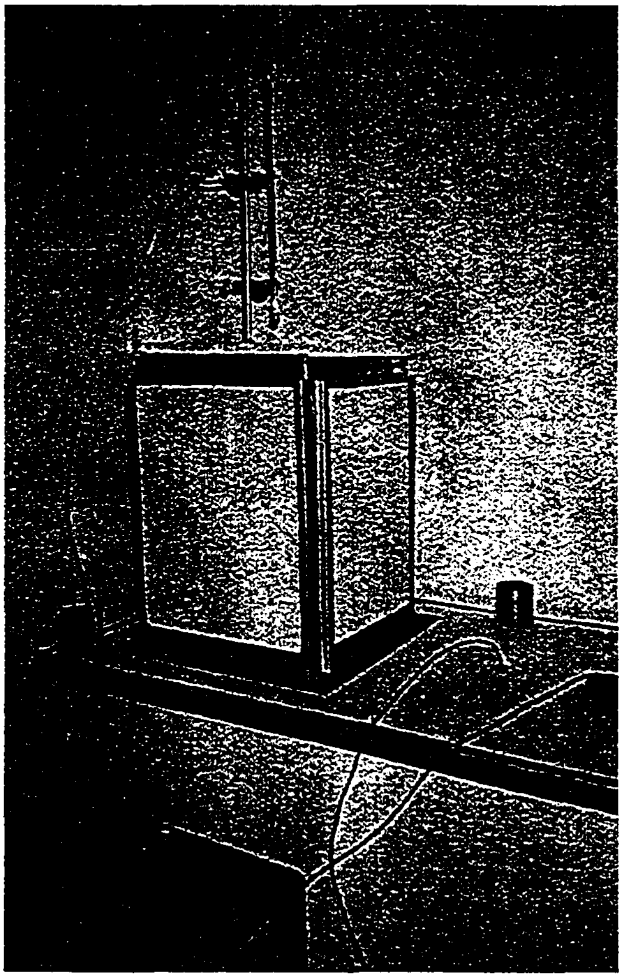


Figure 3.5: Styrofoam structure on top of the freezer, the spray nozzle and the temperature and humidity sensors

Samples were pre-cooled inside the cold room to near 0 °C before starting the experiment. To get a mixture of 70% ice and 30% water in the plastic tray after spraying 1000 mL of samples, some trial runs were carried out with DI water and the following combinations of the flow rate and height of spray nozzle from the bottom of the plastic tray were determined (Table 3.3).

Table 3.3: Combination of flow rate and height of the spray nozzle to produce a mixture of 70% ice and 30% water.

Parameters	Temperatures	
	-10 °C	-25 °C
Flow rate (mL/Min)	25	25
Height of the nozzle (mm)	1400	450

From trial experimental runs it was found that about 800 mL ice and water mixture was produced in the tray from the spraying of 1000 mL of pre-cooled water, where ice portion was almost 560 mL and the water portion was 240 mL. So another 200 mL of sample were assumed to be evaporated in the air and/or fell outside the tray.

Every time before starting the spray freezing experiment, whole system was rinsed with the sample that was going to be used for the experiment. A 1000 mL of samples were sprayed for 40 minutes at a flow rate of 25 mL/min inside the freezer on the plastic tray at cold temperatures. From the mixture of ice and water, water, which is called runoff, was drained, collected, measured and stored in sample bottles and later tested for TOC, COD, color and toxicity. The ice samples were then collected in insulated cylindrical Plexiglas storage columns with netted bottom, which had a diameter of 120 mm and a height of 150 mm. Ice columns were stored in a freezer for several days. Ice samples storage temperatures were same as their spray temperatures.

Some ice samples were melted after 2 days and some were melted after 2 weeks of storage time. The setup for melting was a combination of the setups designed by Gao (1998) and Tsiouris *et. al.* (1985). The melting experiments were carried out inside the cold room and melting was promoted by using a 250 W infrared lamp suspended between 250 mm and 300 mm above the ice surface (Figure 3.6).

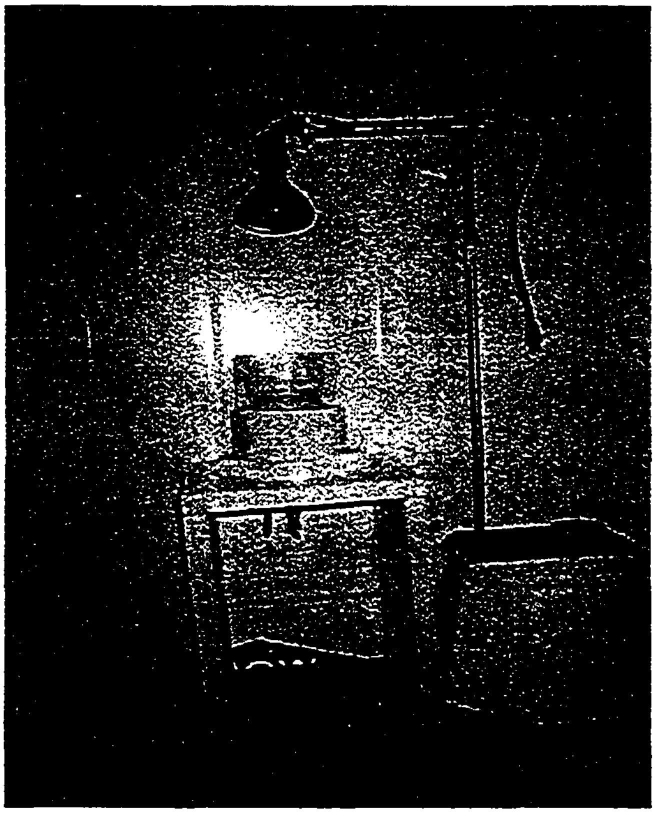


Figure 3.6: Melting arrangement of the ice produced from the spray freezing

In this melting arrangement, there is a Styrofoam structure, which holds a cylindrical plastic container with a valve at the bottom. The insulated Plexiglas storage columns with the ice were placed inside this plastic container and the infrared light was turned on for melting. The insulation for the Plexiglas storage column was used to reduce the edge melting effect during melting. A unidirectional melting from top to bottom was accomplished. The melt water was percolating through the ice column and was collected at the bottom. Melt water was sequentially collected in the sample bottles in four steps from the bottom of the plastic container. The sizes of the volume of sequential melt water for four collection steps are shown in Table 3.4. TOC, COD, color and toxicity were tested for the samples. Step 1 was called the initial melt water and step 4 was called the final melt water.

Table 3.4: Volumes of the sequential melt water collected in four steps during the melting of 560 mL of stored ice.

Steps of Collection	Volume (mL) of Collection	% volume of collection	Cumulative % Volume of Collection
1	40	7.14	7.14
2	80	14.29	21.43
3	160	28.57	50.00
4	280	50.00	100.00

3.4. Design of Experiments

Factorial experimental designs were carried out for both beaker freezing and spray freezing experiments to find out the significant factors that influence the reduction of TOC and COD of both industrial and synthetic wastewaters. Color, only for the pulp mill effluent and the toxicity, for both pulp mill effluent and refinery wastewater, were also measured but the color and toxicity data were only used to find out the correlation of color and toxicity with TOC and COD. Concentrations of the samples measured were converted to concentration ratios, C/C_o, which shows the degree of increase or decrease of concentrations (C) of the samples after treatment, from the initial concentrations (C_o) of the samples.

3.4.1. Beaker Freezing Experiments

Beaker freezing experiments were carried out only for industrial wastewater; pulp mill effluent and refinery wastewater. A 2^3 factorial experimental design with 2 replicates was adopted to see the effect of dilutions, freezing temperatures and stirring on TOC and COD removal. Factor levels are shown in Table 3.5.

Table 3.5: 2^3 factorial design of beaker freezing experiments of pulp mill effluent and refinery wastewater

Factors	Levels	
	Low	High
Dilution	1:10	1:1
Freezing Temperature	-25 °C	-10 °C
Stirring	Without	With

There were 16 runs in this design for both pulp mill effluent and refinery wastewater experiments and those were randomized. Significant factors were determined for the reduction of TOC and COD for both wastewaters, in ice samples. Significant factors were also determined for the increase of TOC and COD for both wastewaters, in unfrozen water samples. Later, the results between pulp mill effluent and refinery wastewater were compared to see if there was any difference between these two wastewaters, considering pulp mill effluent and refinery wastewater as two blocks.

3.4.2. Spray Freezing and Melting Experiments

Spray freezing and ice melting were carried out for industrial and synthetic wastewaters. A 2^2 factorial design with 2 replicates was adopted for pulp mill effluent and refinery wastewater to see the effects of spray temperatures and storage time on TOC and COD removal. The factor levels for 2^2 factorial design are shown in Table 3.6.

Table 3.6: 2^2 factorial design of spray freezing and melting experiments of pulp mill effluent and refinery wastewater

Factors	Levels	
	Low	High
Spray freezing temperature	-25 °C	-10 °C
Ice storage time	2 days	14 days

There were 8 runs for this design and those were randomized for both pulp mill effluent and refinery wastewater spraying experiment. Significant factors were determined for the increase of TOC and COD of the initial melt water for both wastewaters. Significant factors were also determined for the reduction of TOC and COD of the final melt water for both wastewaters. Later, the results between pulp mill effluent and refinery wastewater were compared to see if there was any difference between these two wastewaters, considering pulp mill effluent and refinery wastewater as two blocks.

A 2^3 factorial block design with single replicate was adopted for synthetic wastewaters (linoleic acid and abietic acid) to observe the effects of acid concentrations, spray freezing temperatures and storage times on TOC and COD. The factor levels are shown in Table 3.7. There were 8 runs for this design and those were randomized for both linoleic acid and abietic acid spraying experiment. Linoleic acid and abietic acid samples were considered as two blocks. Significant factors were determined for the increase of TOC and COD of the initial melt water for both wastewaters. Significant factors were also determined for the reduction of TOC and COD of the final melt water for both wastewaters. The block effect was also observed to find out whether the results of linoleic acid and abietic acid samples were significantly different.

Table 3.7: 2^3 factorial block design of spray freezing experiments of linoleic acid and abietic acid

Factors	Levels	
	Low	High
Concentration	5 mg/L	20 mg/L
Spray freezing temperature	-25 °C	-10 °C
Ice storage time	2 days	14 days

Significant factors were determined for the increase of TOC and COD of initial melt water. Significant factors were also determined for the reduction of TOC and COD of final melt water.

3.5. Scanning Electron Microscopy

The JOEL JSM-6301F Scanning Electron Microscope with cryo option was used to examine the morphology of ice specimens. The electron gun was a cold-cathode field emission type designed for ultra high resolution scanning electron microscopy (SEM) with a modern digital image processing system. Instrument specifications are summarized in Table 3.8.

Table 3.8: JSM-6301F Scanning Electron Microscope Specification

Feature	Performance
Magnification: Zoom : Fixed	10X to 500,000X Any magnification
Secondary Electron Image Resolution: at 30 KV : at 1 KV	1.5 nm guaranteed 5 nm guaranteed
Backscattered Electron Image Resolution (at 30 KV)	3.0 nm attainable
Probe Current	10^{-12} to 10^{-10} A
Electron Gun	Cold-cathode field emission
Accelerating Voltage	0.5 to 30 KV, 0.1 KV steps
Emitter	<310> tungsten tip
Alignment	Mechanical and electromagnetic deflection

3.5.1. Ice Sample Preparation

SEM operation was conducted only for the ice samples produced from pulp mill effluent. Spray freezing experiments were carried out for pulp mill effluent in 2 replicates, as were done for its spray freezing experiments. Run numbers for various combinations of spray temperatures and ice storage times for pulp mill effluent are shown in Table 3.9.

Table 3.9: Spray run numbers for various combinations of spray temperature and storage time for pulp mill effluent

Storage time	Spray Temperature	
	-10 °C	-25 °C
2 days	1, 5	2, 6
14 days	3, 7	4, 8

Runs for the samples, required for 14 days of storage, were carried out 14 days before the SEM operation and the runs for the samples, required for 2 days of storage, were carried out 2 days before the SEM operation. Small pieces of ice were collected from the tray from each run after the drainage of unfrozen water (runoff) and stored in a small beaker (100 mL) inside a freezer at the spray temperatures. But unfortunately, SEM operation was only done for the run numbers 1, 2, 3 and 4 within the allotted time.

3.5.2. SEM Operation

SEM operation was conducted in the SEM lab in Earth and Atmospheric Science building at the University of Alberta. Ice samples were transported from the Civil Engineering building to the SEM lab in a box with dry ice so that the samples were not melted. It was found that the ice specimens could not be mounted on the sample exchange holder and placed directly into the specimen stage without superficial melting of the ice surface. The melting is sufficient to obscure the morphology of the ice sample. That is why, the ice samples were super-cooled by submerging those in liquid nitrogen and then fractured within the liquid nitrogen to produce a clean unexposed ice surface. The samples were exposed to condensation when these were withdrawn from liquid nitrogen and placed in specimen holder and glued. So the sublimation was conducted to expose the ice surface under vacuum in the cold stage at a temperature of -40 °C. An image resolution of 1.5 KV was used to monitor sublimation. After the exposure of the surface, the ice samples were cooled to -180 °C for 10 minutes before removal for coating. Then the samples were removed under vacuum using the specimen transfer stage and transferred to a cryo chamber where the samples were gold coated at -180 °C. The samples were double sputter coated with gold for a total thickness of 100 Angstroms. After the coating, the samples were transferred to the specimen chamber of the SEM and examined using an image resolution of 5 KV.

3.6. Analytical Procedures

3.6.1. Total Organic Carbon (TOC)

TOC of the samples were analysed by using Dohrmann TOC Analyser following the method described in section 5310 C of Standard Methods (1998). Only for the analysis of pulp mill effluent, additional 9.6 g of mercuric nitrate [$Hg(NO_3)_2.H_2O$] was used in making of 2% potassium persulfate reagent to avoid the interference in oxidation of organic molecules in samples caused by high concentration of chloride in pulp mill effluent sample. All determinations were conducted in duplicate.

3.6.2. Chemical Oxygen Demand (COD)

COD was determined by closed reflux colorimetric method as described in section 5220 D of Standard Methods (1998). A HACH COD reactor and a Novaspec® II spectrophotometer were used for the tests. All determinations were conducted in duplicate.

3.6.3. Color

Color of the samples were only determined for pulp mill effluent in accordance with Standard H.5P prepared by the Environment Improvement Committee, which was issued by the Physical and Chemical Standard Committee, Technical Section of the Canadian Pulp and Paper Association (1974). The spectrophotometer, which was used to measure the absorption, was the Pharmacia Biotech Ultrospec 3000 UV/visible spectrophotometer. All determinations were conducted in duplicate.

3.6.4. Toxicity

Mircotox toxicity analysis was performed on raw samples of industrial and synthetic wastewaters and the treated samples to determine the acute toxicity. The test involves the use of a marine bacterium *Photobacterium phosphoreum* to determine the toxicity of the samples. A model 500 Microtox analyzer (AZUR Environmental) was used to measure the light emitted by the bacterium as result of its normal metabolic processes. Presence of toxic substance in the sample hampers the metabolic processes of the bacterium and decreases the intensity of the emitted light. The effect of light reduction is measured for various dilutions of the samples. EC_{50} is then determined from the linear regression of the measured light reductions where EC_{50} is the concentration of the test sample at which there is a 50% reduction in bacterial light production (Kennedy *et. al.*, 2000). Higher EC_{50} value means lower toxicity, as EC_{50} value is inversely proportional to the toxicity. EC_{50} values were calculated at 15 minutes from the time of mixing the various dilutions with the bacterium. Toxicity unit (TU) can be determined using Equation 1:

$$TU_{50} = 100/EC_{50} \tag{1}$$

TU eliminates the inverse relationship of EC_{50} with toxicity. As the toxicity of supplied pulp mill effluent and refinery waste was not very high, TU_{20} was determined for these samples, where $TU_{20} = 100/EC_{20}$ (2)

3.6.5. pH

pH was determined in accordance with the section 4500-H+ B of Standard Methods (1992). The pH measurement instrument was the Fisher Scientific Accumet pH Meter 25. The meter had a relative accuracy of ± 0.01 pH units.

4. RESULTS AND DISCUSSIONS

The results obtained from partial freezing in beakers and spray freezing and melting experiments are presented in the following sections. First there are general discussions about the results. After the general discussions, statistical analyses of the results are presented in each section.

4.1. Partial Freezing Experiments in Beakers

The results from the beaker freezing experiments are presented and discussed in this section. Beaker freezing experiments were carried out only for the industrial wastewaters; pulp mill effluent and refinery wastewater. Both original wastewaters and diluted wastewaters were used for the experiments. Wastewaters were diluted to 1:10 of original concentrations. The wastewaters samples were partially frozen and 70% ice and 30% water were produced under different experimental conditions. Both ice and liquid samples were analysed. TOC, COD and toxicity were measured for both wastewater samples, and color was measured only for pulp mill effluent. The impurity concentrations of the ice and unfrozen water samples were normalized to the concentration of the original wastewater samples (C/C_o). All the runs of the beaker tests were replicated and the presented normalized concentration data are the averages of two replicates.

4.1.1. Pulp Mill Effluent

4.1.1.1. Concentration reduction in ice obtained from the partial freezing of original and diluted pulp mill effluent samples

Figure 4.1 and Figure 4.2 show the normalized TOC, COD and color in ice samples produced in beaker freezing tests of original and diluted (1:10) pulp mill effluent,

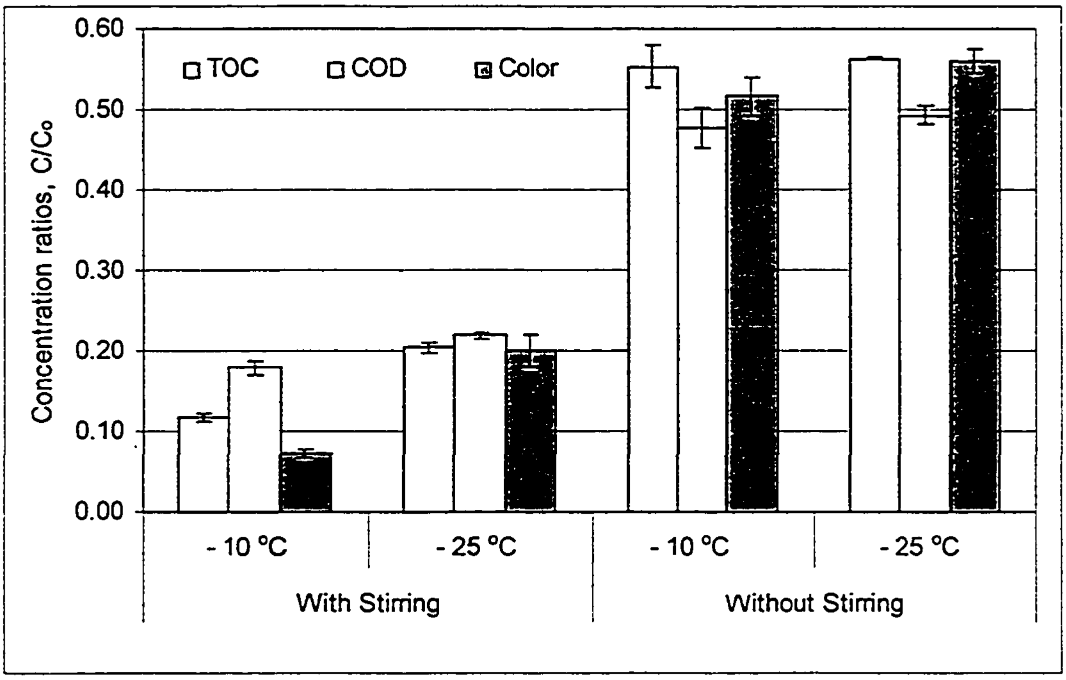


Figure 4.1: Normalized TOC, COD and color in ice samples of original pulp mill effluent in beaker tests (TOC_0 = 241 mg/L, COD_0 = 767 mg/L, $Color_0$ = 889 CU)

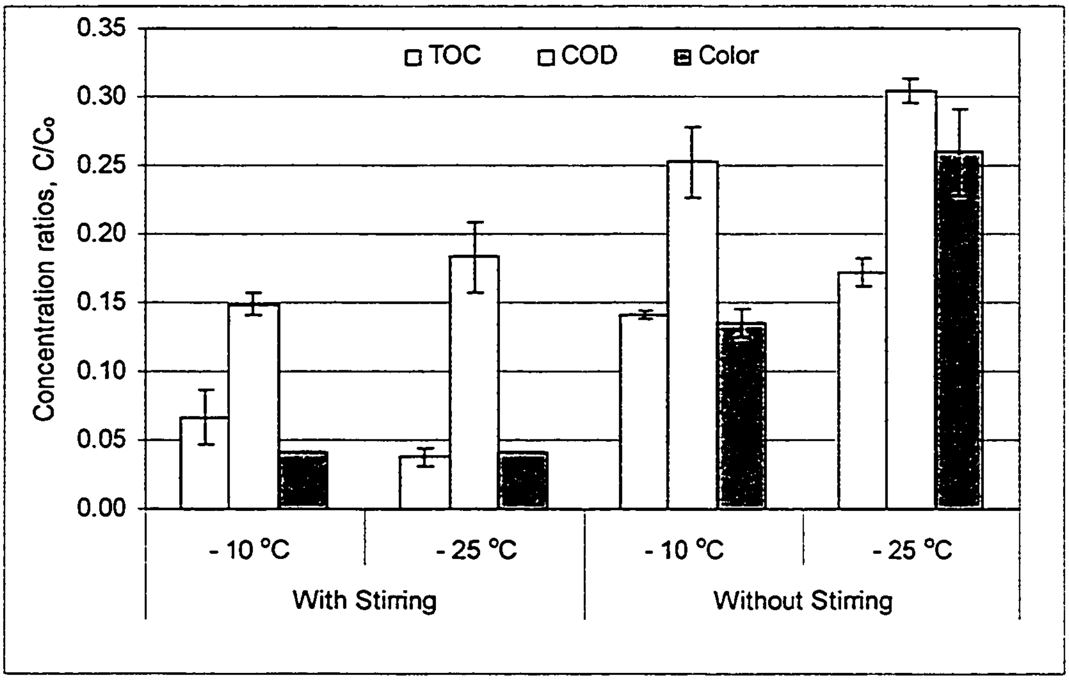


Figure 4.2: Normalized TOC, COD and color in ice samples produced from diluted (1:10) pulp mill effluent in beaker tests (TOC_0 =27.0 mg/L, COD_0 = 84.0 mg/L, $Color_0$ = 92.0 CU)

respectively. The toxicity data were not incorporated in the figures, since all the ice samples were found to be non-toxic. The original pulp mill effluent was found to be toxic (TU= 1.04). So, a 100% toxicity reduction was achieved for the ice samples obtained from the partial freezing experiments of the original pulp mill effluent. Both of the figures clearly indicated that the impurity concentrations were reduced ($C/C_o < 1.0$). The ranges of percent reduction of impurity concentrations in ice samples in beaker tests for original and diluted (1:10) pulp mill effluent samples are shown in Table 4.1.

Table 4.1: The ranges of percent reduction of impurity concentrations in ice samples in beaker tests for original and diluted (1:10) pulp mill effluent samples

Pulp mill effluent samples	TOC (%)	COD (%)	Color (%)
Original (1:1)	44 to 88	51 to 82	44 to 93
Diluted (1:10)	83 to 96	70 to 85	74 to 96

It was observed that a better reduction of impurity concentration was achieved for diluted (1:10) pulp mill effluent samples. The reason was that, the efficiency of rejecting impurities from growing ice crystals is reduced due to the increase of the chances of trapping impurities in ice crystals with the increase of impurity concentration in the sample.

From Figure 4.1, it was observed that the stirring increased the efficiency of impurity separation from the ice crystals and the impurity concentration reduction of the samples was better achieved by applying stirring. The maximum concentration reductions achieved, with and without the application of stirring, for original pulp mill effluent were 93% color and 52% COD, respectively. From Figure 4.2, it was also observed that the maximum concentration reduction achieved with and without the application of stirring for diluted (1:10) pulp mill effluent samples were 96% TOC and color and 87% color, respectively. The increase of the impurity separation efficiency because of the application of stirring was due to the renewal of the sample water on the growing ice crystal surface. When ice crystal grows, it rejects the impurities and the impurity concentration in the liquid phase near the growing ice crystal increases gradually and hence enhances the chances of incorporating impurities in the ice crystals. So, when stirring was applied to the freezing samples, it continuously renewed the water molecules near the growing ice crystal surface and reduced the chances of impurities to be trapped inside the ice crystals (Gay *et. al.*, 2003).

Figure 4.1 and Figure 4.2 also indicate that there was a slight effect of temperature in impurity separation efficiency. Both the figures show that at the warmer temperature (-10 °C) the impurity removal efficiency was higher than that at the colder temperature (-25 °C) irrespective of stirring. The faster cooling rate at colder temperatures caused the ice crystal grow at a faster rate and the solid-liquid interface moves at a higher velocity (Hoekstra and Miller, 1967) and hence, has a higher degree of chances to incorporate impurities in the liquid adjacent to the ice crystal surface inside the growing ice crystals.

4.1.1.2. Concentration increase in unfrozen water samples obtained from the partial freezing of original and diluted pulp mill effluent samples

Figure 4.3 and Figure 4.4 show the normalized TOC, COD and color in unfrozen water samples (30% volume) in partial beaker freezing experiments for original and diluted (1:10) pulp mill effluent, respectively. The normalized toxicity data are presented only in Figure 4.3. Figure 4.4 does not show any toxicity data as the unfrozen water

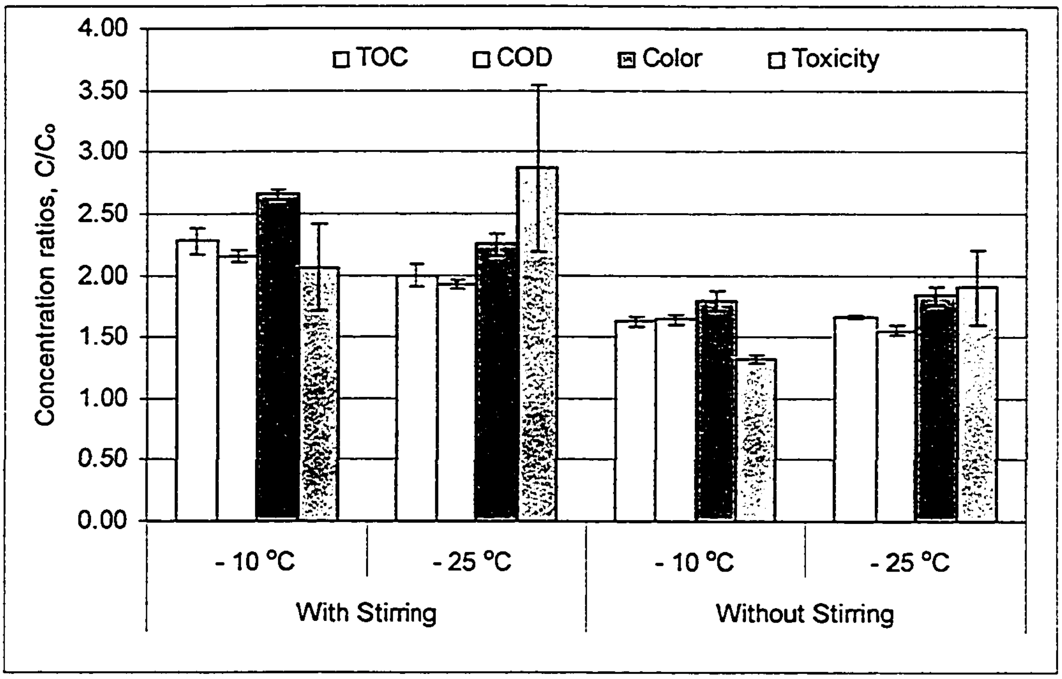


Figure 4.3: Normalized TOC, COD, color and toxicity in unfrozen water samples in beaker tests for original pulp mill effluent (TOC_0 =241 mg/L, COD_0 = 767 mg/L, $Color_0$ = 889 CU and $Toxicity_0$ = 1.04 TU)

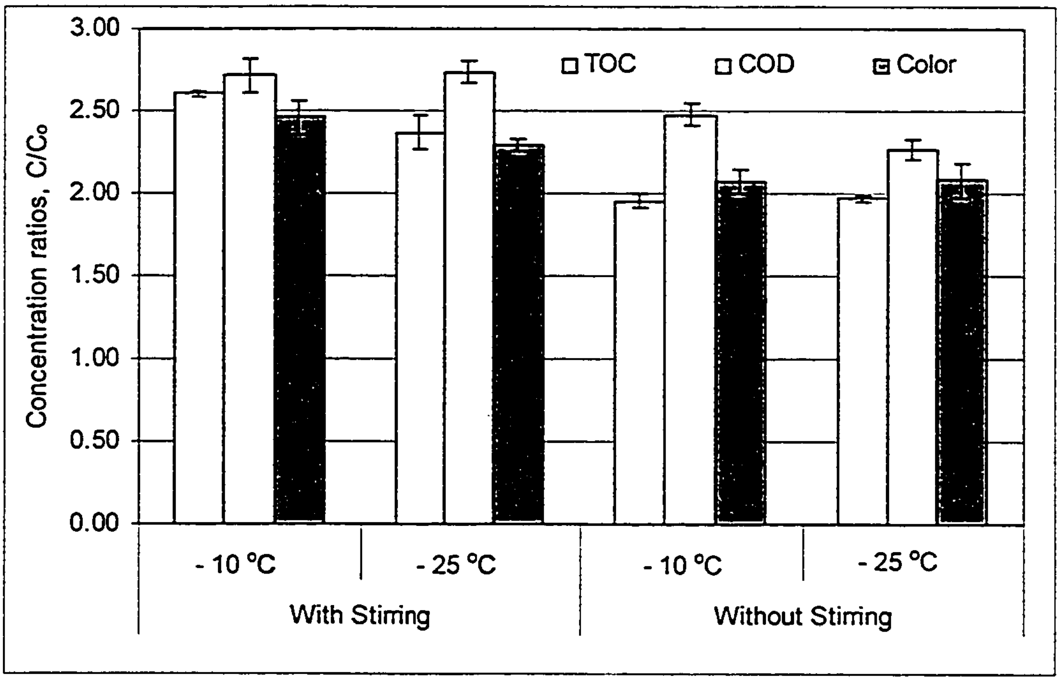


Figure 4.4: Normalized TOC, COD and color in unfrozen water samples in beaker tests for diluted (1:10) pulp mill effluent (TOC_0 =27.0 mg/L, COD_0 = 84.0 mg/L, $Color_0$ = 93.0 CU)

samples obtained from the partial freezing of diluted (1:10) pulp mill effluent were found non-toxic. The reduction of impurity concentrations in ice samples means the increase of impurity concentrations in unfrozen water samples. That is why, Figure 4.3 and Figure 4.4 were the opposite of the Figure 4.1 and Figure 4.2 described in section 4.1.1.1.

From Figure 4.3 and Figure 4.4, it is observed that the unfrozen water samples were more concentrated with impurities ($C/C_o > 1.0$), since the impurities were rejected from the ice samples and concentrated in unfrozen water. The ranges of percent increase of impurity concentrations in unfrozen water samples in beaker tests for original and diluted (1:10) pulp mill effluent samples are shown in Table 4.2.

Table 4.2: The ranges of percent increase of impurity concentrations in unfrozen water samples in beaker tests for original and diluted (1:10) pulp mill effluent

Pulp mill effluent samples	TOC (%)	COD (%)	Color (%)	Toxicity (%)
Original (1:1)	63 to 128	56 to 116	79 to 165	32 to 187
Diluted (1:10)	95 to 161	126 to 174	107 to 146	-

It was observed that higher increases of impurity concentrations in unfrozen water samples occurred for diluted (1:10) pulp mill effluent samples. For the samples with higher concentrations, the efficiency of rejecting impurities from growing ice crystals was reduced because the chances of trapping impurities in the ice crystals increase with increasing impurity concentration in the sample.

From Figure 4.3 and Figure 4.4, it was observed that the pulp mill effluent samples which were stirred during partial freezing experiments produced more concentrated unfrozen water samples than the samples which were not stirred. The maximum increases in concentration observed with stirring and without stirring for original pulp mill effluent were 165% and 84% of color, respectively (Figure 4.3). On the other hand, the maximum increases of concentrations observed with and without the application of stirring for diluted (1:10) pulp mill effluent were 174% of COD and 148% of color, respectively (Figure 4.4). The renewal of the sample water on the growing ice crystal surface due to stirring makes less impurities trapped inside the growing ice crystals and increases the concentration of the impurities in the unfrozen water samples (Gay *et. al.*, 2003). Acute toxicity data were found for the unfrozen water samples obtained from the partial freezing of the original pulp mill effluent. Toxicity values of these samples were increased up to maximum 187%. The increase of toxicity was due to the increase of the impurity concentrations in the samples.

4.1.1.3. Correlation between acute toxicity data and impurity concentrations obtained from the partial freezing experiments of pulp mill effluent

Correlations of acute toxicity with the corresponding impurity concentrations of the samples obtained from the partial freezing experiments of pulp mill effluent were investigated. Microsoft Excel software was used to find out the best fit curve. It also produced the correlation equation and R^2 value. In Figure 4.5 and Figure 4.6, acute toxicity values were plotted against their corresponding TOC and COD values, respectively. Acute toxicity data was only found for the unfrozen water samples obtained from the partial freezing of original pulp mill effluent. No toxicity was observed for the samples produced from the partial freezing of diluted (1:10) pulp mill effluent, where diluted pulp mill effluent was itself found to be non-toxic. Figure 4.5 and Figure 4.6 show similar pattern. There is a trend that the acute toxicity of the samples increased as TOC and COD increased. The trendlines were not shown in the plots as they did not show

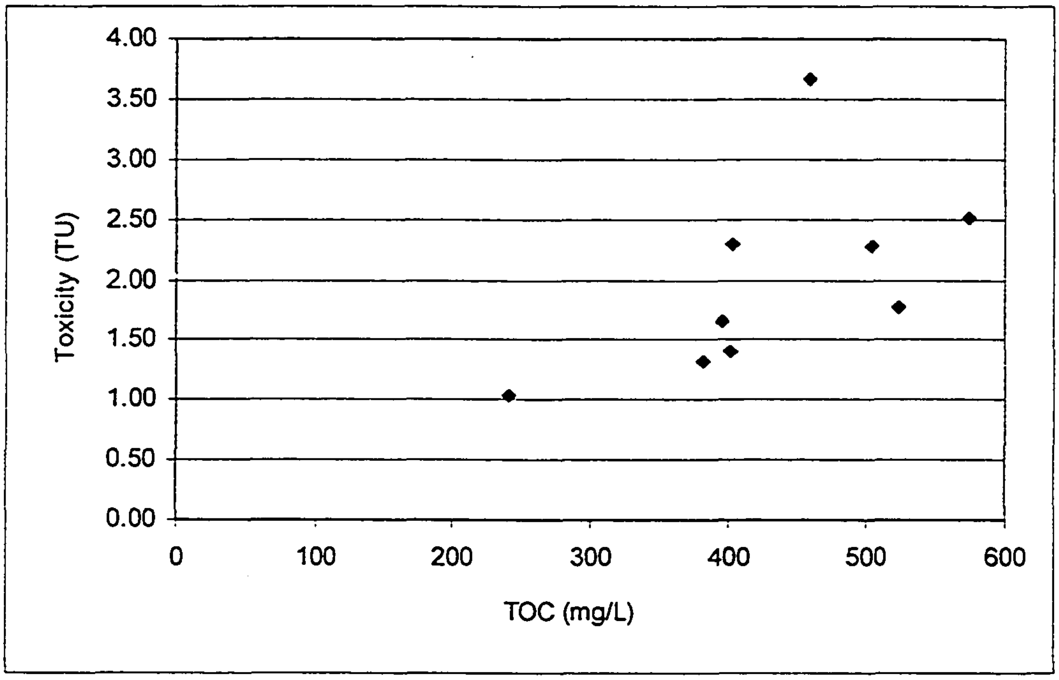


Figure 4.5: Acute toxicity vs. TOC concentrations of the samples obtained from the partial freezing experiment of pulp mill effluent

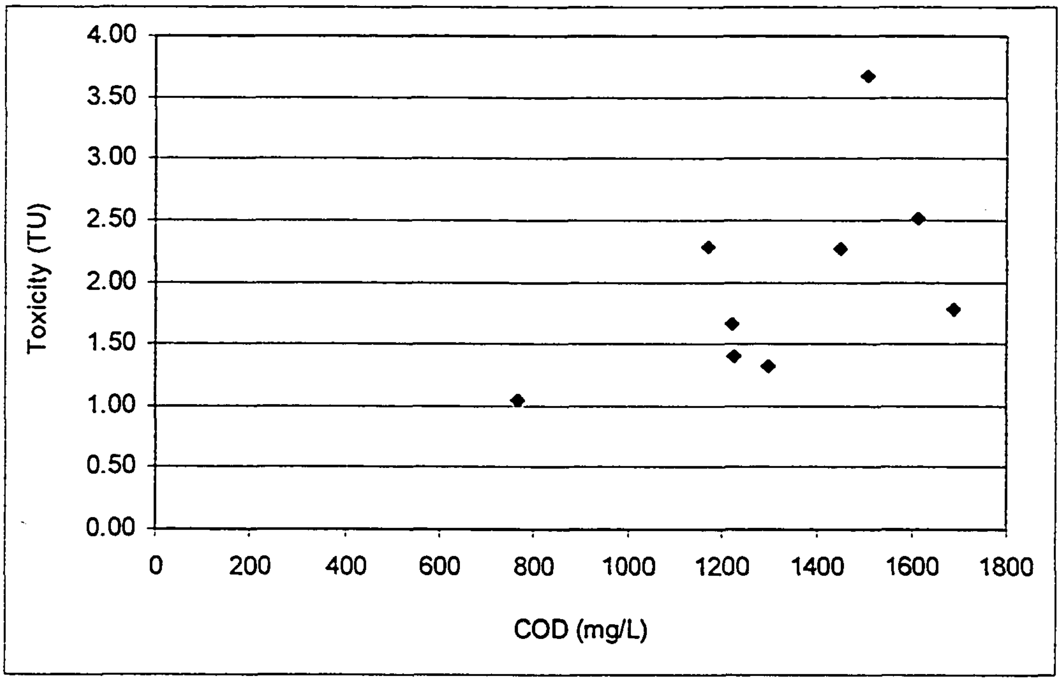


Figure 4.6: Acute toxicity vs. COD concentrations of the samples obtained from the partial freezing experiment of pulp mill effluent

strong correlations between toxicity and TOC and between toxicity and COD. The weak relationship might be due to the fact that the toxicity data are normally associated with a lot of uncertainties and moreover few toxicity data were possible to obtain for pulp mill effluent samples.

4.1.2. Refinery Wastewater

4.1.2.1. Concentration reduction in ice samples obtained from the partial freezing of original and diluted refinery wastewater samples

From the partial freezing experiments of refinery wastewater, similar results as pulp mill effluent partial freezing experiments were observed. No color measurement was done for refinery wastewater. Figure 4.7 and Figure 4.8 show the normalized TOC, COD and toxicity of ice samples obtained from the beaker freezing experiments of original and diluted (1:10) refinery wastewater, respectively. Diluted (1:10) refinery wastewater and the ice samples obtained from the partial freezing of diluted refinery wastewater were found non-toxic. Like pulp mill effluent (section 4.1.1), the impurity concentrations were reduced significantly ($C/C_o < 1.0$) for refinery wastewater in the ice samples. Like pulp mill effluent, it was observed for the refinery wastewater that the stirring increased the efficiency of impurity separation from the ice and better reduction of impurity concentrations was achieved for diluted (1:10) samples than original refinery wastewater samples. The reason is same as discussed for pulp mill effluent in section 4.1.1.1.

The ranges of percent impurity concentration reduction of ice samples in beaker tests for original and diluted (1:10) refinery wastewater are shown in Table 4.3. The reduction efficiency of impurity concentrations by partial freezing of refinery wastewater

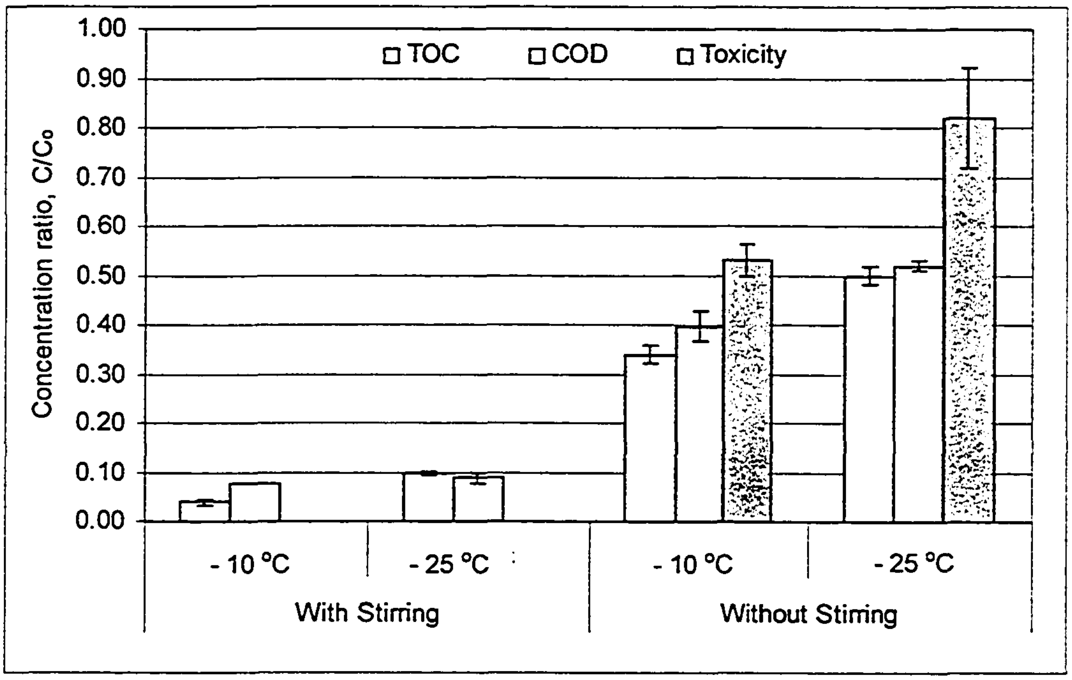


Figure 4.7: Normalized TOC, COD and toxicity in ice samples of original refinery wastewater beaker partial freezing experiments (TOC_0= 14.0 mg/L, COD_0 = 70.0 mg/L, $toxicity_0$ = 1.81 TU)

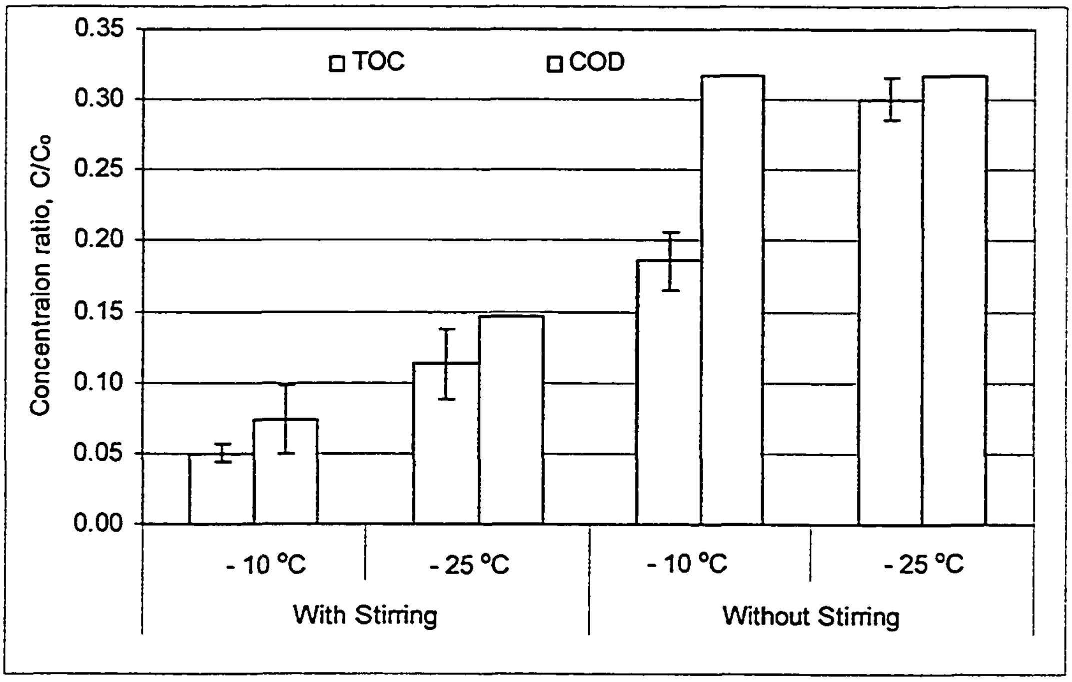


Figure 4.8: Normalized TOC and COD in ice samples of diluted (1:10) refinery wastewater beaker partial freezing experiments (TOC_0 = 1.88 mg/L, COD_0 = 8.34 mg/L)

Table 4.3: The ranges of percent reduction of impurity concentrations in ice samples in beaker tests for original and diluted (1:10) refinery wastewater samples

Refinery wastewater samples	TOC (%)	COD (%)	Toxicity (%)
Original (1:1)	50 to 96	48 to 92	18 to 100
Diluted (1:10)	70 to 95	68 to 93	-

was observed to be higher than that for pulp mill effluent. This might be because of the lower impurity concentration in refinery wastewater (Table 3.2), since it is known that the chances of trapping impurity particle in the growing ice crystals increases with the increase of impurity concentrations in water. Also the chemical nature of the impurities present in pulp mill effluent is different from that of refinery wastewater. Higher inorganic impurities are normally present in refinery wastewater than pulp mill effluent. This could cause the difference as some compounds are easier to be incorporated into the ice structures than others.

Again, the difference in the amount of inorganic impurities present in refinery wastewater and pulp mill effluent (mainly organic impurities) might have played a role in the organic impurity separation efficiency of the wastewaters. It is known that the organic impurity removal efficiency by partial freezing would be reduced if the inorganic impurity concentrations in the solution were increased (Baker, 1970).

Temperature effects were more profound for refinery wastewater experiments than pulp mill effluent experiments. Figure 4.7 and Figure 4.8 indicates that there was an effect of temperature in impurity separation efficiency. Both the figures show that at the warmer temperature (-10 °C) the impurity removal efficiency was higher than that at colder temperature (-25 °C) irrespective of stirring. The reason is same as discussed for pulp mill effluent in section 4.1.1.1.

4.1.2.2. Concentration increase in unfrozen water samples obtained from the partial freezing of original and diluted (1:10) refinery wastewater samples

The normalized impurity concentrations in the unfrozen water samples obtained from the partial beaker freezing experiment of original (TOC, COD and toxicity) and diluted (TOC and COD) refinery wastewater are shown in Figure 4.9 and Figure 4.10, respectively. The diluted refinery wastewater itself was not toxic and the concentrated samples of the unfrozen water samples obtained from the partial freezing of the diluted samples were also not toxic. Like the pulp mill effluent, unfrozen water samples of refinery wastewater also showed an increase in impurity concentrations ($C/C_o > 1.0$). Greater increases of impurity concentrations in unfrozen water samples occurred for diluted (1:10) refinery wastewater samples. Higher impurity concentrations in unfrozen water samples were observed for the refinery wastewater samples which were stirred during partial freezing experiments than the samples which were not stirred.

The ranges of percent increase of impurity concentrations in unfrozen water samples in beaker tests for refinery wastewater samples are shown in Table 4.4. Compared to the pulp mill effluent, the increase of impurity concentrations in unfrozen water samples obtained from the partial freezing of refinery wastewater samples was higher. It was obvious because, the removal of impurities from ice samples of refinery wastewater was higher than that of pulp mill effluent.

Table 4.4: The ranges of percent increase of impurity concentrations in unfrozen water samples in beaker tests for original and diluted (1:10) refinery wastewater

Refinery wastewater samples	TOC (%)	COD (%)	Toxicity (%)
Original (1:1)	80 to 207	95 to 169	216 to 526
Diluted (1:10)	112 to 209	111 to 179	-

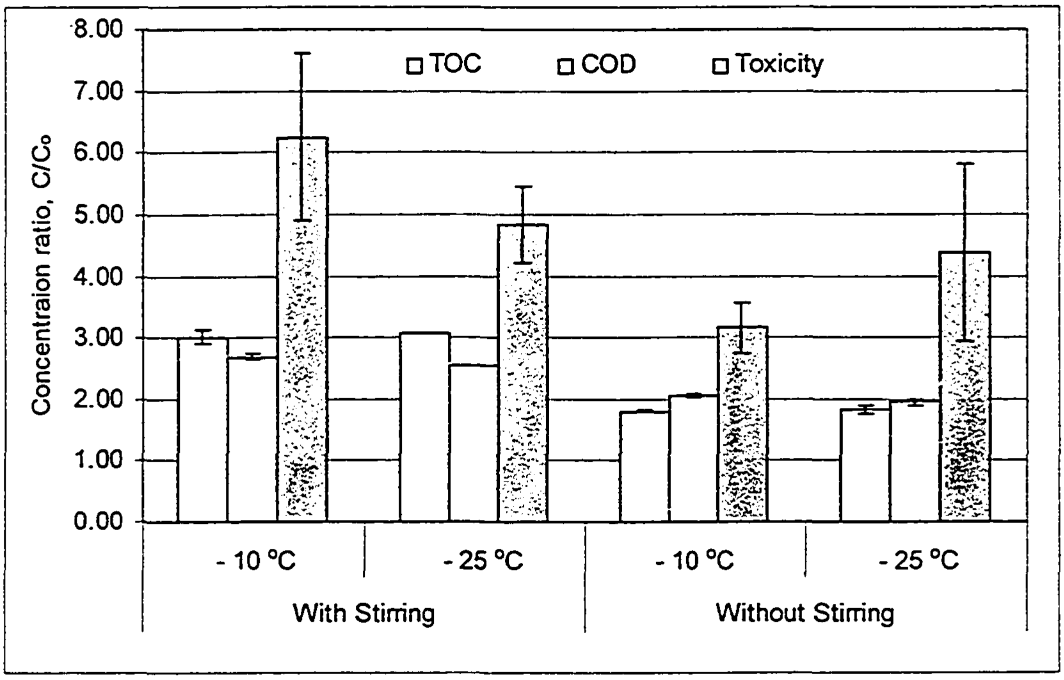


Figure 4.9: Normalized TOC, COD and toxicity in unfrozen water samples of original refinery wastewater beaker partial freezing experiments (TOC_0 = 14.0 mg/L, COD_0 = 70.0 mg/L, $toxicity_0$ = 1.81 TU)

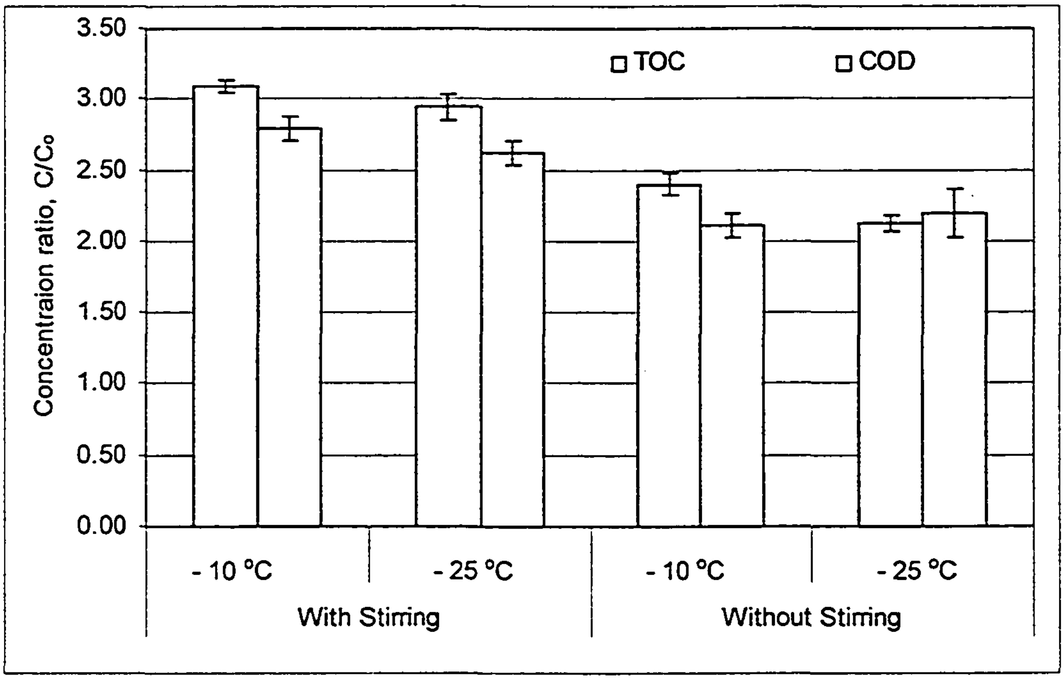


Figure 4.10: Normalized TOC and COD in unfrozen water samples of diluted (1:10) refinery wastewater beaker freezing experiments (TOC_0 = 1.88 mg/L, COD_0 = 8.34 mg/L)

4.1.2.3. Correlation between acute toxicity data and impurity concentrations obtained from the partial freezing experiments of refinery wastewater

Correlations between acute toxicity and the corresponding impurity concentrations of the samples obtained from the partial freezing of refinery wastewater were also investigated. In Figure 4.11 and Figure 4.12, acute toxicity values were plotted against their corresponding TOC and COD values, respectively, obtained from the partial freezing experiments of refinery wastewater. Acute toxicity was observed to be higher for the refinery wastewater than that of pulp mill effluent; though the impurity concentrations of refinery wastewater were lower than that of pulp mill effluent. This might be because of the presence of the elements of higher toxicity in refinery wastewater than the pulp mill effluent or due to the sensitivity of test bacteria to refinery wastewater. The diluted samples of the refinery wastewater were not toxic and the ice and unfrozen water obtained from the partial freezing experiments of the diluted refinery wastewater were also not toxic.

Figure 4.11 and Figure 4.12 show similar pattern. There is a trend that acute toxicity of the samples decreased as TOC and COD decreased. The correlation between acute toxicity and TOC and that between acute toxicity and COD can be linear or non-linear. More data are needed to confirm any correlation. But the trend of reduction of toxicity with the reduction of TOC and COD was more obvious for refinery wastewater samples than that obtained for pulp mill effluent samples (section 4.1.1.3). This might have been caused by the fact that more toxicity data were obtained for refinery wastewater samples.

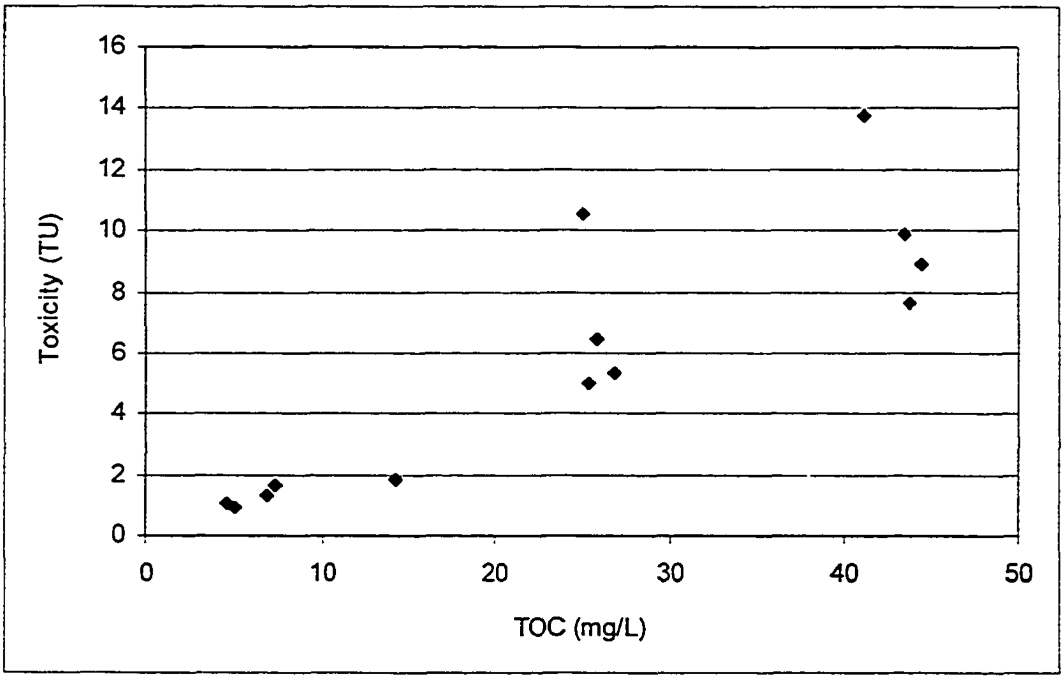


Figure 4.11: Correlation between acute toxicity and TOC of the samples obtained from the partial freezing experiments of refinery wastewater

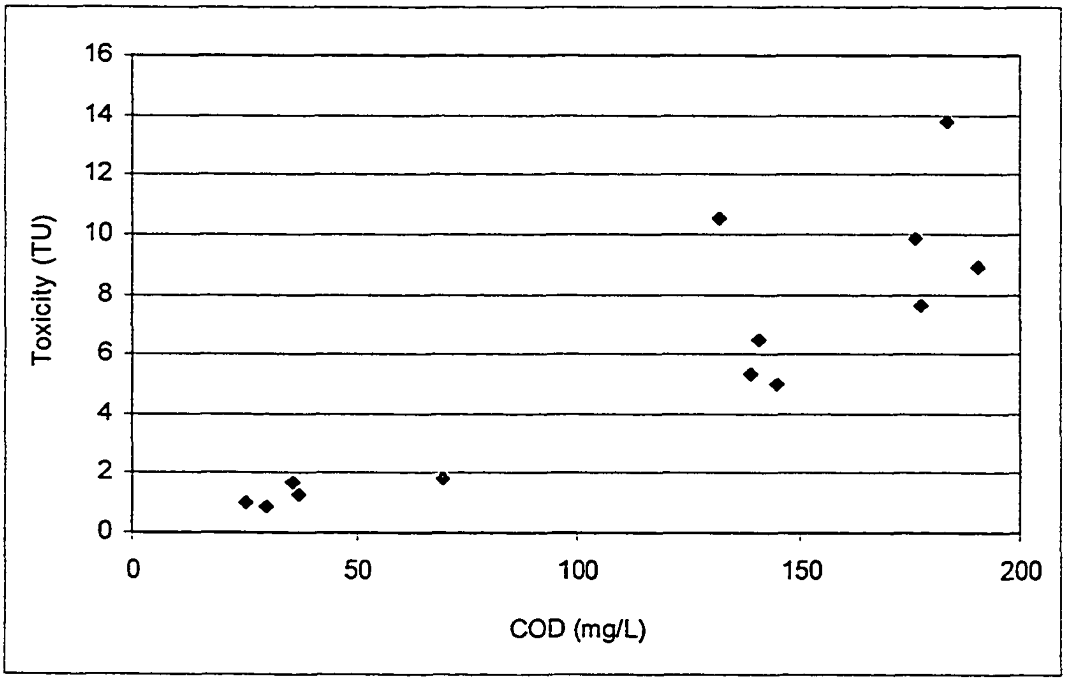


Figure 4.12: Correlation between acute toxicity and COD of the samples obtained from the partial freezing experiments of refinery wastewater

4.1.3. Statistical analysis of the impurity concentrations of ice and unfrozen water samples produced from beaker partial freezing experiment

A statistical analysis was performed on the TOC and COD concentration ratio data of the ice and unfrozen water samples obtained from the partial freezing experiments of pulp mill effluent and refinery wastewater to find out the significant factors for the impurity separation efficiency of partial freezing. Null hypothesis of the analysis was that the factors had no effect on impurity reduction. The p-value is the probability that the sample could have been drawn from the population being tested given the assumption that the null hypothesis is true. A p-value of 0.05 indicates that there is only a 5% chance of drawing the sample being tested if the null hypothesis was actually true. A p-value close to zero indicates that the null hypothesis is false. Table 4.5 shows the p-values for the factors and interactions calculated from a 2^3 factorial experiment with 2 replicates where pulp mill effluent and refinery wastewater were considered as 2 blocks (ANOVA tables are in Appendix B). Since greater reduction of impurity in ice samples means greater increase of impurity in unfrozen water samples, the factorial analysis should provide the same result for both ice and unfrozen water samples.

At 95% confidence level, the factors which have the p-values less than 0.05 are considered to be significant. From Table 4.5 it is observed that the temperature factor was significant for both TOC and COD concentration ratio data for ice samples. The temperature factor was not significant for unfrozen water samples at 95% confidence level, but they could be significant at 85% and 83% confidence level for TOC (p-value = 0.1547) and COD (p-value = 0.1732) concentration data of unfrozen water samples. From the results of impurity separation for pulp mill effluent and refinery wastewater, it was observed that the efficiency of separation was higher for wastewater frozen at -10 °C. The dilution and stirring factors were clearly significant for both ice and unfrozen water samples. From the results of impurity separation for pulp mill effluent and refinery wastewater, it was observed that the efficiency of separation was higher for diluted samples than original samples and when stirring was applied.

Table 4.5: p-values of the factors affecting the ice and unfrozen water samples TOC and COD in the beaker tests of pulp mill effluent and refinery wastewater

Sources of variation	p-values			
	Ice samples		Unfrozen water samples	
	TOC	COD	TOC	COD
Temperature (A)	0.0136	0.0163	0.1547	0.1732
Dilution (B)	0.0000	0.0000	0.0006	0.0000
Stirring (C)	0.0000	0.0000	0.0000	0.0000
Block (Pulp/Refinery)	0.2423	0.0314	0.0000	0.0233
AB	0.4528	0.8527	0.3845	0.6594
AC	0.4853	0.8527	0.4666	0.7315
BC	0.0000	0.0000	0.1194	0.6594
ABC	0.5906	0.2873	0.7795	0.7811

Note: At 95% confidence level, p-value = 0.05

Results obtained from pulp mill effluent were significantly different from refinery wastewater as blocking effect was significant for both ice and unfrozen water samples, expect for the TOC concentration data of ice samples (p-value = 0.2423). It was observed from the TOC and COD concentration ratio data of pulp mill effluent and refinery wastewater that the overall separation efficiency was higher for refinery wastewater than pulp mill effluent.

Temperature interactions with dilution (AB) and stirring (AC) were not significant. Only stirring interaction with dilution factor (BC) was clearly significant for both TOC and COD concentration ratio data of ice samples. From the result of TOC and COD concentration ratios of both pulp mill effluent and refinery wastewater, it was observed that stirring was more effective in impurity separation for original pulp mill effluent and refinery wastewater than for diluted pulp mill effluent and refinery wastewater. Three factor interaction of temperature, dilution and stirring (ABC) was also not significant.

4.2. Spray Freezing and Melting Experiment

Spray freezing and melting experiments were conducted for both industrial (pulp mill effluent and refinery wastewater) and synthetic wastewaters (linoleic acid and abietic acid). During the spray freezing experiments, a mixture of ice (70%) and water (30%) was produced in a tray for each run. The water was drained out of the tray which is called the runoff and collected for analysis. The ice samples, produced from each run, were stored at spray temperature. The stored ice was then melted and the meltwater was sequentially collected for analysis. The results of these experiments are reported into two main sections; impurity separation by runoff and impurity removal from the stored spray ice by melting. The results are discussed in the following sections.

4.2.1. Impurity separation by runoff

The experimental results of the impurity concentrations of the runoff samples are presented in this section. Runoff samples were analysed for TOC, COD, color and toxicity. The impurity concentrations of the runoff samples were normalized to that of original wastewater samples (C/C_o).

4.2.1.1. Impurity separation by runoff during spray freezing experiments of industrial wastewater: pulp mill effluent and refinery wastewater

For both pulp mill effluent and refinery wastewater, four runs of spray freezing experiments were conducted at each temperature (-10 °C and -25 °C) and fours sets of impurity concentration ratio data; TOC, COD and color (only for pulp mill effluent), were obtained at each temperature. For each wastewater, toxicity was only measured for two runoffs generated at each temperature. Average concentration ratios of TOC, COD, color and toxicity of the runoffs produced from the spray freezing are presented in Figure 4.13 and Figure 4.14. It was observed that the impurity concentrations of the runoffs were higher than those of original pulp mill effluent and refinery wastewater, respectively ($C/C_o > 1$). So a certain amount of impurities were carried away by the runoffs from the ice produced from the spray freezing of pulp mill effluent and refinery wastewater (Gao, 1998; Wuite *et al.*, 1999).

Impurity concentration ratios of the runoffs produced from pulp mill effluent and refinery wastewater are listed in Table 4.6. The TOC and COD concentration ratio data of the runoffs produced from pulp mill effluent and refinery wastewater were comparable. Only the toxicity ratio data for the runoffs produced from refinery wastewater were much

Table 4.6: Impurity concentration ratios (C/C_o) of the runoffs produced from pulp mill effluent and refinery wastewater in spray freezing experiments

Wastewater	Spray Temperature (°C)	TOC	COD	Color	Toxicity
Pulp mill	-10	1.97	1.93	1.98	1.86
	-25	1.74	1.72	1.76	1.47
Refinery	-10	1.96	2.14	-	2.51
	-25	1.67	1.81	-	2.88

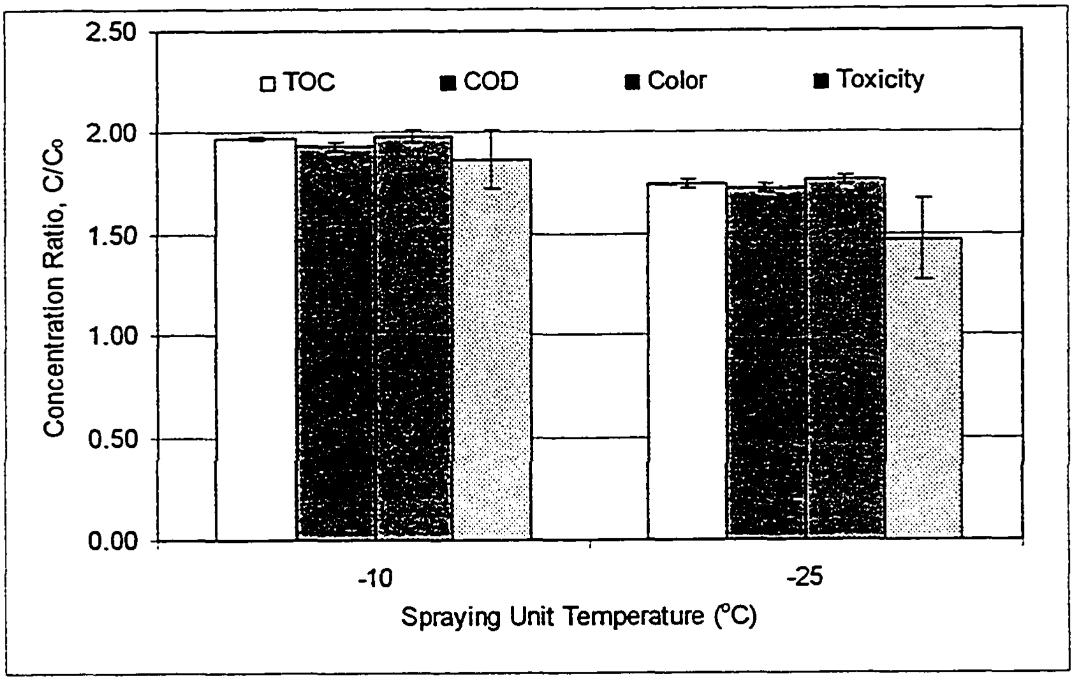


Figure 4.13: Normalized TOC, COD, color and toxicity of runoff at -10 °C and -25 °C for pulp mill effluent (TOC_0 = 254 mg/L, COD_0 = 768 mg/L, $Color_0$ = 912 CU and $toxicity_0$ = 1.27 TU)

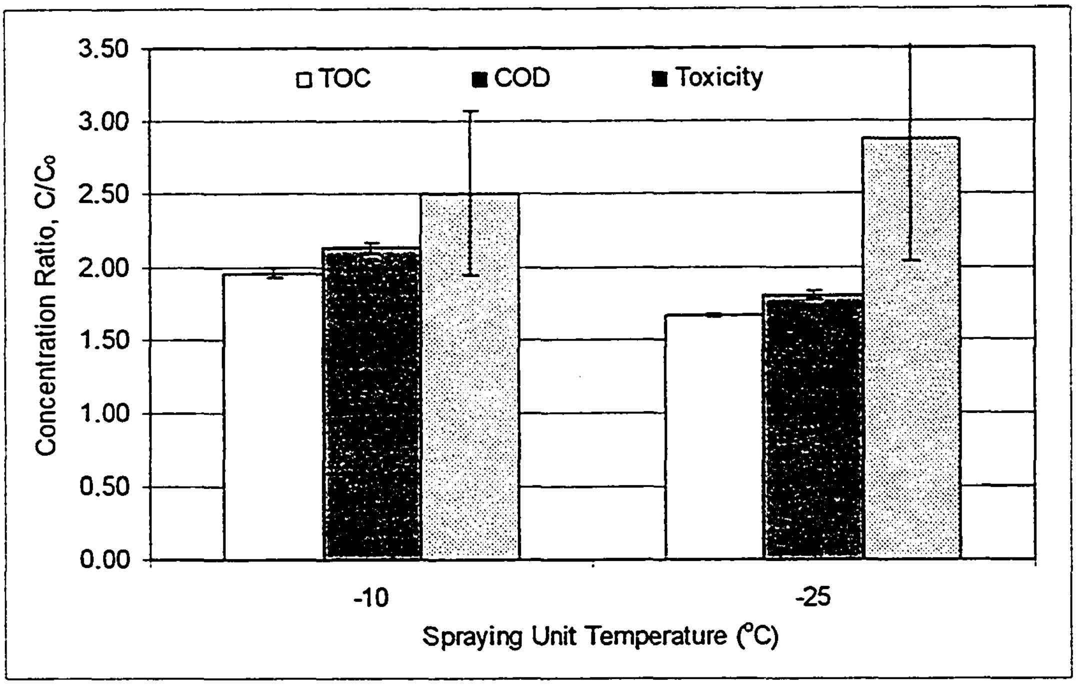


Figure 4.14: Normalized TOC, COD, and toxicity of runoff at -10 °C and -25 °C for refinery wastewater (TOC_0 = 15.1 mg/L, COD_0 = 72.3 mg/L and $toxicity_0$ = 2.39 TU)

higher than those produced from pulp mill effluent. The concentration ratios of the runoffs produced from refinery wastewater were slightly higher than those produced from pulp mill effluent.

It was observed for both of the wastewaters that the higher impurity separation efficiencies by runoffs were observed at the warmer temperature (-10 °C) of spray freezing, as the concentration ratios of the runoffs had higher values at warmer temperature (-10 °C) than at colder temperature (-25 °C). It is known that partial freezing of the wastewater droplets occurs during the spray freezing. The warmer temperatures cause slower movement of the solid-liquid interface of the growing ice crystals and reduce the chance of entrapping impurities in the ice crystals (Hoekstra and Miller, 1967). Unlike all the concentration ratio data, only the toxicity ratio of the runoffs generated from refinery wastewater showed a higher value (2.88) at colder temperature than warmer temperature (Figure 4.14). This might have been caused by experimental error. The toxicity ratio data was the average of the toxicity ratios of two replicates which toxicity ratios were 3.72 and 2.04. Here 3.72 was much higher than 2.04 and might be an erroneous data, which increased the average toxicity ratio value of the runoff generated at the colder temperature.

4.2.1.2. Impurity separation by runoff during spray freezing experiments of synthetic wastewaters: linoleic acid and abietic acid

For both linoleic acid and abietic acid, two runs of spray freezing for 5 mg/L solution and two runs of spray freezing for 20 mg/L solution were conducted at -10 °C and similar runs were conducted also at -25 °C. So, two sets of impurity concentration ratio data; TOC, COD and toxicity, were obtained for each combination of sample concentration and temperature for both acid solutions. Figure 4.15 and Figure 4.16 show the results obtained from freezing of linoleic acid and those of abietic acid solutions are presented in Figure 4.17 and Figure 4.18. As shown in Figure 4.15 to Figure 4.18, the impurity concentrations of the runoffs were higher than the impurity concentrations of original linoleic acid and abietic acid solutions ($C/C_o > 1$).

Impurity concentration ratios of the runoffs produced from linoleic acid and abietic acid are listed in Table 4.7. It was observed that a better impurity separation by runoffs was achieved for lower concentration solutions (5 mg/L) of linoleic acid at both temperatures, as higher impurity concentration ratio data (C/C_o) were observed for lower concentration solutions (5 mg/L) of linoleic acid.

Table 4.7: Impurity concentration ratios (C/C_o) of the runoffs produced from linoleic acid and abietic acid in spray freezing experiments

Solutions	Concentration (mg/L)	Spray Temperature (°C)	TOC (C/C_o)	COD (C/C_o)	Toxicity (C/C_o)
Linoleic acid	5	-10	1.69	1.93	5.72
		-25	1.65	1.63	2.33
	20	-10	1.65	1.66	1.75
		-25	1.58	1.54	1.76
Abietic acid	5	-10	1.73	1.88	2.10
		-25	1.58	1.77	2.46
	20	-10	1.62	1.81	2.05
		-25	1.58	1.52	2.75

Temperature effect was also noticed for impurity separation by runoffs. Warmer temperature showed better impurity separation, as the impurity concentration ratios of the runoffs produced from both 5 mg/L and 20 mg/L linoleic acid solutions had higher values

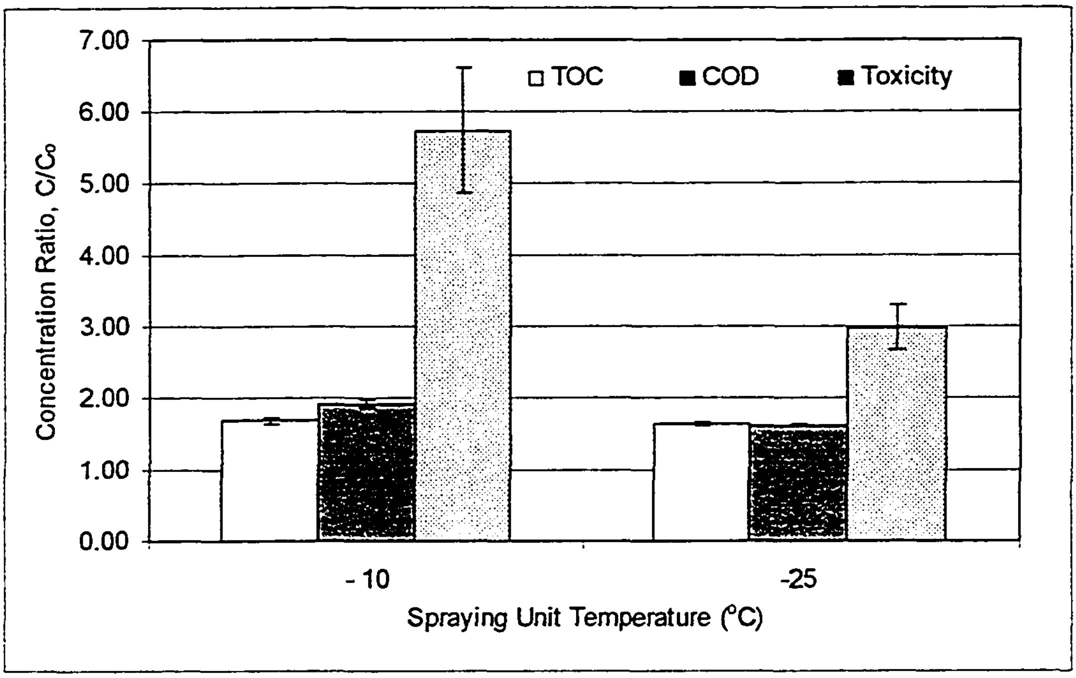


Figure 4.15: Normalized TOC, COD and toxicity of runoff at -10 °C and -25 °C for 5 mg/L linoleic acid sample (TOC_0 = 5.14 mg/L, COD_0 = 26.4 mg/L and $toxicity_0$ = 4.44 TU)

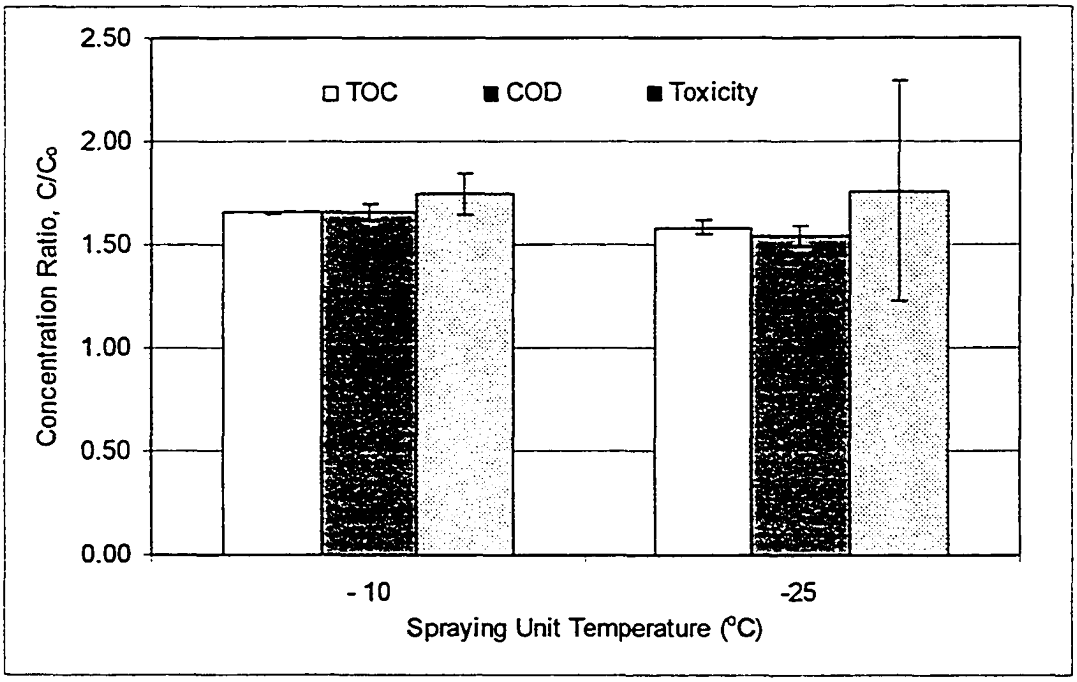


Figure 4.16: Normalized TOC, COD and toxicity of runoff at -10 °C and -25 °C for 20 mg/L linoleic acid sample (TOC_0 = 12.7 mg/L, COD_0 = 54.0 mg/L and $toxicity_0$ = 27.6 TU)

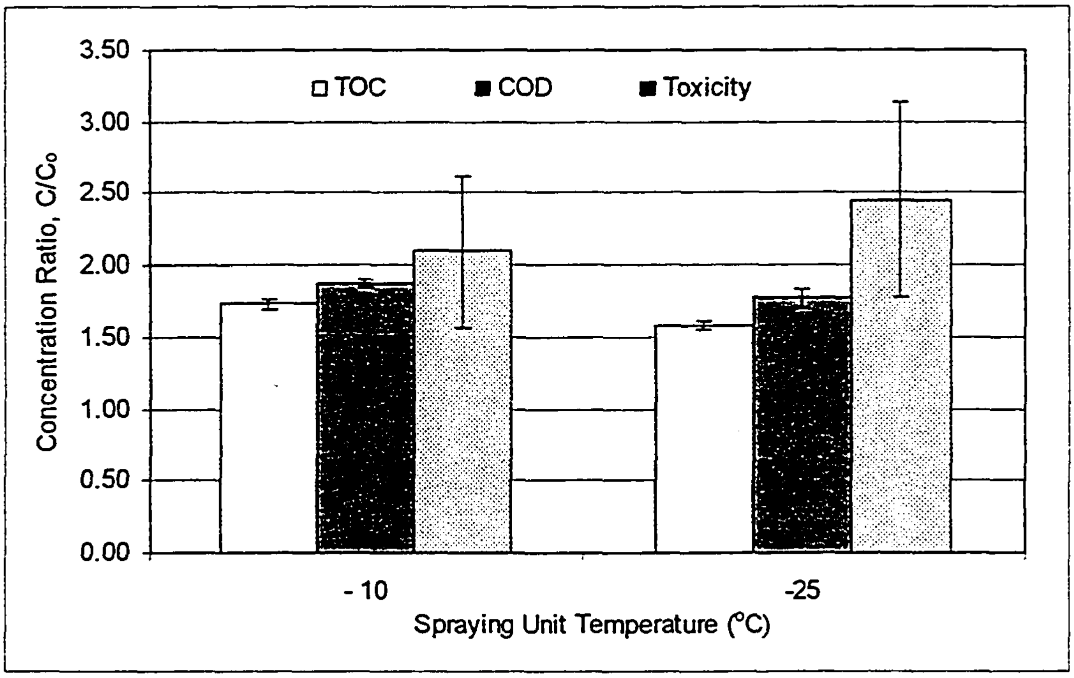


Figure 4.17: Normalized TOC, COD and toxicity of runoff at -10 °C and -25 °C for 5 mg/L abietic acid sample (TOC_0 = 4.57 mg/L, COD_0 = 20.6 mg/L and $toxicity_0$ = 2.62 TU)

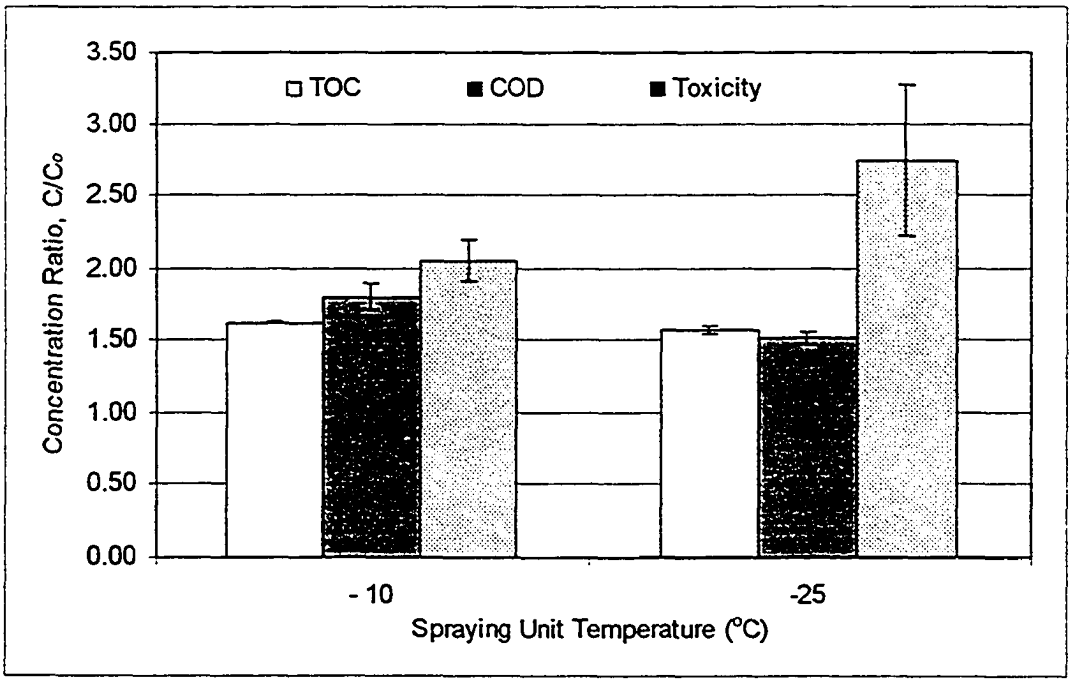


Figure 4.18: Normalized TOC, COD and toxicity of runoff at -10 °C and -25 °C for 20 mg/L abietic acid sample (TOC_0 = 14.5 mg/L, COD_0 = 70.0 mg/L and $toxicity_0$ = 15.7 TU)

at warmer temperature than at colder temperature (Figure 4.15 and Figure 4.16). The toxicity ratio of the runoff produced from the spraying of 5 mg/L linoleic acid solution at -10 °C showed unexpectedly higher value (5.72) which might be a result of measurement error.

Same as the results of linoleic acid solutions, it was observed that a better impurity separation by runoffs was achieved for lower concentration solutions (5 mg/L) of abietic acid at both colder and warmer temperatures, as the impurity concentration ratios (C/C_o) of the runoffs produced from 5 mg/L abietic had higher values than those produced from 20 mg/L abietic acid solutions. The only exception was the toxicity ratio data, which might have been caused by the error in toxicity measurement.

Warmer temperature showed better impurity separation, as the impurity concentration ratios of the runoffs produced from both 5 mg/L and 20 mg/L abietic acid solutions had higher values at warmer temperature than at colder temperature (Figure 4.17 and Figure 4.18). Here, the only exception was the toxicity ratio data. The toxicity ratios of the runoffs produced from the spraying of abietic acid solution at -25 °C showed higher value than those produced at -10 °C, which are inconsistent with the TOC and COD concentration data. This might also be a result of measurement error.

4.2.2. Impurity removal from the stored spray ice by melting

The experimental results of the impurity concentrations of the meltwater samples are presented in this section. Meltwaters were collected sequentially in four consecutive steps. The first portion of meltwater was approximately 7.14% of the total ice volume, and the second, third and fourth portions were approximately 14.3%, 28.6% and 50.0%, respectively, where first 7.14% of the meltwaters were called the initial meltwaters and the last 50.0% of the meltwaters were called the final meltwaters. Meltwater samples were analysed for TOC, COD, color and toxicity. The impurity concentrations of the meltwater samples were normalized to that of original wastewater samples (C/C_o). The normalized impurity concentration ratios were plotted against the cumulative meltwater volume %, which were approximately 7.14%, 21.4%, 50.0% and 100%. The patterns of the graphs were similar to those plotted for ice meltwaters by Johannessen and Henriksen (1977), Brimblecombe *et. al.* (1987) and Gao *et. al.* (2004b).

4.2.2.1. Impurity removal from the stored spray ice, produced from the pulp mill effluent, by melting:

Four runs of spray freezing of pulp mill effluent were carried out at both temperatures (-10 °C and -25 °C) to produce ice samples. Two of the four ice samples produced at -10 °C were stored for 2 days and the other two for 2 weeks. Same storage time was used for the ice samples produced at -25 °C. So there were two replicates and hence two sets of impurity concentration data for each combination of spray temperature and ice storage time. TOC, COD and color were measured for all the samples of each replicate. Only the toxicity was measured for one replicate.

Figure 4.19 to Figure 4.22 show the variation of impurity concentrations (TOC, COD, color and toxicity) of the meltwater during the melting of the ice produced from the spray freezing of pulp mill effluent at -10 °C. Also, the Figure 4.23 to Figure 4.26 show the variation of impurity concentrations (TOC, COD, color and toxicity) of the meltwater during the melting of the ice produced from the spray freezing of pulp mill effluent at -25 °C. From all the figures it was commonly observed that the impurity concentrations of initial meltwater were higher than that of original pulp mill effluent

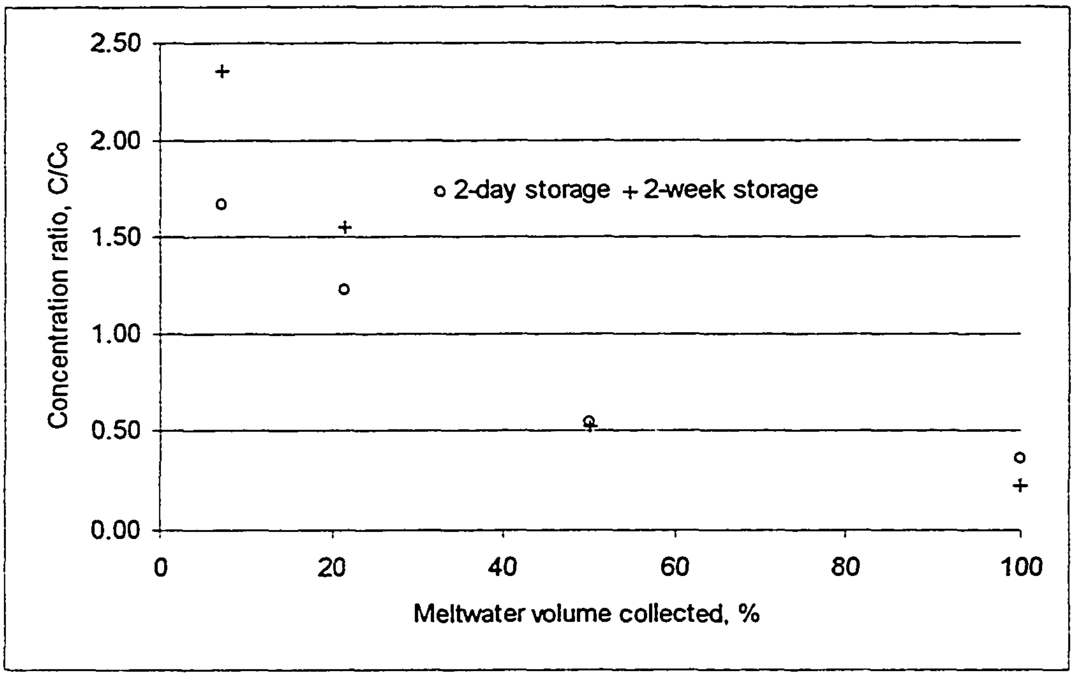


Figure 4.19: Variation of the normalized TOC concentration in the sequential meltwater of the spray ice made from pulp mill effluent at -10 °C, C_0 = 254 mg/L

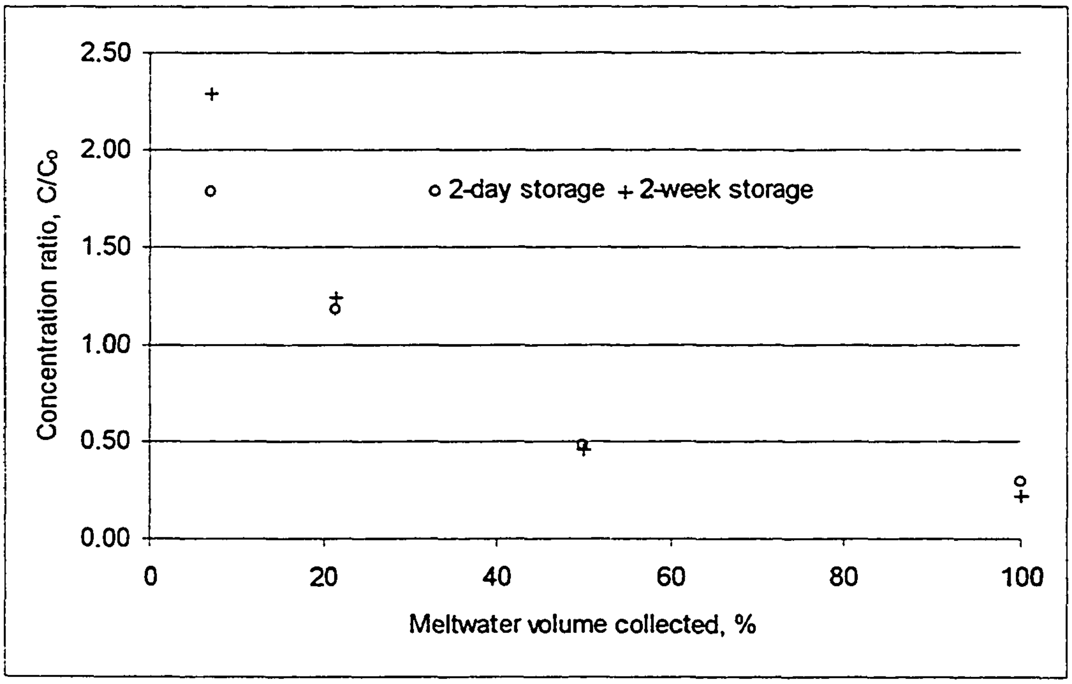


Figure 4.20: Variation of the normalized COD concentration in the sequential meltwater of the spray ice made from pulp mill effluent at -10 °C, C_0 = 768 mg/L

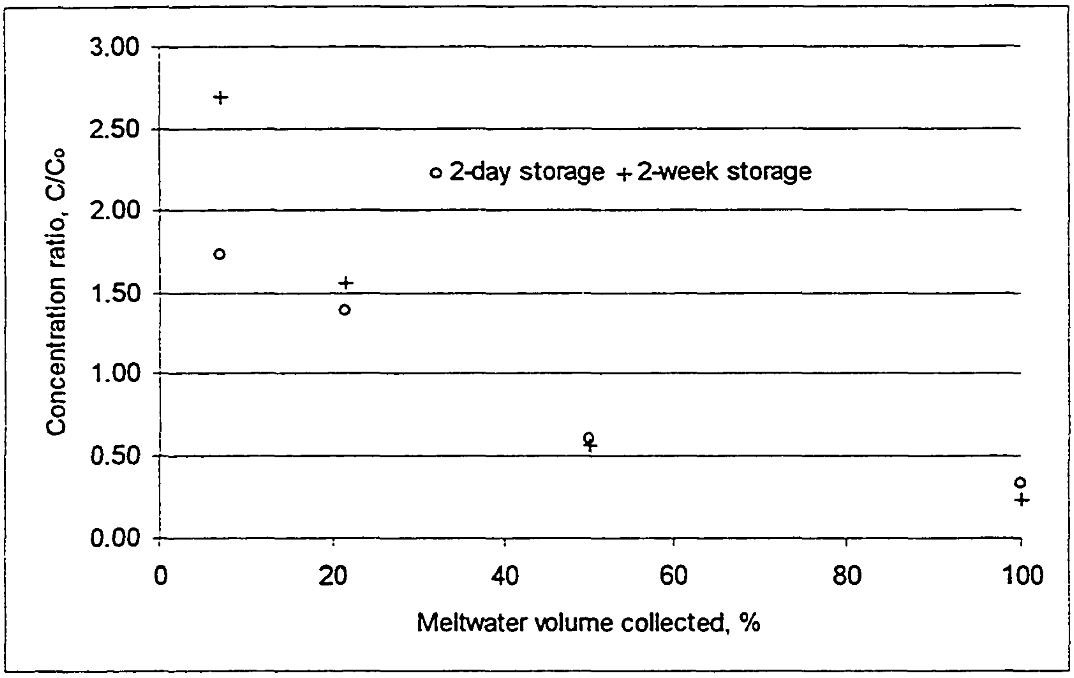


Figure 4.21: Variation of the normalized color concentration in the sequential meltwater of the spray ice made from pulp mill effluent at -10 °C, C_0 = 912 CU

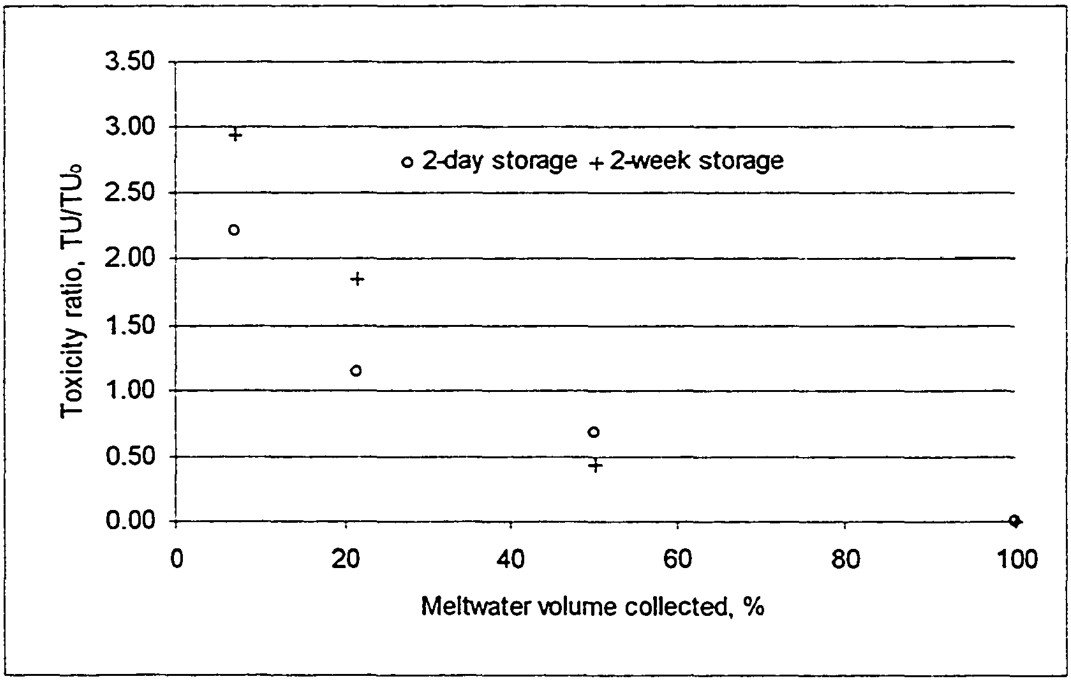


Figure 4.22: Variation of the normalized toxicity in the sequential meltwater of the spray ice made from pulp mill effluent at -10 °C, TU_0 = 1.27 TU

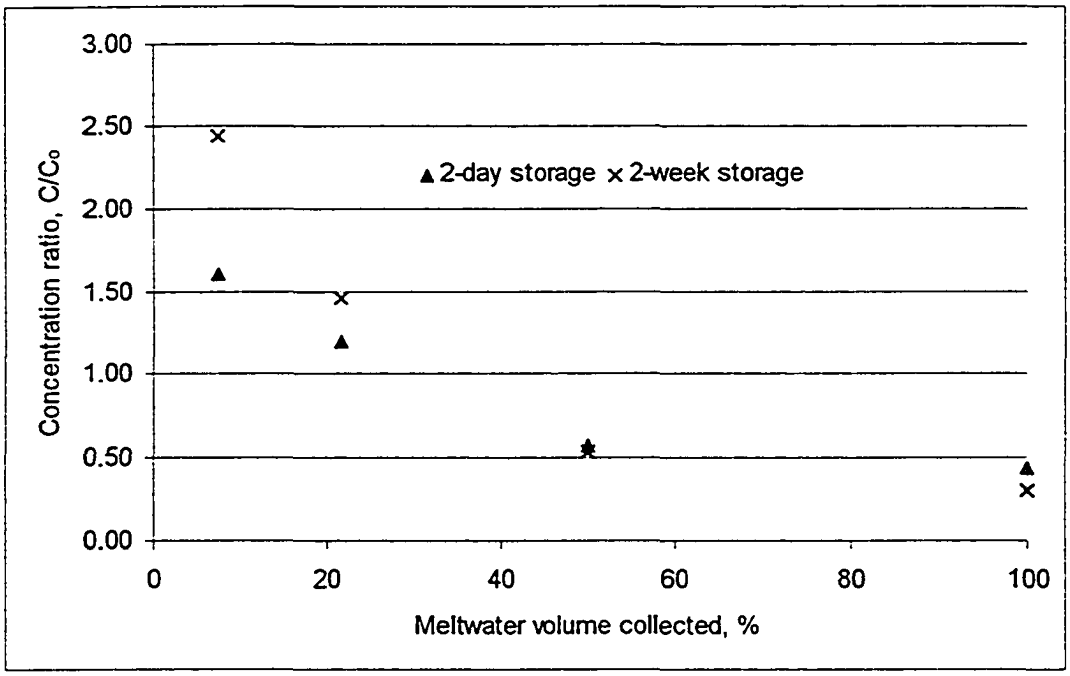


Figure 4.23: Variation of the normalized TOC concentration in the sequential meltwater of the spray ice made from pulp mill effluent at -25 °C, C_0 = 254 mg/L

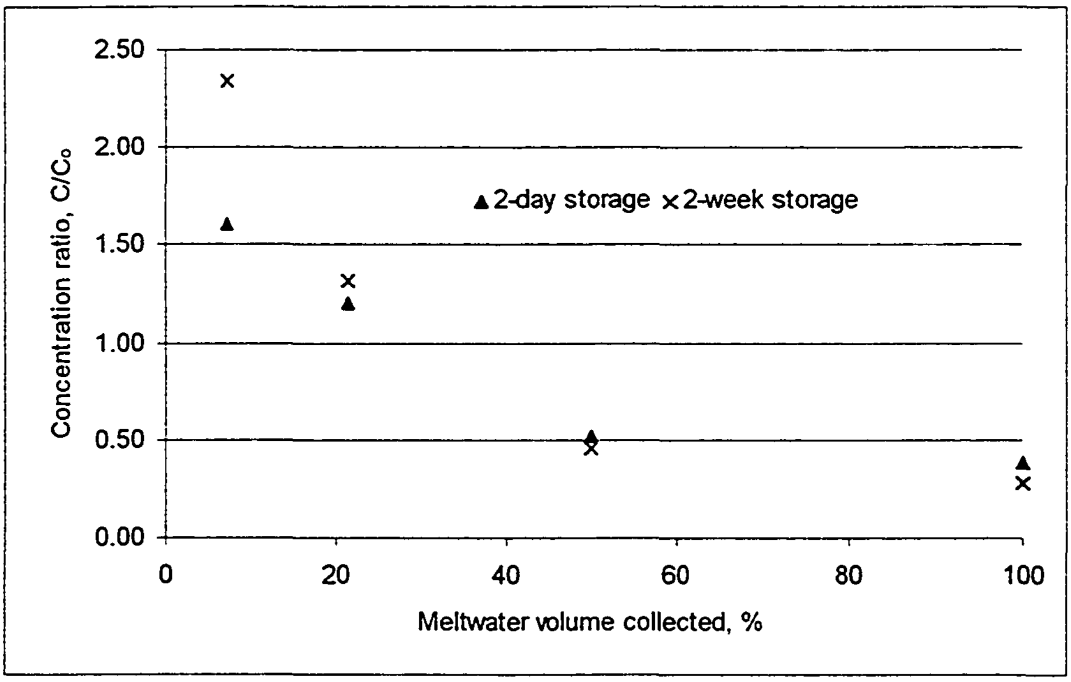


Figure 4.24: Variation of the normalized COD concentration in the sequential meltwater of the spray ice made from pulp mill effluent at -25 °C, C_0 = 768 mg/L

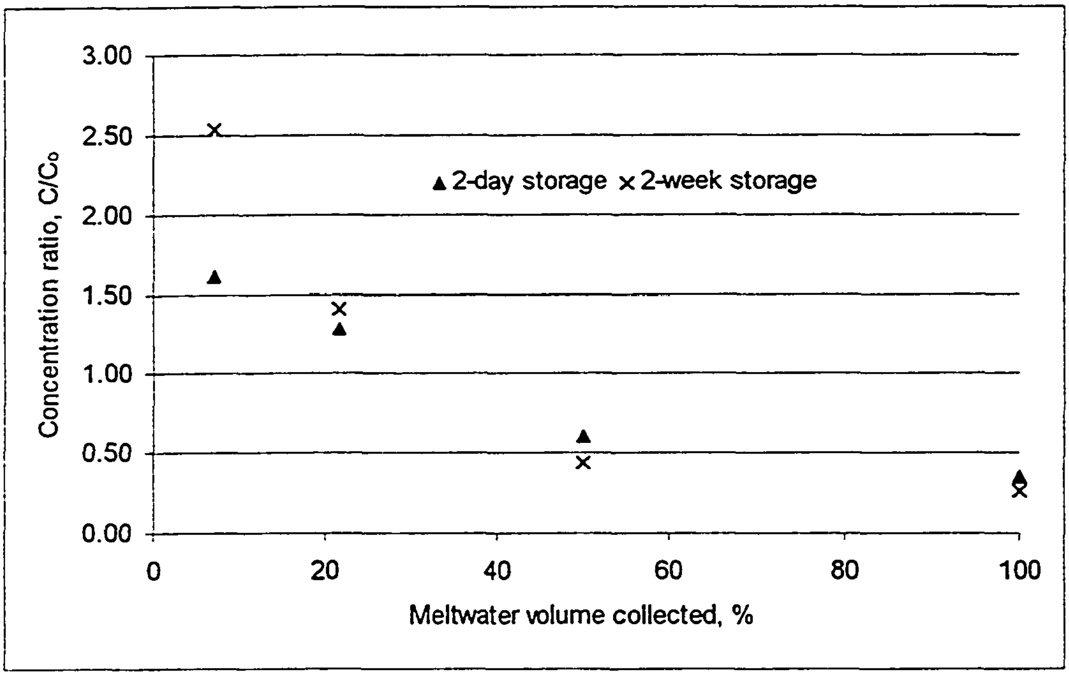


Figure 4.25: Variation of the normalized color concentration in the sequential meltwater of the spray ice made from pulp mill effluent at -25 °C, C_0 = 912 CU

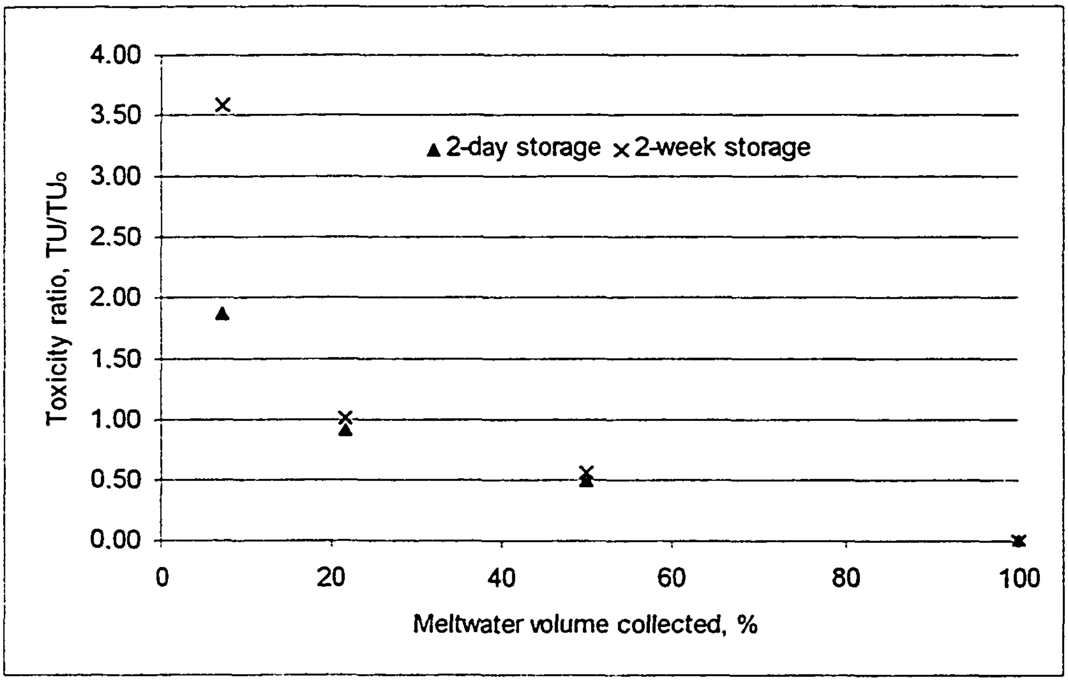


Figure 4.26: Variation of the normalized toxicity in the sequential meltwater of the spray ice made from pulp mill effluent at -25 °C, TU_0 = 1.27 TU

($C/C_o > 1$) (Seip *et al.*, 1980; Gao *et al.*, 2004b; Wuite *et al.*, 1999). Again, it was also commonly observe that the impurity concentrations of final meltwater were lower than that of original pulp mill effluent ($C/C_o<1$). A chemical fractionation occurred during the melting process. Initial meltwater percolated through the ice columns and carried away most of the impurities, leaving less of impurities in the ice columns for the subsequent meltwater to wash away to get the clearer meltwater gradually.

The impurity concentration ratios of the initial meltwaters of the spray ice produced from pulp mill effluent at -10 °C (Figure 4.19 to Figure 4.22) and -25 °C (Figure 4.23 to Figure 4.26) are listed in Table 4.8.

Table 4.8: Impurity concentration ratios (C/C_o) of the initial meltwaters of the spray ice produced from pulp mill effluent

Spray Temperature	Storage Time	TOC (C/C_o)	COD (C/C_o)	Color (C/C_o)	Toxicity (C/C_o)
-10 °C	2 days	1.67	1.78	1.72	2.20
	2 weeks	2.36	2.29	2.69	2.95
-25 °C	2 days	1.61	1.61	1.60	1.87
	2 weeks	2.44	2.34	2.53	3.59

From Table 4.8, there is a clear indication that the ice stored for longer period (2 weeks) had more impurity concentrations in its initial meltwater. The reason might be that the ice grains grow with the storage time and the impurities readjust their position and concentrate to the surface of the ice crystals (Johannessen and Henriksen, 1978). So, for the older ice, more impurities are readily washed away when the initial meltwater percolate down through the ice columns than for the younger ice.

Also, it was observed that the initial meltwater of the ice produced at -10 °C had slightly higher impurity concentration ratios than the initial meltwater of the ice produced at -25 °C. This temperature effect was more profound at shorter storage time (2 days). In the process of ice formation the chances of impurities to be captured in the ice structure is more at colder temperatures, because of the faster rate of freezing. As a result, runoffs with lower impurity concentrations were produced at colder spray temperature than the warmer temperature which left lower concentrations of impurities on the surface of the ice grains and hence the initial meltwater impurity concentrations were low for the ice produced at colder temperature. But the effect of temperatures on the impurity concentrations of initial meltwater was minimized by the longer ice storage time because of the readjustments of impurities on the ice crystal surface with the storage time (Johannessen and Henriksen, 1978), where it is believed to concentrate.

Table 4.9 shows the percent reduction of impurity concentrations in the final 50% of the meltwater. It was noticed that the final 50% of the meltwaters of the ice produced from the pulp mill effluent was not toxic. Other impurity concentrations were reduced up to 57% to 78%. This result can be compared with other pulp mill effluent treatment methods like ozonation or advanced oxidation. Color of pulp mill effluent can be reduced by 58 to 67% with 50 mg/L ozone dose (Mohammed and Smith, 1992). Using advanced oxidation process (ozone with hydrogen peroxide) Murphy *et al.* (1993) achieved 50% color reduction of final effluent of a pulp mill. It was observed that higher impurity reduction for the final 50% of the meltwaters was achieved for the ice samples which had longer storage time (2 weeks) and which were produced at -10 °C. This was because the initial meltwater impurity concentrations were higher for the ice samples which had

Table 4.9: Percent reduction of impurity concentrations in the final 50% of the meltwaters of the spray ice produced from pulp mill effluent

Spray Temperature	Storage Time	TOC (%)	COD (%)	Color (%)	Toxicity (%)
-10 °C	2 days	64	71	67	Not toxic
	2 weeks	77	78	77	Not toxic
-25 °C	2 days	57	61	65	Not toxic
	2 weeks	69	72	73	Not toxic

longer storage time (2 weeks) and hence more impurities were removed from the ice samples by initial meltwaters leaving purer ice behind. The impurity separation by the runoffs and by the initial meltwaters was better achieved at a warmer temperature than at the colder temperature. So, after the runoff and initial meltwater collections, ice samples produced at warmer temperature and stored for longer time had less impurity concentrations than the ice samples produced at colder temperature and stored for shorter time. That is why the percent reduction of impurity concentrations in the final 50% of the meltwaters of the spray ice produced at warmer temperature was higher.

Correlations between acute toxicity and the corresponding impurity concentrations of the samples obtained from the spray freezing and melting experiments of pulp mill effluent were evaluated. Figure 4.27 and Figure 4.28 shows linear correlation between acute toxicity and TOC and that between acute toxicity and COD, respectively. Toxicity data of the original pulp mill effluent, runoffs samples and meltwater samples were incorporated into the plots. Figure 4.27 and Figure 4.28 show similar trend and it is observed that the acute toxicity of the samples decreased linearly as TOC and COD decreased. The correlation between acute toxicity and TOC and that between acute toxicity and COD were strong as the R^2 values were 0.83 and 0.80, respectively.

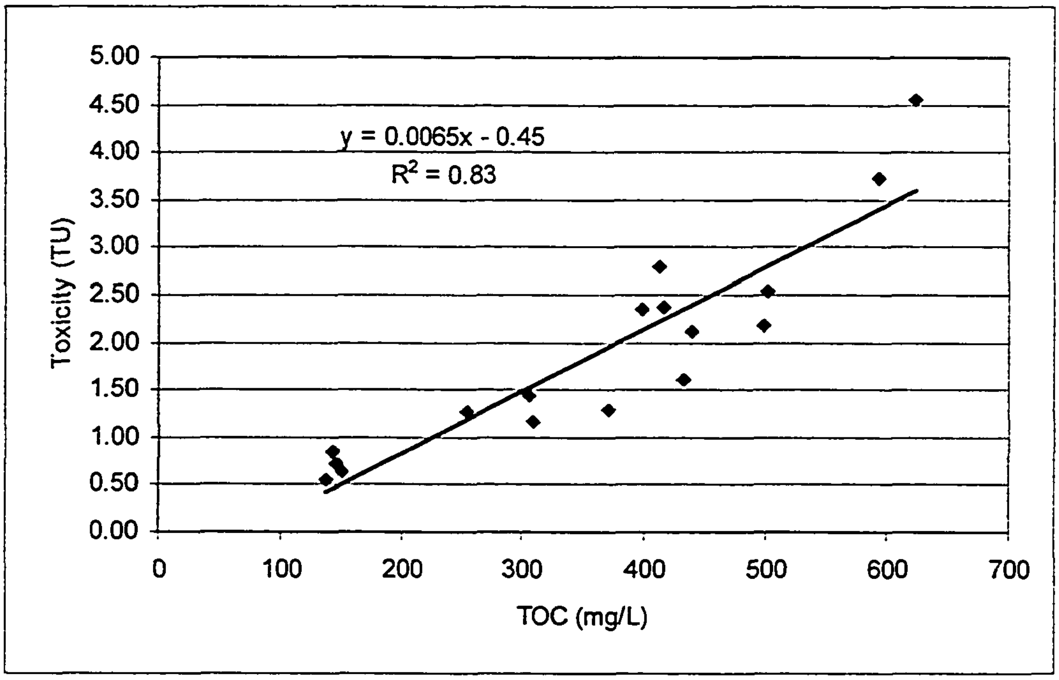


Figure 4.27: Correlation between acute toxicity and TOC of the samples obtained from the spray freezing experiments of pulp mill effluent

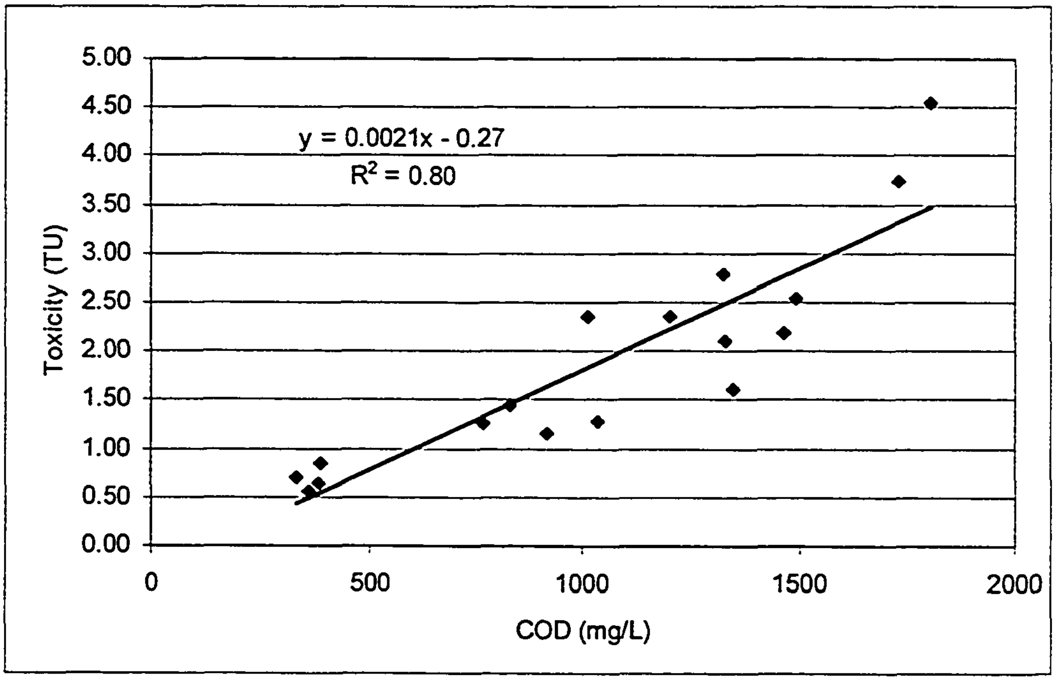


Figure 4.28: Correlation between acute toxicity and COD of the samples obtained from the spray freezing experiments of pulp mill effluent

4.2.2.2. Impurity removal from the stored spray ice, produced from refinery wastewater, by melting

The spray freezing and ice melting procedures for the refinery wastewater were the same as pulp mill effluent described in section 4.2.2.1.

Figure 4.29 to Figure 4.31 show the variation of impurity concentrations (TOC, COD and toxicity) of the meltwater during the melting of the ice produced from the spray freezing of refinery wastewater at -10 °C. Also the Figure 4.32 to Figure 4.34 show the variation of impurity concentrations (TOC, COD and toxicity) of the meltwater during the melting of the ice produced from the spray freezing of refinery wastewater at -25 °C. The pattern of the plots are similar to that of pulp mill effluent, where the impurity concentrations of initial meltwater were higher than that of original refinery wastewater ($C/C_o>1$) and the gradual decrease of impurity concentration ratios of the meltwater caused the impurity concentrations of final meltwater to be lower than that of original refinery wastewater ($C/C_o<1$).

The impurity concentration ratios of the initial meltwaters of the spray ice produced from refinery wastewater at -10 °C (Figure 4.29 to Figure 4.31) and -25 °C (Figure 4.32 to Figure 4.34) are listed in Table 4.10. Most of the impurity concentration ratio data of the initial meltwaters of the ice produced from refinery wastewaters showed higher corresponding values than that of the ice produced from pulp mill effluent. The runoffs generated from the spray freezing of refinery wastewaters also showed higher values impurity concentration ratios than the corresponding values of impurity concentration ratios of the runoffs generated from the spray freezing of pulp mill effluent. So, it can be assumed that the surface of the ice crystals after runoffs had higher

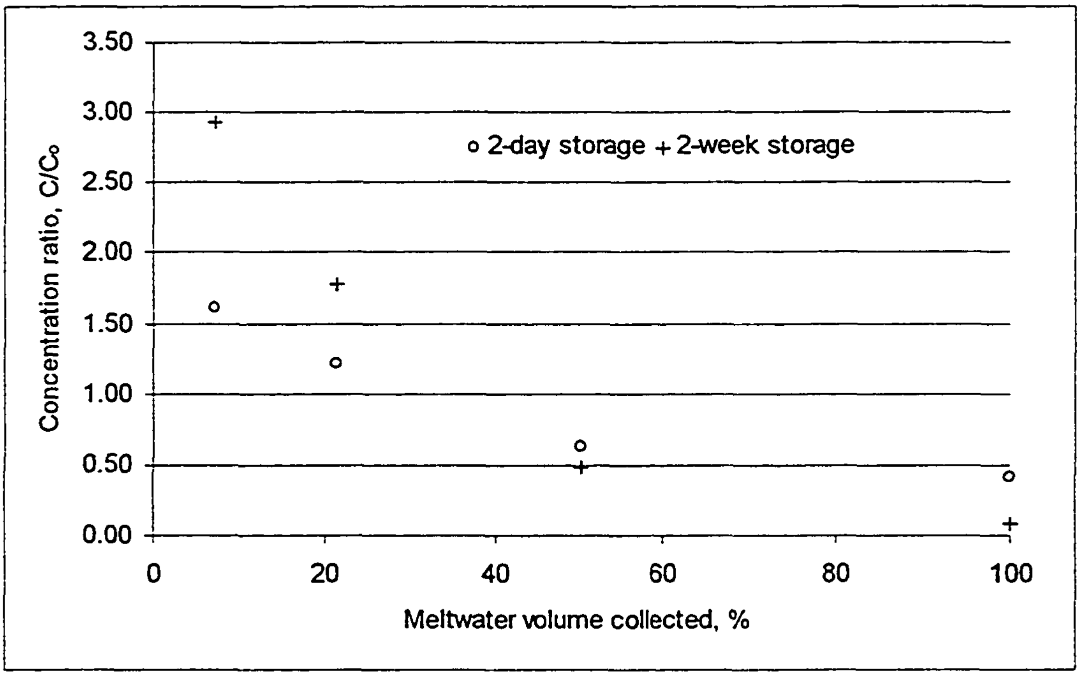


Figure 4.29: Variation of the normalized TOC concentration in the sequential meltwater of the spray ice made from refinery wastewater at -10 °C, C_0 = 15.1 mg/L

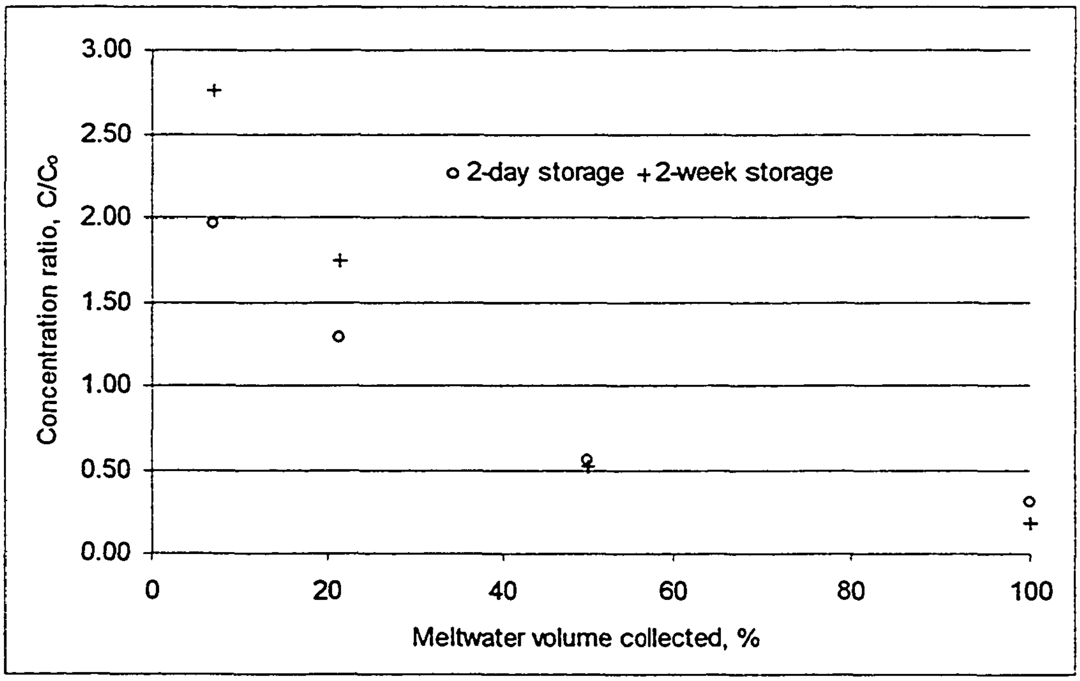


Figure 4.30: Variation of the normalized COD concentration in the sequential meltwater of the spray ice made from refinery wastewater at -10 °C, C_0 = 72.3 mg/L

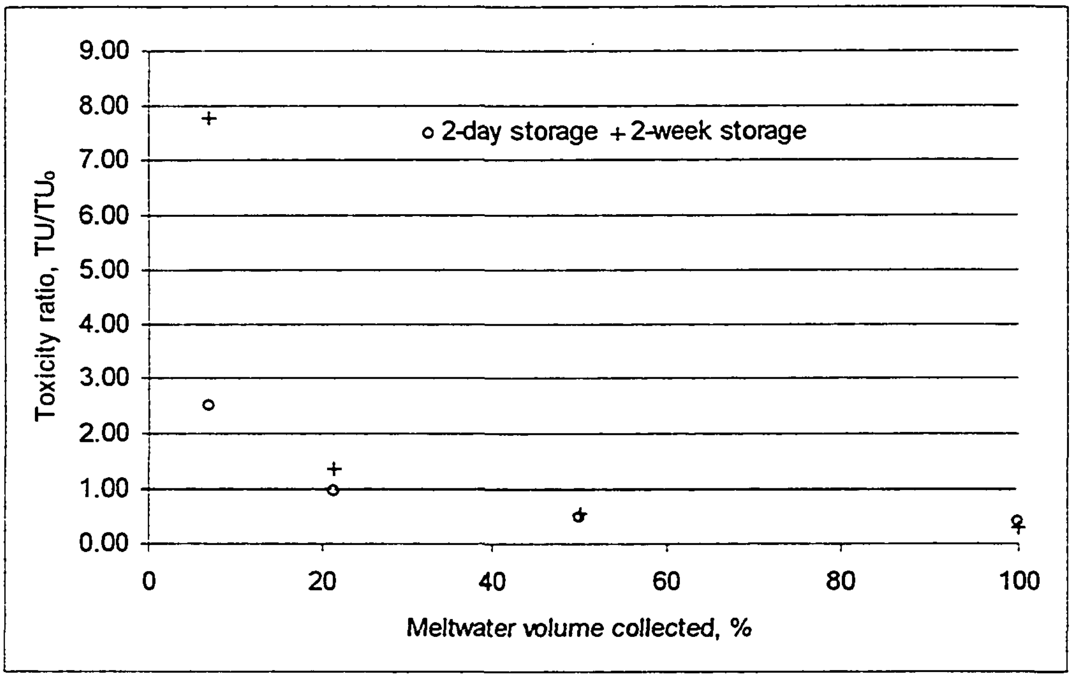


Figure 4.31: Variation of the normalized toxicity in the sequential meltwater of the spray ice made from refinery wastewater at -10 °C, $TU_0 = 2.39$ TU

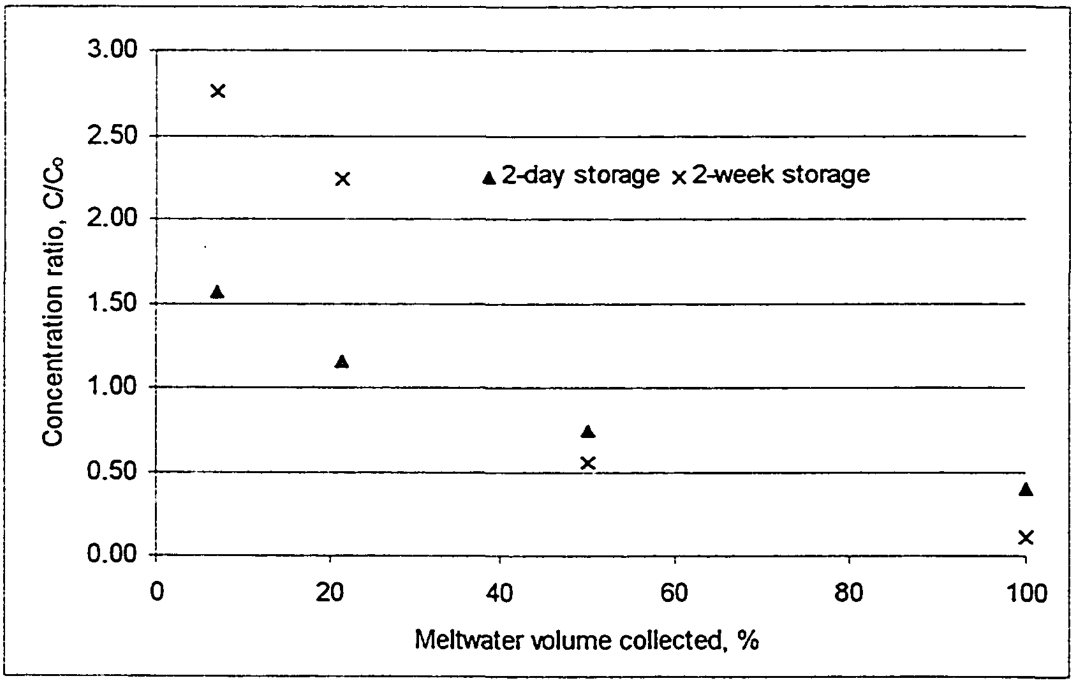


Figure 4.32: Variation of the normalized TOC concentration in the sequential meltwater of the spray ice made from refinery wastewater at -25 °C, $C_0 = 15.1$ mg/L

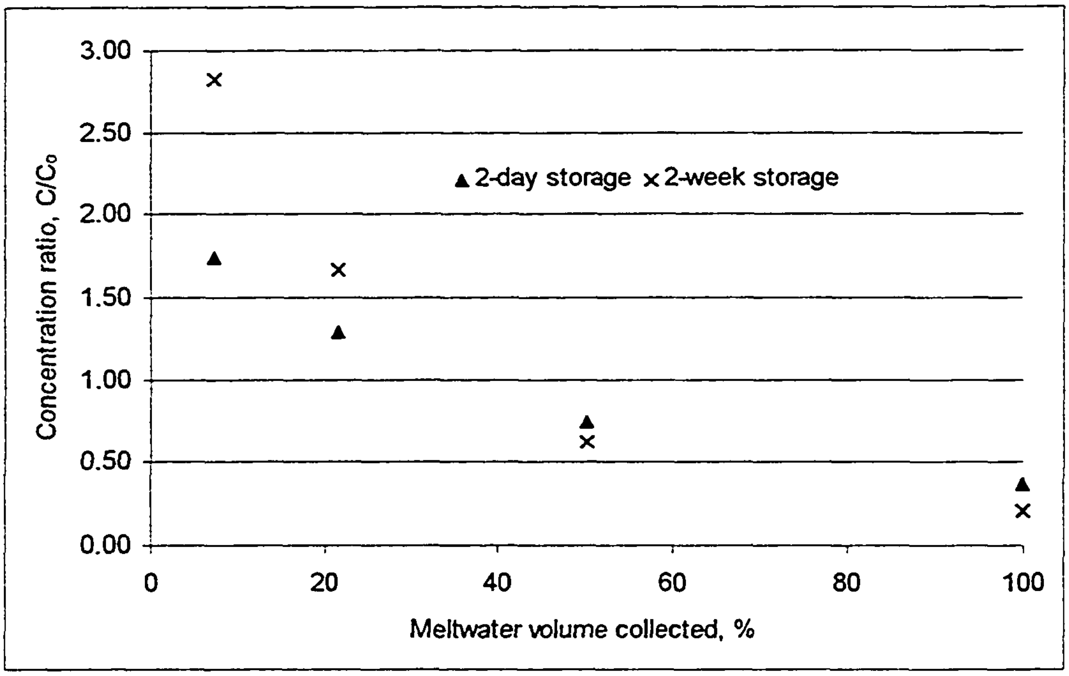


Figure 4.33: Variation of the normalized COD concentration in the sequential meltwater of the spray ice made from refinery wastewater at -25 °C, $C_0 = 72.3$ mg/L

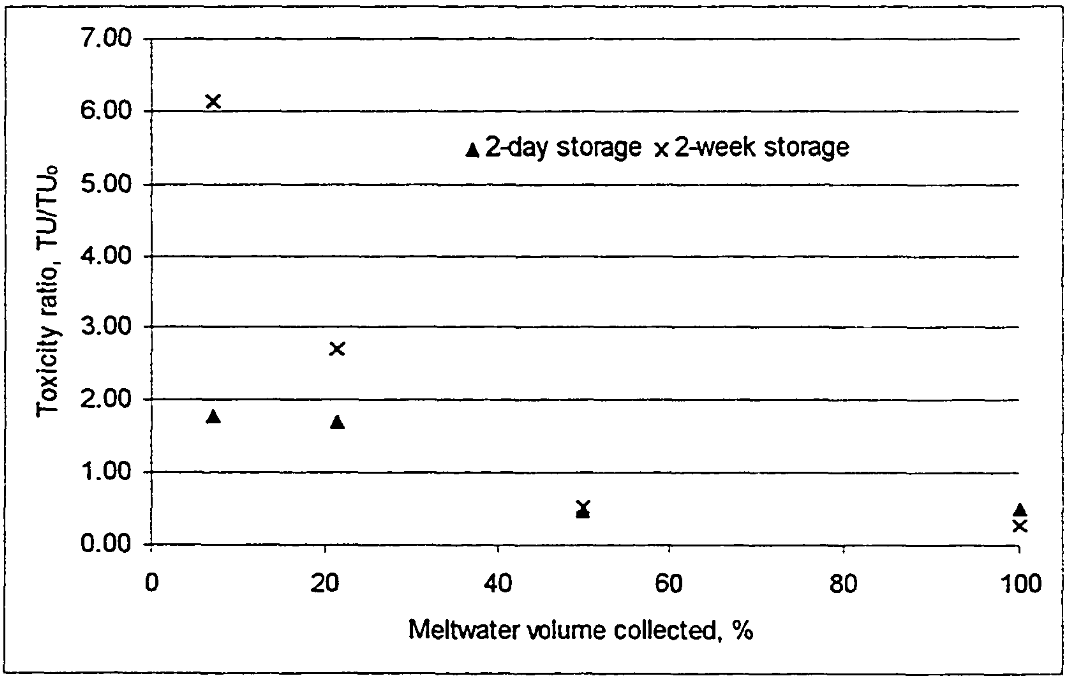


Figure 4.34: Variation of the normalized toxicity in the sequential meltwater of the spray ice made from refinery wastewater at -25 °C, $TU_0 = 2.39$ TU

Table 4.10: Impurity concentration ratios (C/C_o) of the initial meltwaters of the spray ice produced from refinery wastewater

Spray Temperature	Storage Time	TOC (C/C_o)	COD (C/C_o)	Toxicity (C/C_o)
-10 °C	2 days	1.60	1.96	2.50
	2 weeks	2.93	2.75	7.78
-25 °C	2 days	1.75	1.74	1.78
	2 weeks	2.76	2.83	6.13

impurity concentration ratios for refinery wastewaters than pulp mill effluent. Also, the difference of the nature of the wastewaters could play a role. The readjustments of the impurity elements in the ice crystal could be different for different wastewaters. It was observed that the ice stored for a longer period (2 weeks) had more impurity concentrations in its initial meltwater. The initial meltwater of the ice produced at warmer temperature (-10 °C) had slightly higher impurity concentration ratios than the initial meltwater of the ice produced at colder temperature (-25 °C). The temperature effect was more profound at shorter storage time (2 days). All of these results are similar to that of pulp mill effluent and were discussed in section 4.2.2.1.

Table 4.11 shows the percent reduction of impurity concentrations in the final 50% of the meltwater samples of the ice produced from refinery wastewater. Unlike the case of pulp mill effluent, it was noticed that the final 50% of the meltwaters of the ice produced from the refinery wastewater remained toxic at a lower level. But for the case of pulp mill effluent, the final 50% of the meltwater samples were not toxic. It can be caused by the presence of higher toxic element in refinery wastewater, though higher separation of impurities was achieved for refinery wastewater than pulp mill effluent.

Table 4.11: Percent reduction of impurity concentrations in the final 50% of the meltwaters of the spray ice produced from refinery wastewater

Spray Temperature	Storage Time	TOC (%)	COD (%)	Toxicity (%)
-10 °C	2 days	58	70	59
	2 weeks	91	82	69
-25 °C	2 days	60	64	48
	2 weeks	89	79	73

TOC and COD impurity concentrations were reduced up to 58% to 91%. It was observed that higher impurity reduction for the final 50% of the meltwaters was achieved for the ice samples which had longer storage time (2 weeks) and which were produced at warmer temperature (-10 °C). This was because the initial meltwater impurity concentrations were higher for the ice samples which had longer storage time (2 weeks) and hence more impurities were removed from the ice samples by initial meltwaters leaving purer ice behind. At warmer temperatures, the impurity separation by the runoffs and by the initial meltwaters was better achieved than at colder temperature. So, after the runoff and initial meltwater collections, ice samples produced at the warmer temperature and stored for longer time had less impurity concentrations than the ice samples produced at colder temperature and stored for shorter time. That is why the percent reduction of impurity concentrations in the final 50% of the meltwaters of the spray ice produced at warmer temperature was higher.

Toxicity removal of refinery wastewater by spray freezing and melting experiments was further investigated by evaluating the correlations between acute toxicity and the corresponding impurity concentrations of the samples obtained from the spray freezing and melting experiments. Figure 4.35 and Figure 4.36 shows exponential correlation between acute toxicity and TOC and that between acute toxicity and COD, respectively. Toxicity data of the original refinery wastewater, runoffs samples and meltwater samples were incorporated into the plots.

Figure 4.35 and Figure 4.36 produce similar trend and it is observed that the acute toxicity of the samples decreased exponentially as TOC and COD decreased. There were strong exponential correlations between the toxicity and the impurity concentrations, since R^2 values for the correlations between acute toxicity and TOC and between acute toxicity and COD were 0.91 and 0.92, respectively.

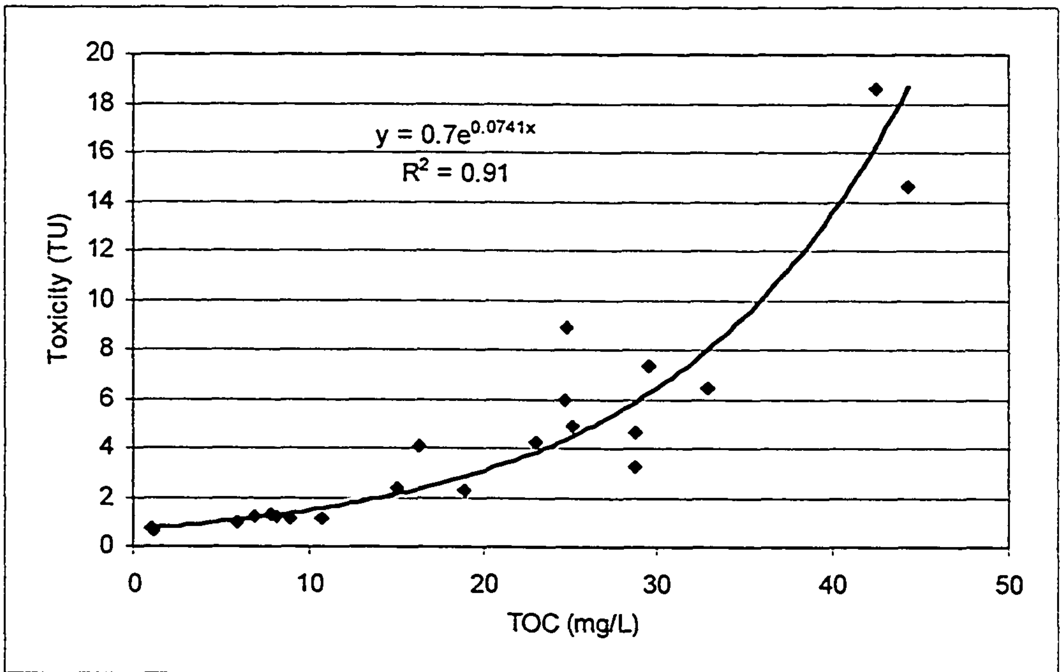


Figure 4.35: Correlation between acute toxicity and TOC of the samples obtained from the spray freezing experiments of refinery wastewater

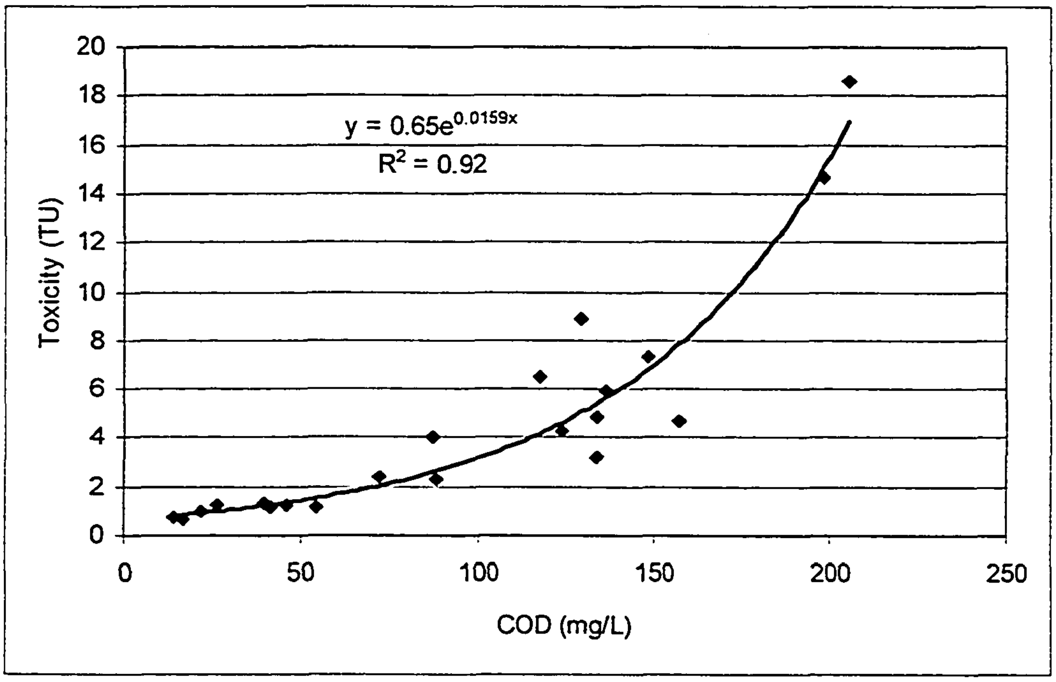


Figure 4.36: Correlation between acute toxicity and COD of the samples obtained from the spray freezing experiments of refinery wastewater

4.2.2.3. Statistical analysis of the meltwater impurity concentrations of the ice samples produced from the pulp mill effluent and refinery wastewater

A statistical analysis was performed on the TOC and COD concentration ratio data of the initial and final meltwater samples of the ice produced from the spray freezing of pulp mill effluent and refinery wastewater to find out the significant factors for the impurity separation efficiency of initial meltwater and final meltwater. Table 4.12 shows the p-values for the factors and interactions calculated from a 2^2 factorial experiment with 2 replicates where pulp mill effluent and refinery wastewater were considered as 2 blocks.

From Table 4.12 it is observed that the spray temperature factor was not statistically significant at 95% confidence level except for the COD concentration ratio data of final meltwater (p-value = 0.0001). It was observed in the section 4.2.2.1. and

Table 4.12: p-values of the factors affecting the initial and final meltwater TOC and COD in pulp mill effluent and refinery wastewater ice melting experiment

Sources of variation	p-values			
	Initial meltwater		Final meltwater	
	TOC	COD	TOC	COD
Block (Pulp/Refinery)	0.0639	0.0003	0.0431	0.0086
Temperature (A)	0.6214	0.2842	0.2563	0.0001
Storage Time (B)	0.0000	0.0000	0.0001	0.0000
AB	0.9791	0.0569	0.7501	0.1252

Note: At 95% confidence level p-value = 0.05

section 4.2.2.2. that there was a slight effect of spray temperature on the meltwater impurity concentrations, where the warmer spray temperature caused higher impurity concentration in initial meltwater and lower impurity concentration in final meltwater, but statistically the effect was not enough to be significant. Therefore, as long as the same percentage of runoff was produced from the spray freezing operation, the temperature will not be a factor influencing the impurity reduction efficiency.

The ice storage time factor was clearly significant for both TOC and COD concentration data (p-values are almost zero). It was observed in the section 4.2.2.1. and section 4.2.2.2. that there was a clear effect of ice storage time on the meltwater impurity concentrations, where for longer storage time the impurity concentrations were higher in initial meltwaters and the impurity concentrations were lower in final meltwaters.

The spray temperature and ice storage time interaction was not statistically significant at 95% confidence level except for the COD concentration data of initial meltwater (p-value = 0.0569). It was observed in the section 4.2.2.1. and section 4.2.2.2. that the effect of spray temperature on the meltwater impurity concentrations was reduced as the ice storage time was increased, but the interaction effect might not be enough to be statistically significant at 95% confidence level.

The block effect was significant at 95% confidence level as the p-values were less than 0.005, except for the TOC concentration data of initial meltwater (p-value = 0.0639). So the impurity removal efficiency was significantly different for pulp mill effluent and refinery wastewater. It was observed in the section 4.2.2.1. and section 4.2.2.2. that the impurity concentration ratios of the initial meltwaters of the ice produced from refinery wastewater was higher than that of the initial meltwaters of the ice produced from the pulp mill effluent. Impurity concentration ratios of the final meltwaters of the ice produced from refinery wastewater was lower than that of the final meltwaters of the ice produced from the pulp mill effluent. The reasons behind the differences in pulp mill effluent and refinery wastewater results were discussed in section 4.2.2.2.

4.2.2.4. Impurity removal from the stored spray ice produced from linoleic acid solutions, by melting

Linoleic acid samples of the concentration of 5 mg/L and 20 mg/L were used for the spray freezing and ice melting of linoleic acid solutions. Two runs of spray freezing of linoleic acid solutions for each concentration were carried out at both temperatures (-10 °C and -25 °C) to produce ice samples. One of the two ice samples for each concentration, produced at -10 °C was stored for 2 days and the other for 2 weeks. Same was done for the ice samples produced at -25 °C. TOC, COD and toxicity of the meltwaters were measured and so, there were only one set of impurity concentration data (TOC, COD and toxicity) for each combination of linoleic acid concentrations, spray temperatures and ice storage time.

Figure 4.37 to Figure 4.39 show the variation of impurity concentrations (TOC, COD and toxicity) of the meltwater during the melting of the ice produced from the spray freezing of linoleic acid samples of concentration 5 mg/L at -10 °C. Figure 4.40 to Figure 4.42 show the variation of impurity concentrations (TOC, COD and toxicity) of the meltwater during the melting of the ice produced from the spray freezing of linoleic acid samples of concentration 20 mg/L at -10 °C. Figure 4.43 to Figure 4.45 show the variation of impurity concentrations (TOC, COD and toxicity) of the meltwater during the melting of the ice produced from the spray freezing of linoleic acid samples of concentrations 5 mg/L at -25 °C. Figure 4.46 to Figure 4.48 show the variation of impurity concentrations (TOC, COD and toxicity) of the meltwater during the melting of the ice produced from the spray freezing of linoleic acid samples of concentrations 20 mg/L at -25 °C.

The meltwaters of the ice samples, produced from the spray freezing of linoleic acid solutions of concentrations 5 mg/L and 20 mg/L, showed the same pattern as pulp mill effluent (section 4.2.2.1.) and refinery wastewater (section 4.2.2.2.). The initial meltwater had higher impurity concentration than that of original linoleic acid solutions ($C/C_o>1$). The impurity concentration of the meltwater decreased gradually and finally the impurity concentrations of final meltwater were lower than that of original linoleic acid solutions ($C/C_o<1$). The only additional step taken for linoleic acid solutions was the use of two different concentrations of linoleic acid to produce ice by spraying to observe the concentration effect on meltwater impurity separation.

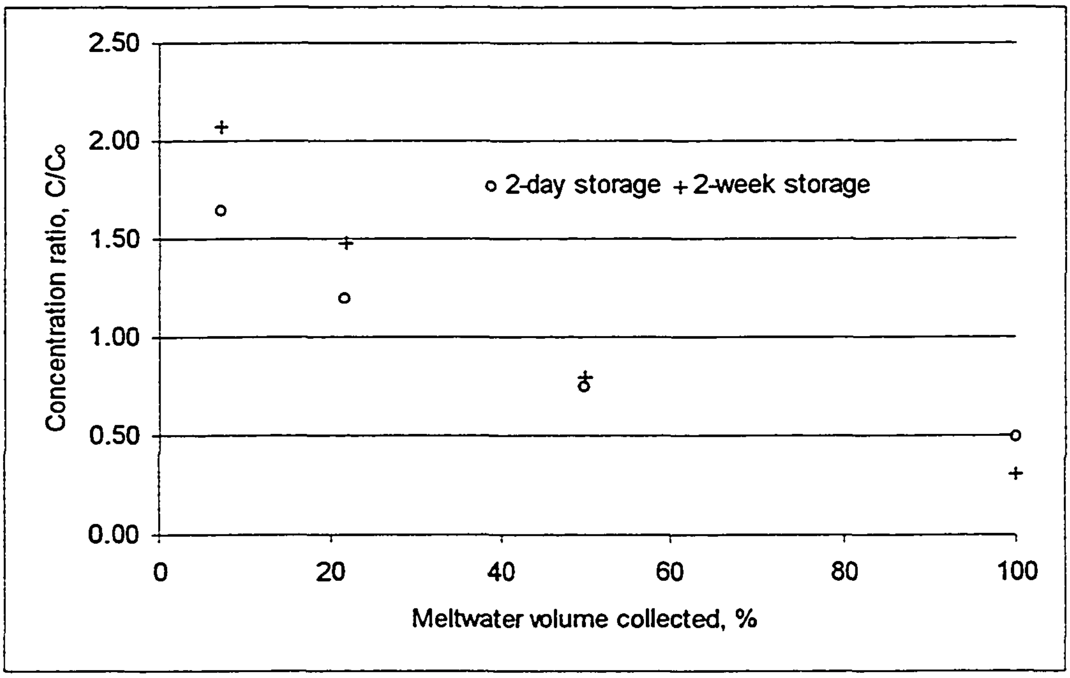


Figure 4.37: Variation of the normalized TOC concentration in the sequential meltwater of the spray ice made from 5 mg/L linoleic acid at -10 °C, $C_0 = 5.14$ mg/L

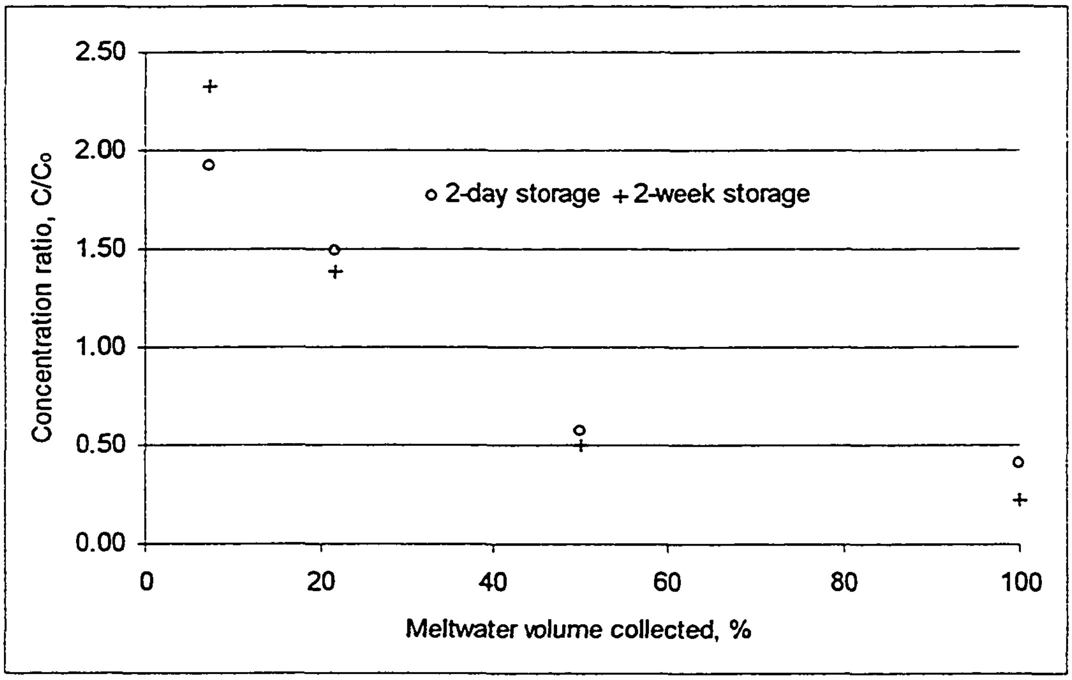


Figure 4.38: Variation of the normalized COD concentration in the sequential meltwater of the spray ice made from 5 mg/L linoleic acid at -10 °C, $C_0 = 26.4$ mg/L

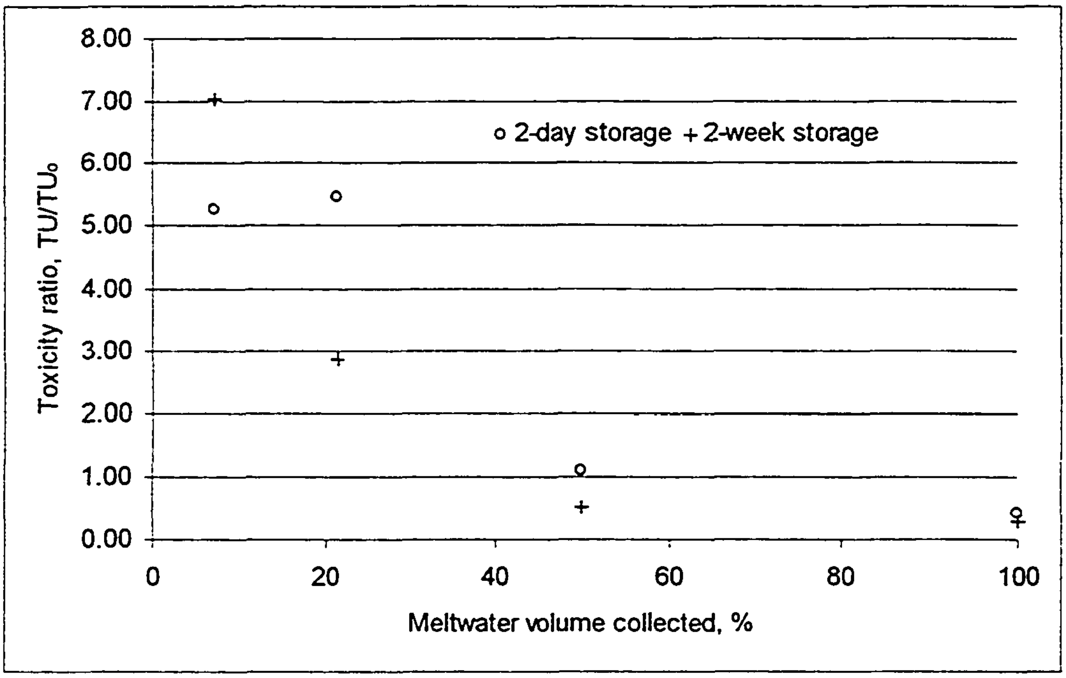


Figure 4.39: Variation of the normalized toxicity in the sequential meltwater of the spray ice made from 5 mg/L linoleic acid at -10 °C, $TU_0 = 4.44$ TU

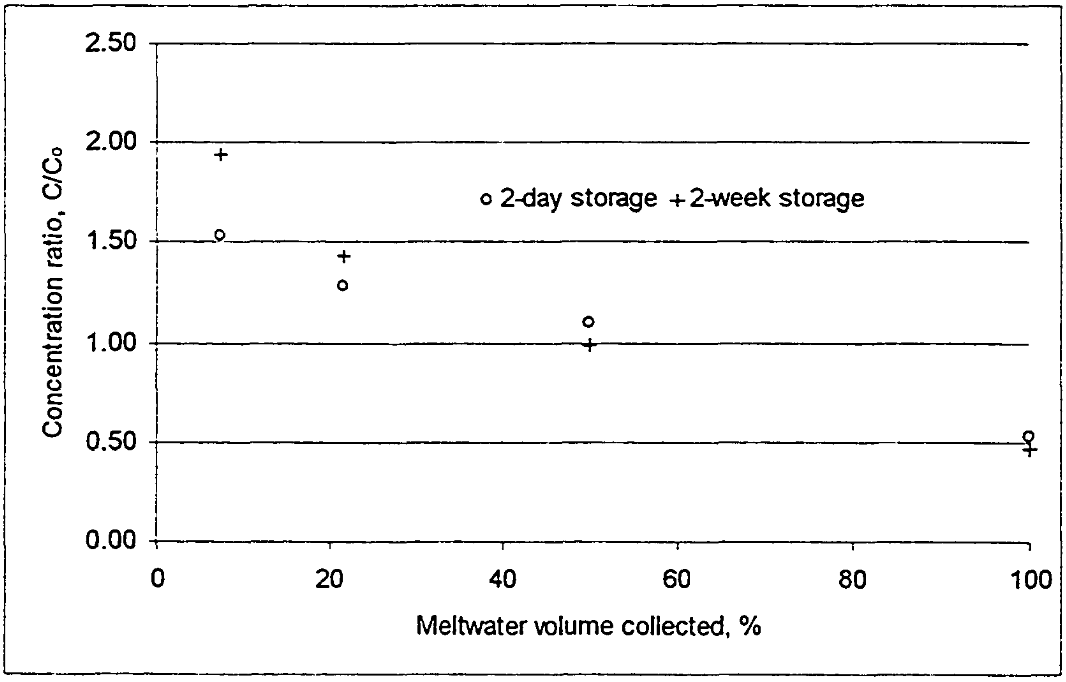


Figure 4.40: Variation of the normalized TOC concentration in the sequential meltwater of the spray ice made from 20 mg/L linoleic acid at -10 °C, $C_0 = 12.7$ mg/L

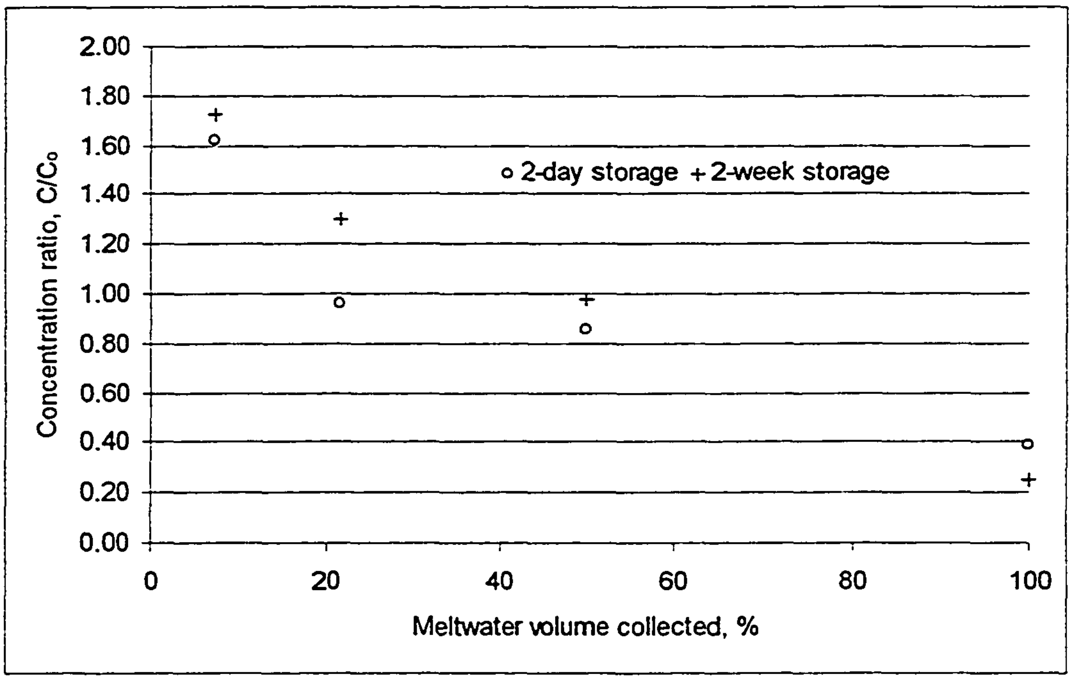


Figure 4.41: Variation of the normalized COD concentration in the sequential meltwater of the spray ice made from 20 mg/L linoleic acid at -10 °C, $C_0 = 54.0$ mg/L

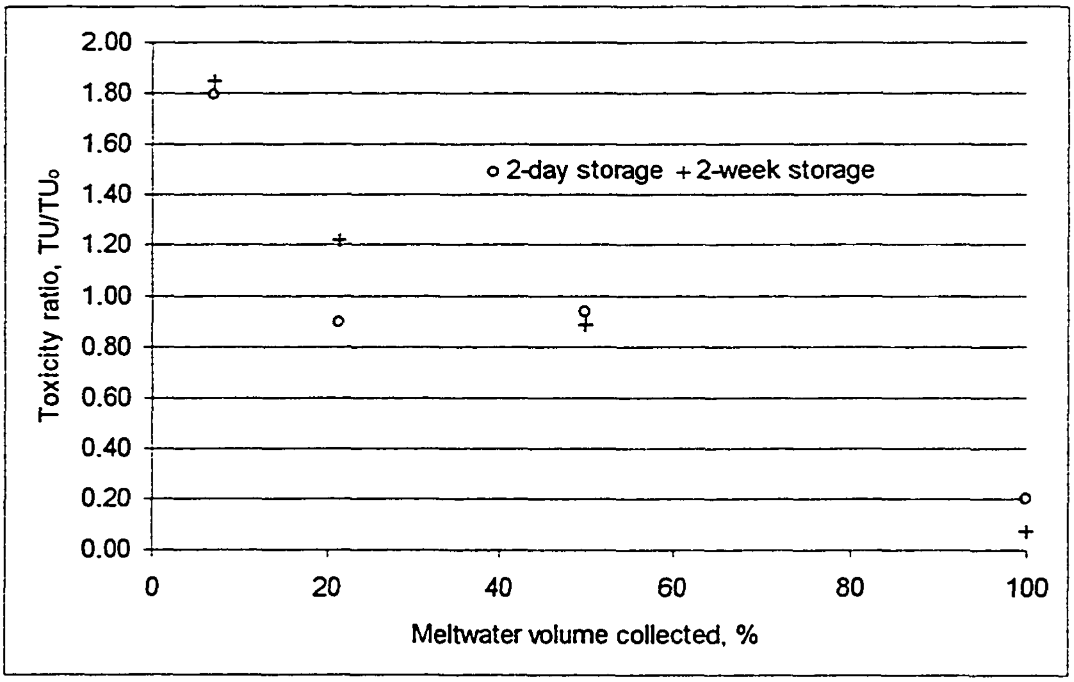


Figure 4.42: Variation of the normalized toxicity in the sequential meltwater of the spray ice made from 20 mg/L linoleic acid solution at -10 °C, $TU_0 = 27.6$ TU

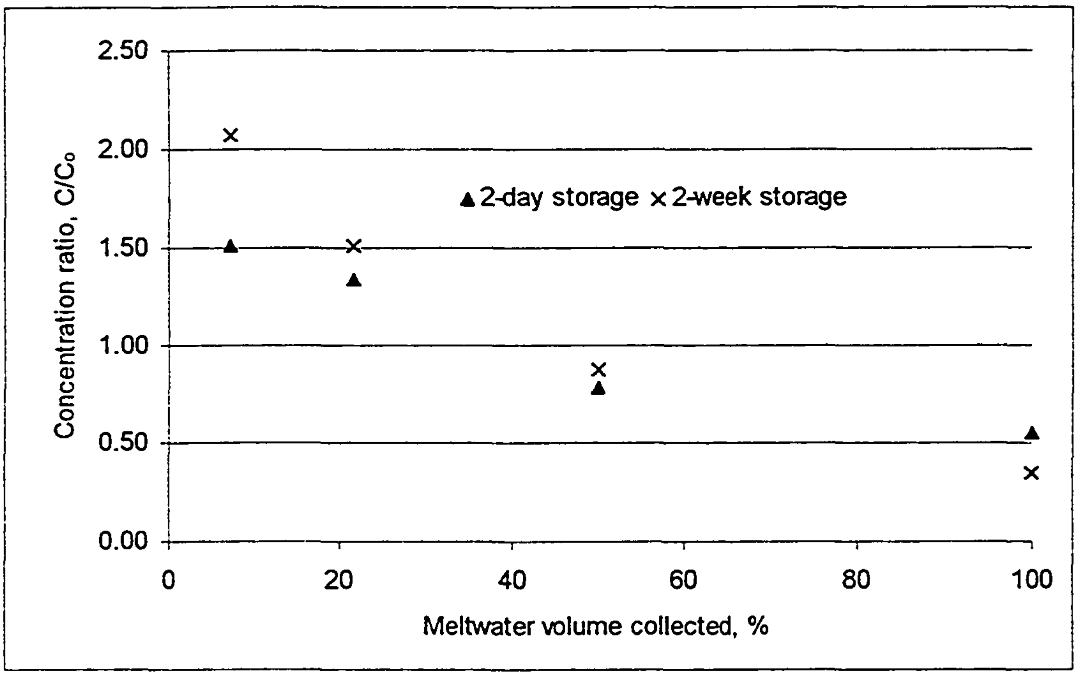


Figure 4.43: Variation of the normalized TOC concentration in the sequential meltwater of the spray ice made from 5 mg/L linoleic acid at -25 °C, C_0 = 5.14 mg/L

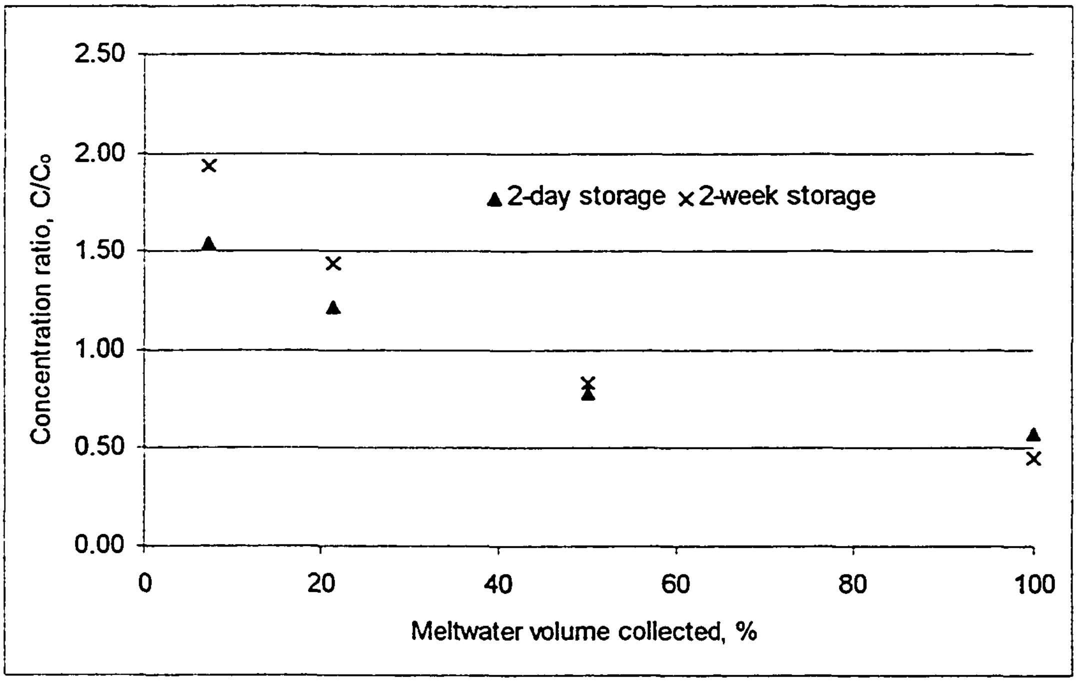


Figure 4.44: Variation of the normalized COD concentration in the sequential meltwater of the spray ice made from 5 mg/L linoleic acid at -25 °C, C_0 = 26.4 mg/L

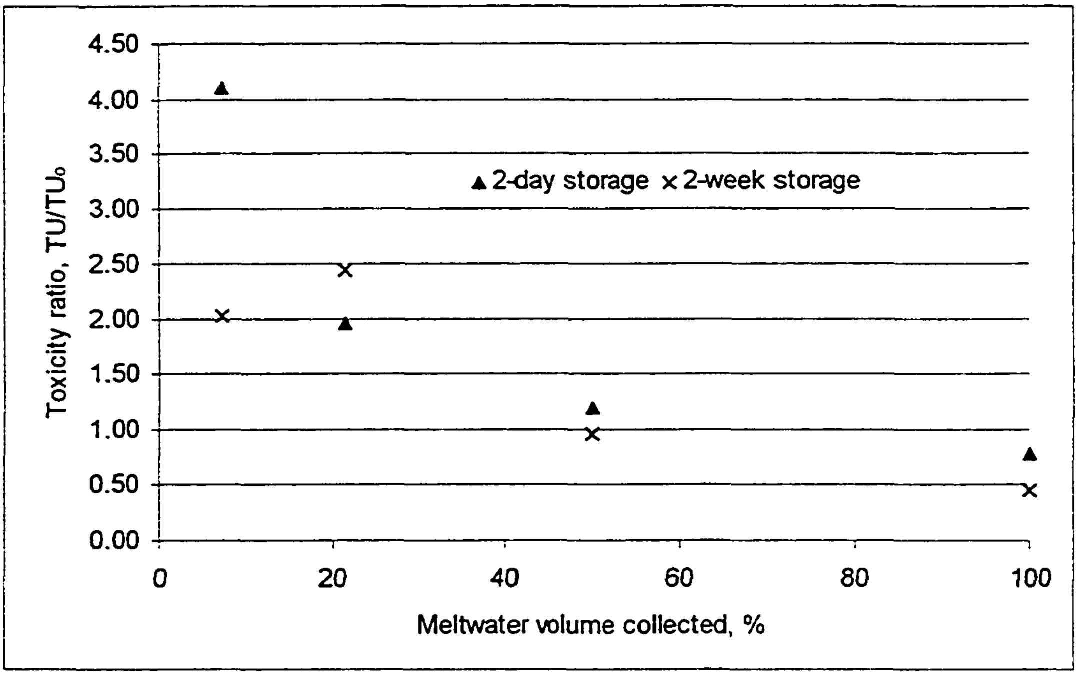


Figure 4.45: Variation of the normalized toxicity in the sequential meltwater of the spray ice made from 5 mg/L linoleic acid at -25 °C, $TU_0 = 4.44$ TU

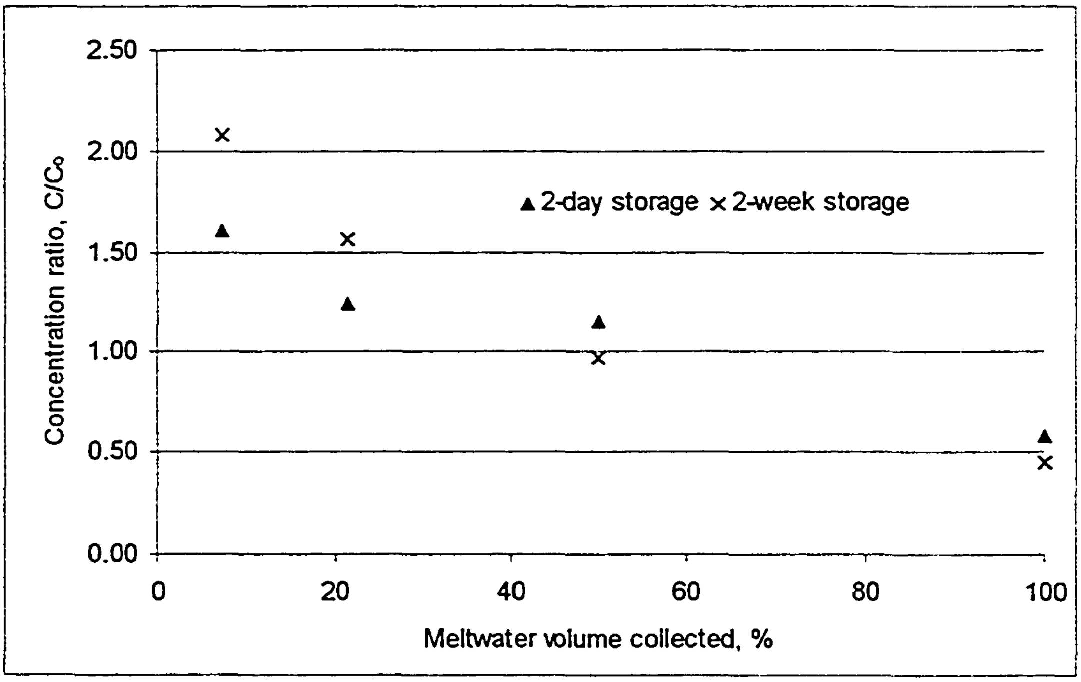


Figure 4.46: Variation of the normalized TOC concentration in the sequential meltwater of the spray ice made from 20 mg/L linoleic acid at -25 °C, $C_0 = 12.7$ mg/L

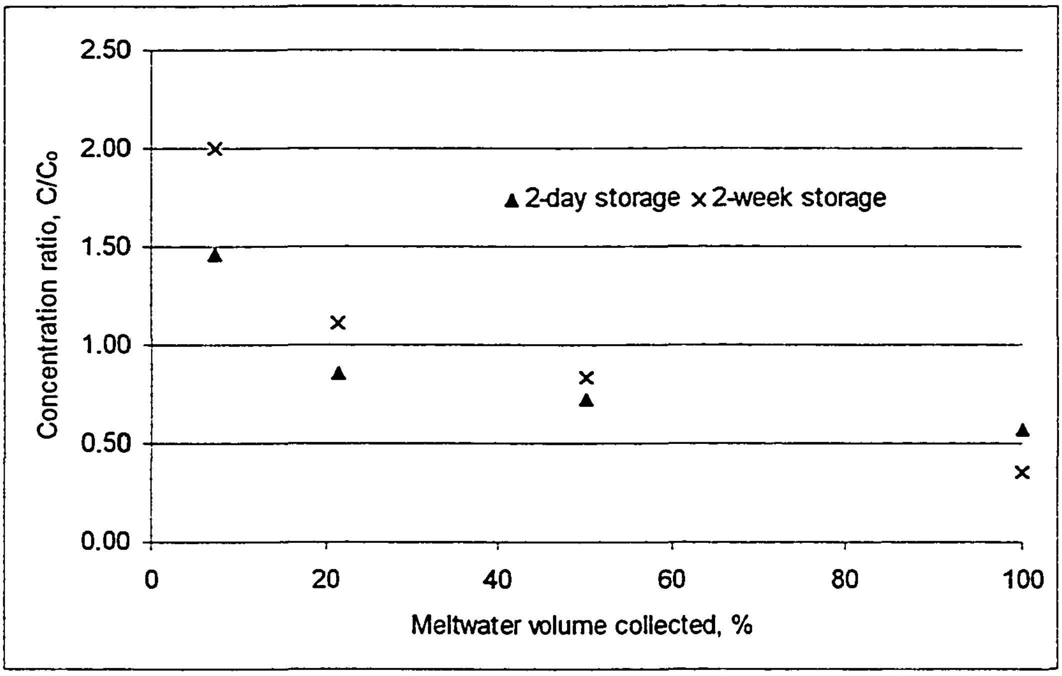


Figure 4.47: Variation of the normalized COD concentration in the sequential meltwater of the spray ice made from 20 mg/L linoleic acid at -25 °C, C_0 = 54.0 mg/L

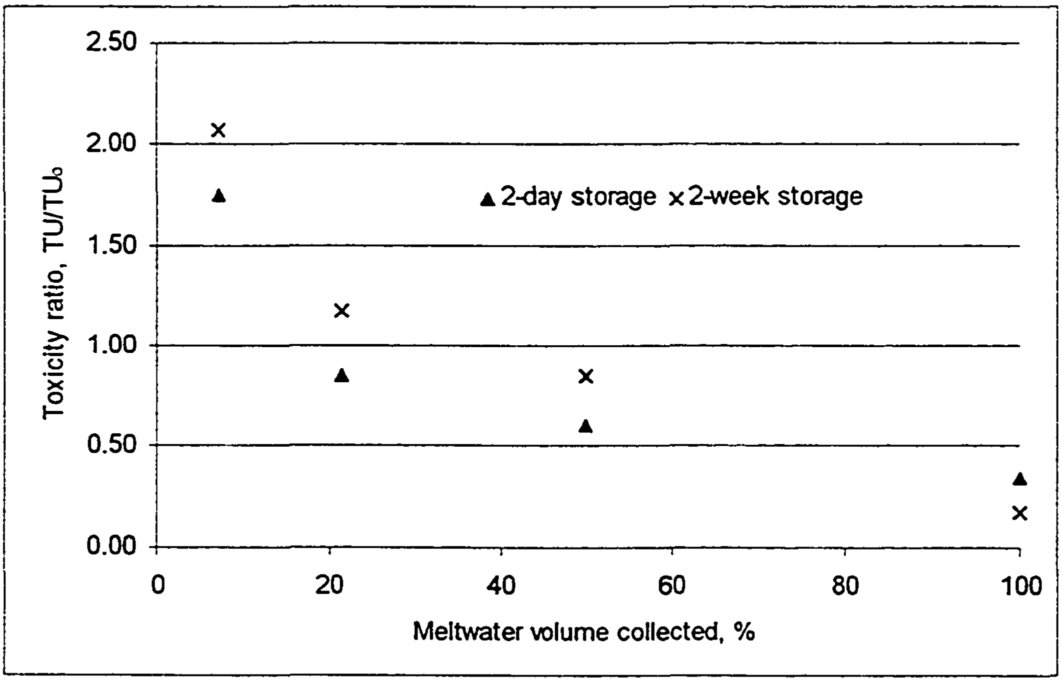


Figure 4.48: Variation of the normalized toxicity in the sequential meltwater of the spray ice made from 20 mg/L linoleic acid at -25 °C, TU_0 = 27.6 TU

Impurity concentration ratios of the initial meltwaters of the spray ice produced from 5 mg/L and 20 mg/L linoleic acid solutions at -10 °C and -25 °C are listed in Table 4.13. It was a noticed from the data that results obtained from the meltwaters of ice samples of linoleic acid are similar to that of pulp mill effluent and refinery wastewater discussed in section 4.2.2.1 and section 4.2.2.2.

Table 4.13: Impurity concentration ratios (C/C_o) of the initial meltwaters of the spray ice produced from linoleic acid solutions

Spray Temperature	Acid Concentration	Storage Time	TOC (C/C_o)	COD (C/C_o)	Toxicity (C/C_o)
-10 °C	5 mg/L	2 days	1.65	1.92	5.28
		2 weeks	2.07	2.32	7.03
	20 mg/L	2 days	1.53	1.62	1.79
		2 weeks	1.94	1.73	1.85
-25 °C	5 mg/L	2 days	1.51	1.54	4.10
		2 weeks	2.07	1.94	2.03
	20 mg/L	2 days	1.61	1.46	1.75
		2 weeks	2.08	2.00	2.07

Like pulp mill effluent and refinery wastewater, it was commonly observed from the figures for the linoleic acid solutions that the ice stored for longer time had more impurity concentrations in its initial meltwater. It was also observed that the initial meltwater of the ice produced at warmer temperature (-10 °C) had slightly higher impurity concentration ratios than the corresponding initial meltwater of the ice produced at the colder temperature (-25 °C) for most of the cases and the temperature effect was more profound at shorter storage time (2 days). The additional information that was obtained from the linoleic acid spray and melting experiment was about the effect of linoleic acid solution concentration. It was observed from the figures that the initial meltwaters of the ice produced from the spray freezing of the linoleic acid solution of lower concentration (5 mg/L) had the higher concentration ratios for most of the cases. Toxicity of the initial meltwater samples also increased ($C/C_o>1$). Few toxicity ratio results showed much higher values (5.28, 7.03 and 4.10).

Table 4.14 shows the percent reduction of impurity concentrations in the final 50% of the meltwater samples of the ice produced from linoleic acid solutions. Some of the results were similar as those of pulp mill effluent and refinery waste in section 4.2.2.1 and section 4.2.2.2, respectively. The only additional information obtained was about the effect of the linoleic acid concentration on the impurity reduction of the final 50% meltwater.

Table 4.14: Percent reduction of impurity concentrations in the final 50% of the meltwaters of the spray ice produced from linoleic acid solutions

Spray Temperature	Solution Concentration	Storage Time	TOC (%)	COD (%)	Toxicity (%)
-10 °C	5 mg/L	2 days	51	59	59
		2 weeks	69	77	70
	20 mg/L	2 days	47	62	80
		2 weeks	53	75	93
-25 °C	5 mg/L	2 days	45	43	21
		2 weeks	66	55	54
	20 mg/L	2 days	42	43	66
		2 weeks	55	65	83

TOC and COD impurity concentrations were reduced 42% to 77%. Toxicity was reduced as much as 93%. It suggests that the spray freezing can be an effective method to reduce toxicity of fatty acid in wastewater, since other treatment methods have drawbacks in treating toxic wastewater. Resin and fatty acid can inhibit the methanogenic bacterial activity biological treatment. Again, advanced oxidation process or ozone treatment of linoleic acid can produce by-products which are more toxic (Wright, 2002).

It was observed that higher impurity reduction for the final 50% of the meltwaters was achieved for the ice samples which had longer storage time (2 weeks) and which were produced at the warmer temperature (-10 °C). The linoleic acid concentration effects were also observed and it was found that the impurity concentration reduction efficiency was slightly higher for lower concentration for corresponding values obtained for higher concentration. Since, the runoff impurity concentration ratios for the 5 mg/L linoleic acid samples, was higher than that of 20 mg/L linoleic acid samples, final meltwaters of the ice produced from lower concentration (5 mg/L) linoleic acid samples had relatively lower impurity concentration ratios than the final meltwaters of the ice produced from higher concentration (20 mg/L) linoleic acid samples. But the toxicity reduction results showed higher toxicity reduction for higher linoleic acid concentration (20 mg/L). It was observed that the toxicity reduction results were greatly different from the TOC or COD reduction results. Higher reduction of TOC and COD should cause higher reduction of toxicity. It is difficult to explain the reason behind that. Replication of the runs could have been conducted to verify the toxicity results. Again, the toxicity analysis is very sensitive and sometimes two very different toxicity results can be obtained for the same sample.

Figure 4.49 and Figure 4.50 illustrate linear correlations between acute toxicity and the corresponding TOC and COD concentration of the samples obtained from the spray freezing and melting experiments of linoleic acid solution. Toxicity data of the

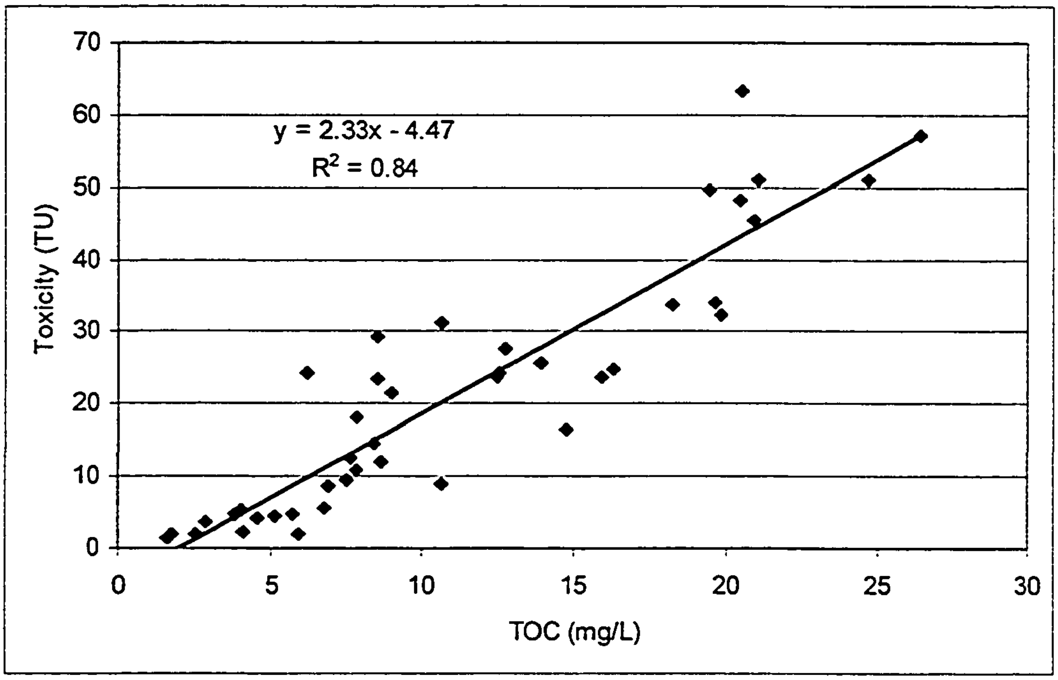


Figure 4.49: Correlation between acute toxicity and TOC of the samples obtained from the spray freezing experiments of linoleic acid

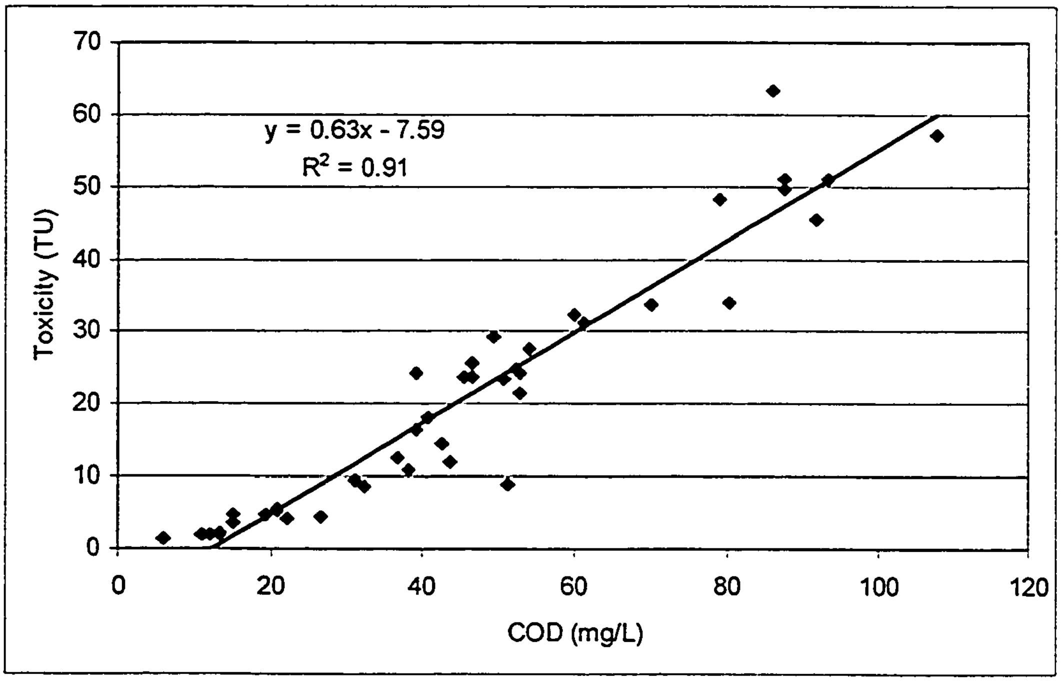


Figure 4.50: Correlation between acute toxicity and COD of the samples obtained from the spray freezing experiments of linoleic acid

linoleic acid samples, runoffs samples and meltwater samples were incorporated into the plots. Figure 4.49 and Figure 4.50 show a similar trend and it is observed that the acute toxicity of the samples decreased linearly as TOC and COD decreased. High R^2 values of 0.84 and 0.91 were obtained for the correlation between acute toxicity and TOC and between acute toxicity and COD, respectively.

4.2.2.5. Impurity removal from the stored spray ice, produced from abietic acid solutions, by melting

Like linoleic acid samples, abietic acid of the concentration of 5 mg/L and 20 mg/L were also used for the spray freezing and ice melting of abietic acid solutions. Runs of spray freezing and melting of abietic acid solution, for each concentration of 5 mg/L and 20 mg/L, were carried out in the same way as were carried out for linoleic acid (section 4.2.2.4.). Same sets of TOC, COD and toxicity data, as linoleic acid solutions, of the meltwaters were found for abietic acid solutions.

Figure 4.51 to Figure 4.53 show the variation of impurity concentrations (TOC, COD and toxicity) of the meltwater during the melting of the ice produced from the spraying of abietic acid samples of concentration 5 mg/L at -10 °C. Figure 4.54 to Figure 4.56 show the variation of impurity concentrations of the meltwater during the melting of the ice produced from the spraying of abietic acid samples of concentration 20 mg/L at -10 °C. Figure 4.57 to Figure 4.59 show the variation of impurity concentrations of the meltwater during the melting of the ice produced from the spraying of abietic acid samples of concentrations 5 mg/L at -25 °C. Figure 4.60 to Figure 4.62 show the variation of impurity concentrations of the meltwater during the melting of the ice produced from the spraying of abietic acid samples of concentrations 20 mg/L at -25 °C.

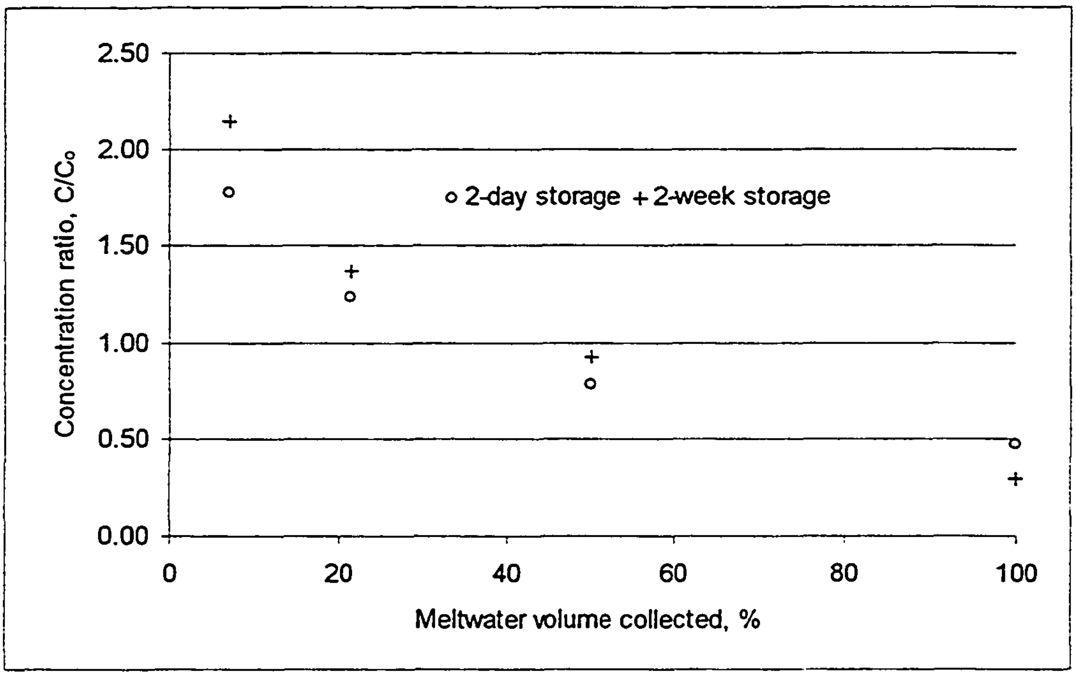


Figure 4.51: Variation of the normalized TOC in the sequential meltwater of the spray ice made from 5 mg/L abietic acid solution at -10 °C, C_0 = 4.57 mg/L

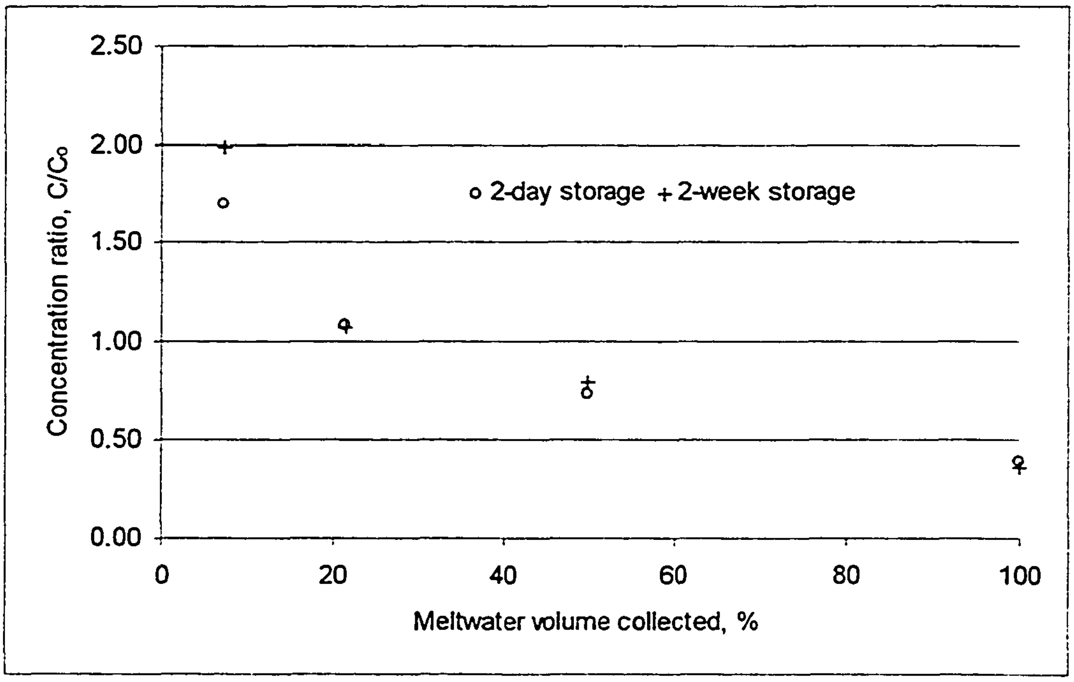


Figure 4.52: Variation of the normalized COD in the sequential meltwater of the spray ice made from 5 mg/L abietic acid solution at -10 °C, C_0 = 20.6 mg/L

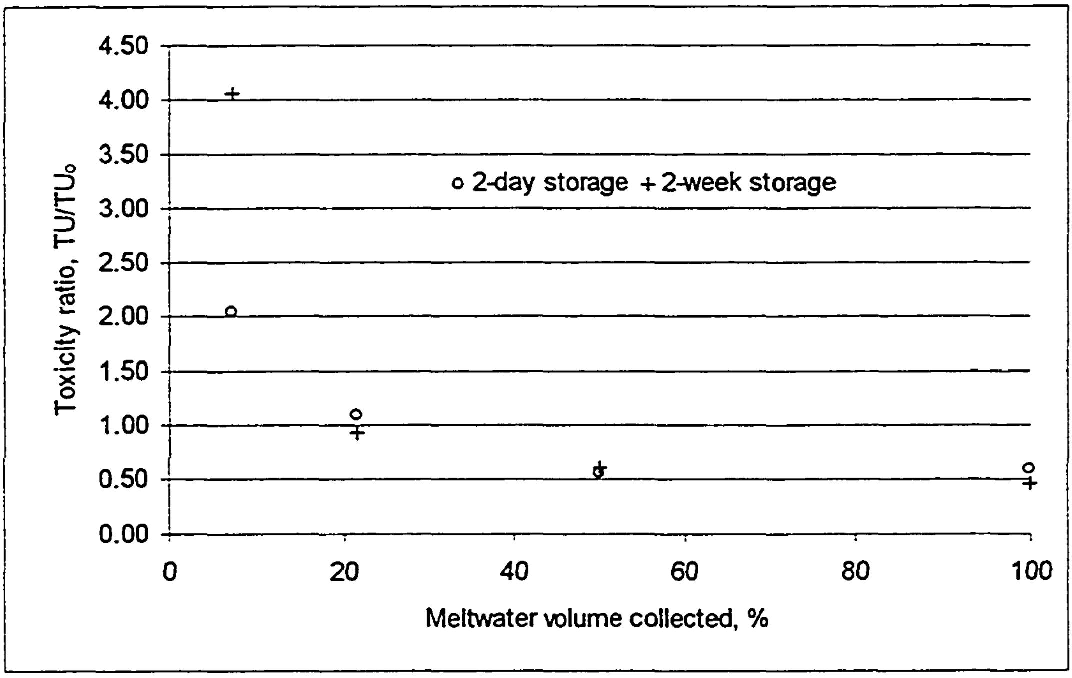


Figure 4.53: Variation of the normalized toxicity in the sequential meltwater of the spray ice made from 5 mg/L abietic acid solution at -10 °C, $TU_0 = 2.62$ TU

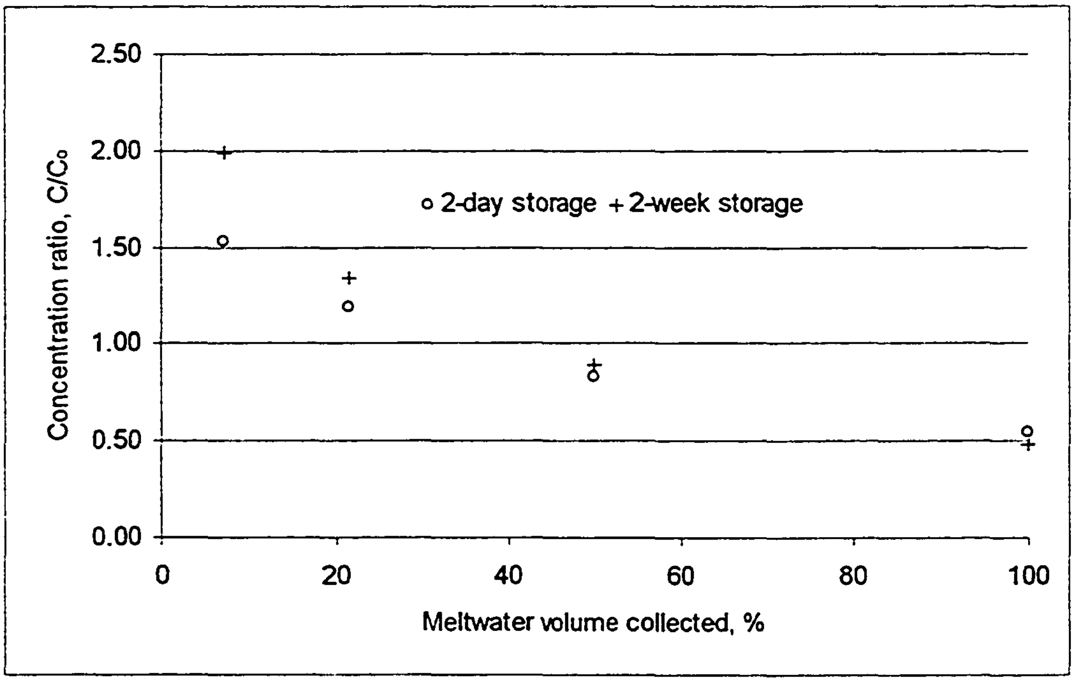


Figure 4.54: Variation of the normalized TOC in the sequential meltwater of the spray ice made from 20 mg/L abietic acid solution at -10 °C, $C_0 = 14.7$ mg/L

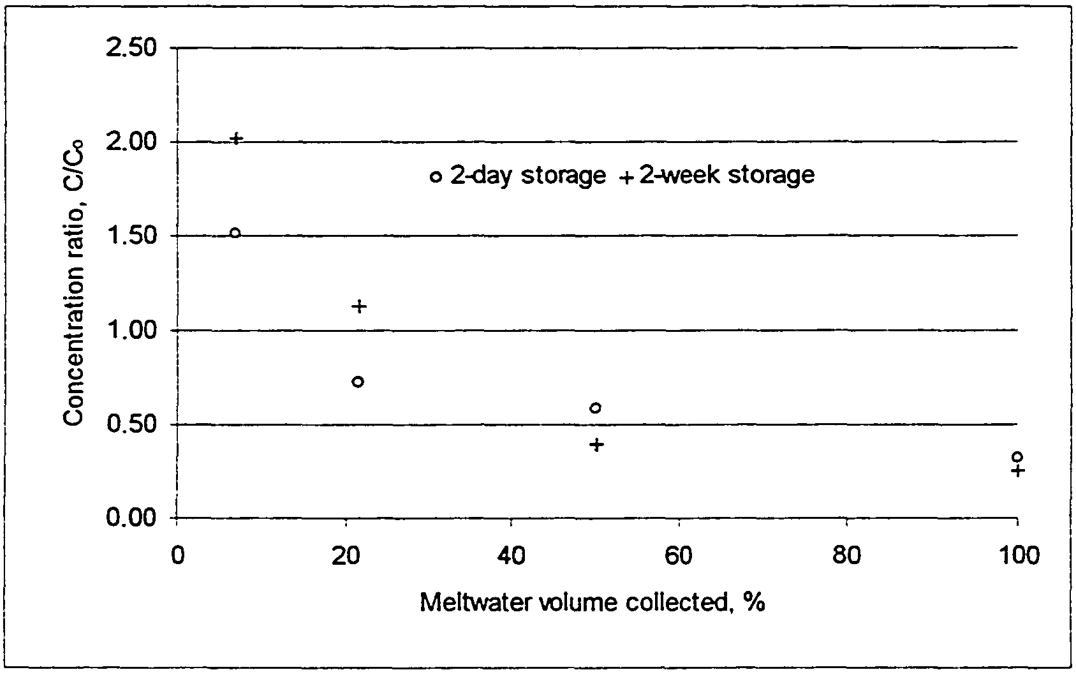


Figure 4.55: Variation of the normalized COD in the sequential meltwater of the spray ice made from 20 mg/L abietic acid solution at -10 °C, $C_0 = 70.0$ mg/L

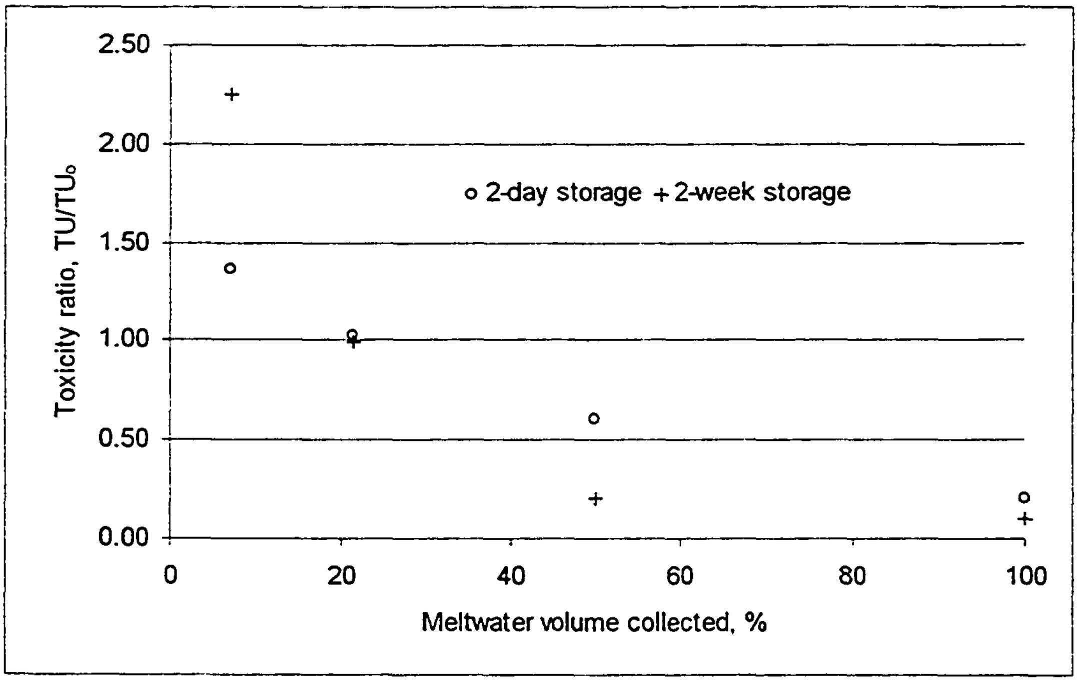


Figure 4.56: Variation of the normalized toxicity in the sequential meltwater of the spray ice made from 20 mg/L abietic acid solution at -10 °C, $TU_0 = 15.7$ TU

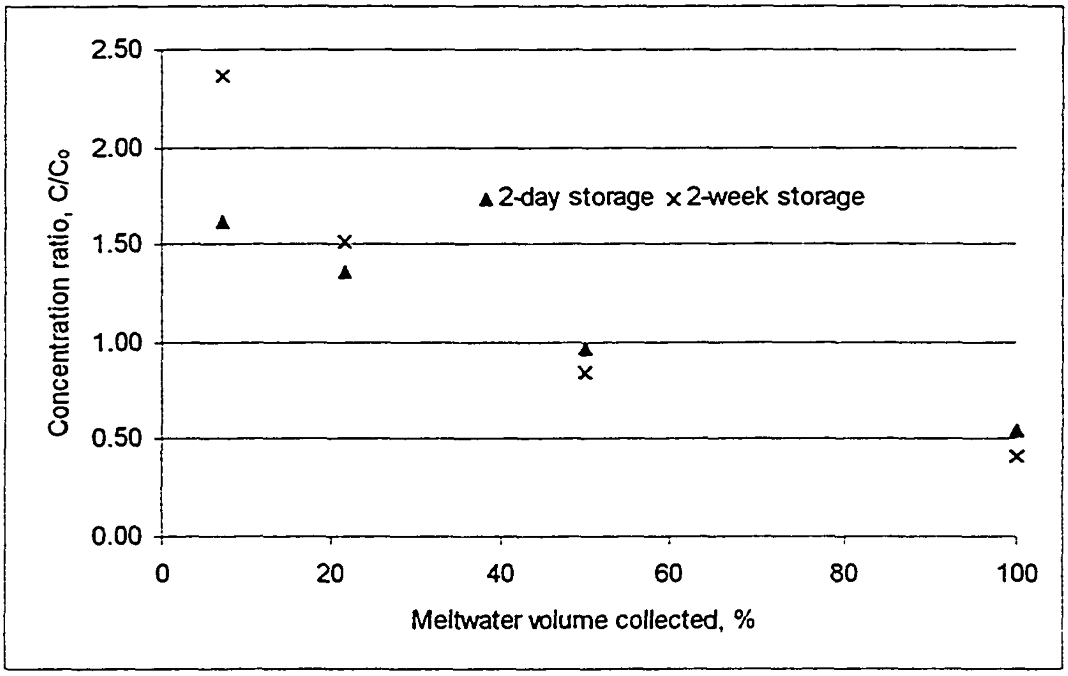


Figure 4.57: Variation of the normalized TOC in the sequential meltwater of the spray ice made from 5 mg/L abietic acid solution at -25 °C, $C_0 = 4.57$ mg/L

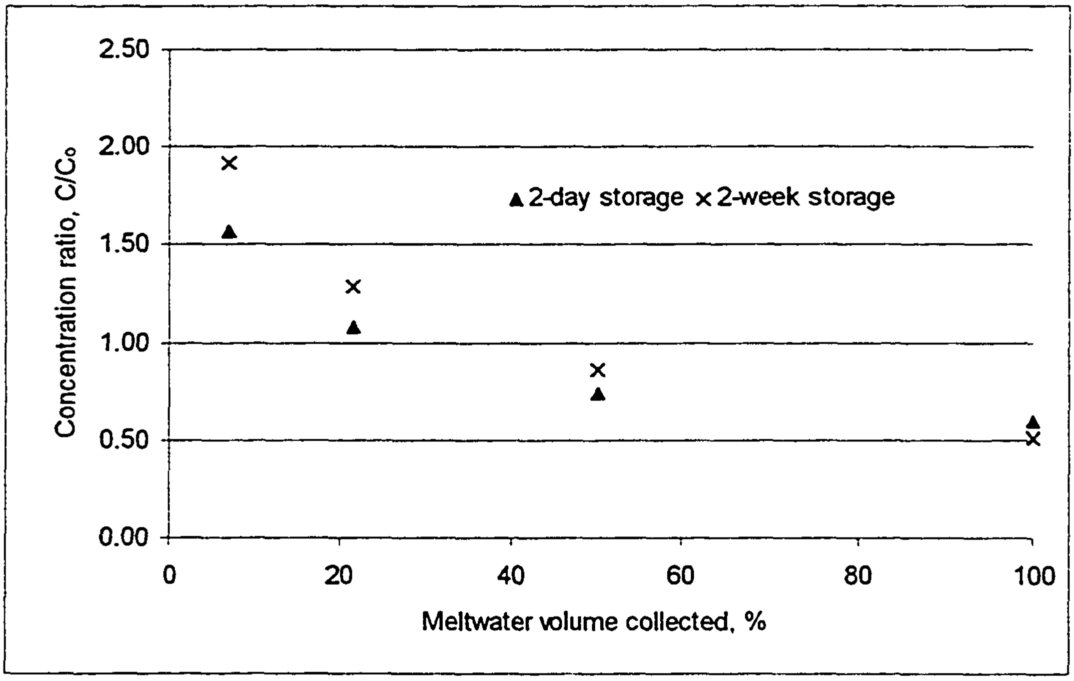


Figure 4.58: Variation of the normalized COD in the sequential meltwater of the spray ice made from 5 mg/L abietic acid solution at -25 °C, $C_0 = 20.6$ mg/L

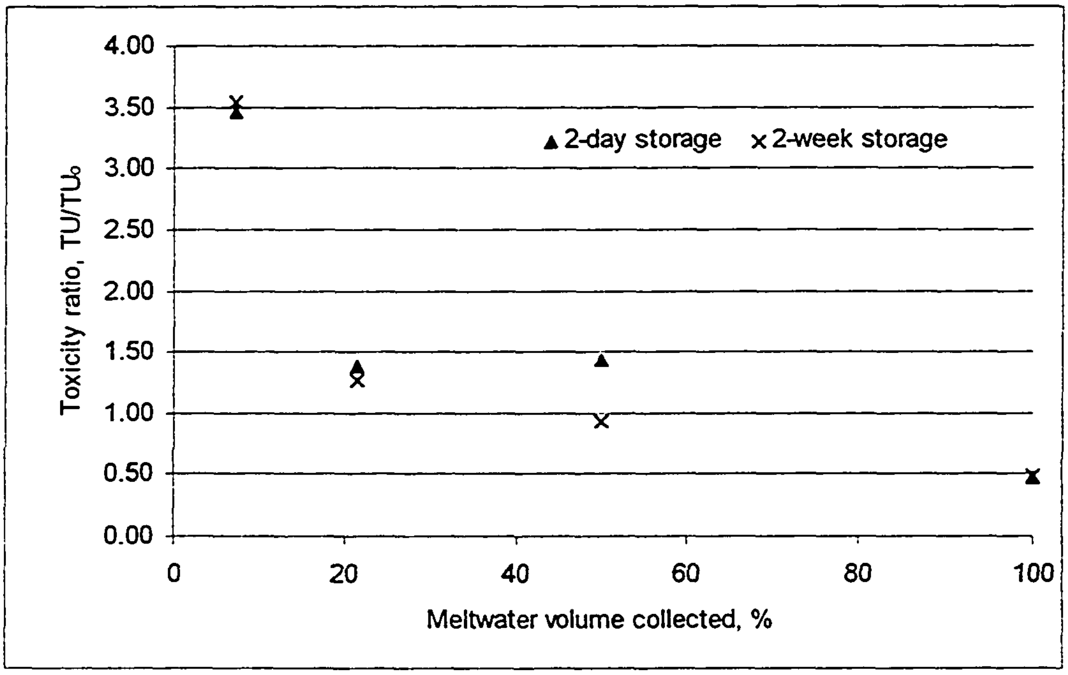


Figure 4.59: Variation of the normalized toxicity in the sequential meltwater of the spray ice made from 5 mg/L abietic acid solution at -25 °C, $TU_0 = 2.62$ TU

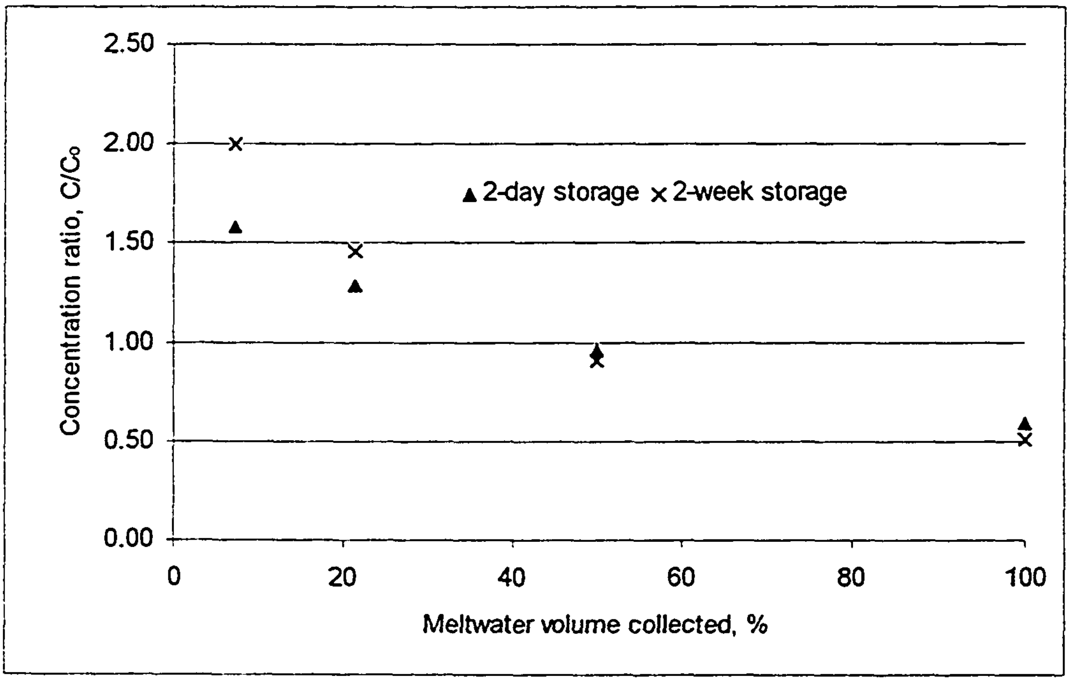


Figure 4.60: Variation of the normalized TOC in the sequential meltwater of the spray ice made from 20 mg/L abietic acid solution at -25 °C, $C_0 = 14.7$ mg/L

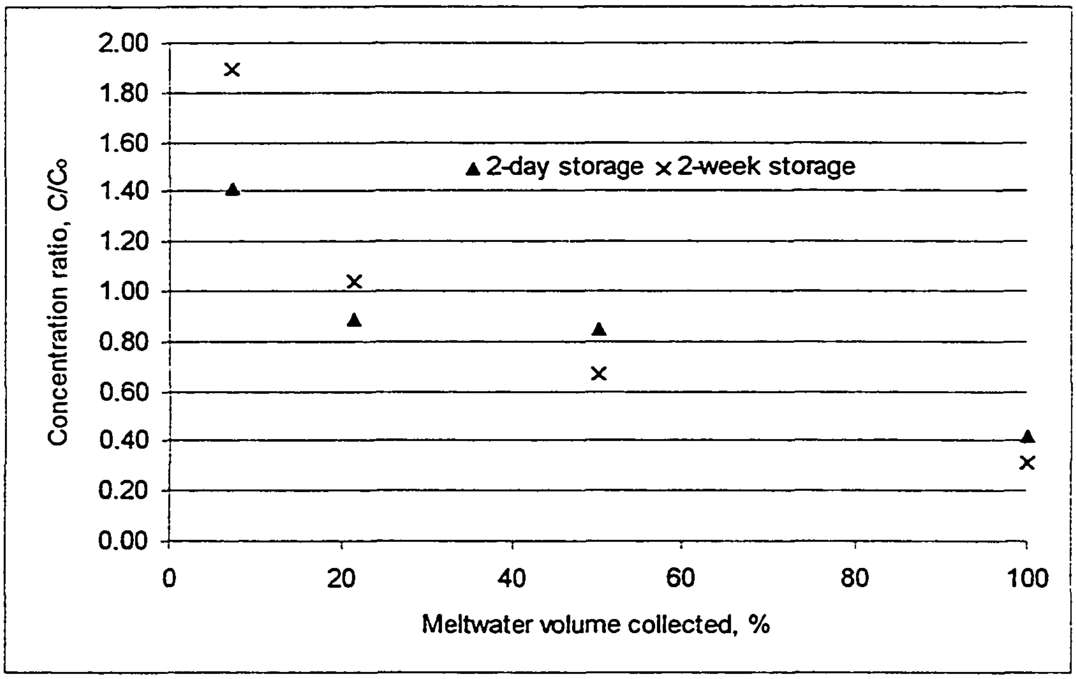


Figure 4.61: Variation of the normalized COD in the sequential meltwater of the spray ice made from 20 mg/L abietic acid solution at -25 °C, $C_0 = 70.0$ mg/L

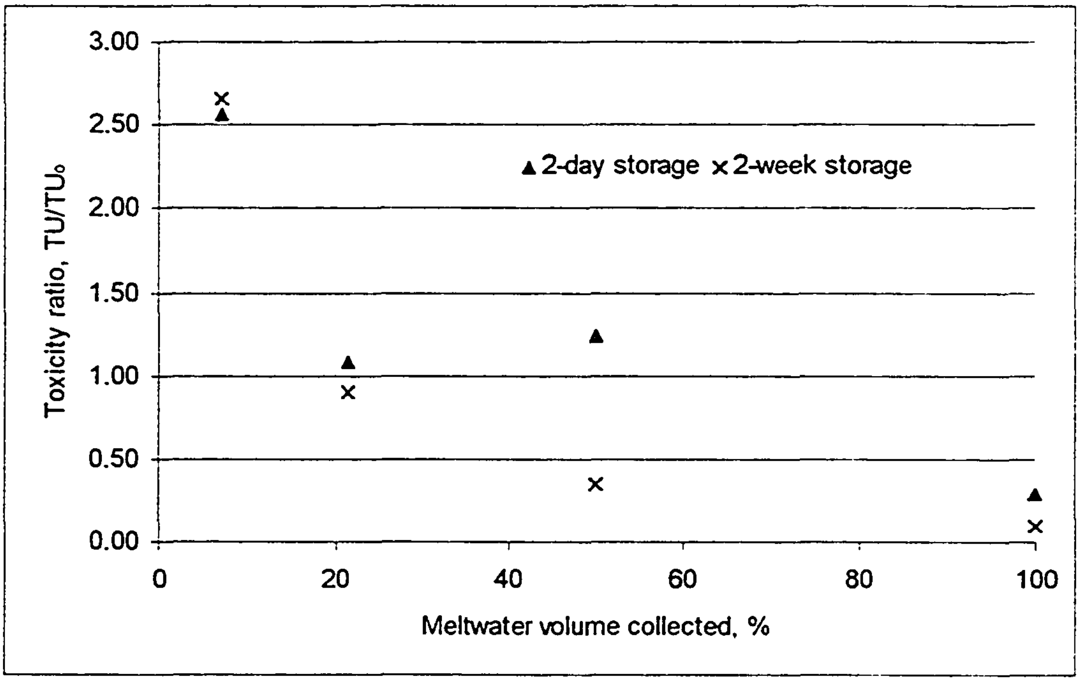


Figure 4.62: Variation of the normalized toxicity in the sequential meltwater of the spray ice made from 20 mg/L abietic acid solution at -25 °C, $TU_0 = 15.7$ TU

The meltwaters of the ice samples, produced from the spray freezing of abietic acid solutions of concentrations 5 mg/L and 20 mg/L, showed the same pattern as was shown for pulp mill effluent, refinery wastewater and linoleic acid in section 4.2.2.1, section 4.2.2.2 and section 4.2.2.4, respectively. The initial meltwaters had higher impurity concentration ratios than that of original abietic acid solutions ($C/C_o>1$). The impurity concentration ratios of the meltwater decreased gradually and the impurity concentrations of final meltwater became lower than that of original abietic acid solutions ($C/C_o<1$). Like the case of linoleic acid, the only additional step taken for abietic acid solutions was the use of two different concentrations to produce ice by spraying to observe the concentration effect on meltwater impurity separation.

Table 4.15 shows the concentration ratios of impurities of the initial meltwaters of the spray ice produced from abietic acid solutions. It was noticed that the results obtained from the meltwaters of ice samples of abietic acid are similar to that of linoleic acid discussed in section 4.2.2.4.

Table 4.15: Impurity concentration ratios (C/C_o) of the initial meltwaters of the spray ice produced from abietic acid solutions

Spray Temperature	Acid Concentration	Storage Time	TOC (C/C_o)	COD (C/C_o)	Toxicity (C/C_o)
-10 °C	5 mg/L	2 days	1.78	1.70	2.03
		2 weeks	2.15	1.99	4.05
	20 mg/L	2 days	1.53	1.51	1.37
		2 weeks	1.99	2.02	2.25
-25 °C	5 mg/L	2 days	1.62	1.56	3.45
		2 weeks	2.36	1.92	3.55
	20 mg/L	2 days	1.59	1.41	2.56
		2 weeks	2.00	1.89	2.66

Results in Table 4.15 shows that the ice stored for longer periods had more impurity concentrations in its initial meltwater. It was also observed that the initial meltwater of the ice produced at warmer temperature (-10 °C) had slightly higher impurity concentration ratios than the initial meltwater of the ice produced at colder temperature (-25 °C) in most of the cases and the temperature effect was more profound at the shorter storage time.

Like linoleic acid solution, the additional information that was obtained from the abietic acid spray and melting experiment was the effect of concentration. Initial meltwaters of the ice produced from the spray freezing of the abietic acid solution of lower concentration (5 mg/L) had the higher concentration ratios for most of the cases.

Table 4.16 shows the percent reduction of impurity concentrations in the final 50% of the meltwater samples of the ice produced from abietic acid solutions. Results were similar to those of linoleic acid discussed in 4.2.2.4. TOC and COD impurity concentrations were reduced up to 40% to 75%. Toxicity was reduced as much as 90%. Like linoleic acid, it was also observed for the abietic acid that higher impurity reduction for the final 50% of the meltwaters was achieved for the ice samples which had longer storage time (2 weeks) and which were produced at warmer temperature (-10 °C). The only difference in the final meltwater impurity concentration ratios of abietic acid samples with that of linoleic acid samples was the COD concentration ratio data. It was found that the COD concentration ratios of final 50% meltwater were slightly higher for the ice produced from the higher concentration (20 mg/L) samples of abietic acid than that produced from the lower concentration (5 mg/L) samples. But TOC concentration ratio data of abietic acid and other impurity concentration ratio data obtained from other wastewaters showed that the impurity separation efficiency was higher for lower concentration wastewater samples. It was also observed that the toxicity reduction was better achieved for higher concentration abietic acid (20 mg/L). Similar results were observed for linoleic acid. Replication of the runs was needed to verify the toxicity data.

Table 4.16: Percent reduction of impurity concentrations in the final 50% of the meltwaters of the spray ice produced from abietic acid solutions

Spray Temperature	Solution Concentration	Storage Time	TOC (%)	COD (%)	Toxicity (%)
-10 °C	5 mg/L	2 days	53	61	41
		2 weeks	71	64	53
	20 mg/L	2 days	46	68	79
		2 weeks	52	75	89
-25 °C	5 mg/L	2 days	45	40	52
		2 weeks	59	49	51
	20 mg/L	2 days	41	58	70
		2 weeks	49	69	90

Linear correlations between acute toxicity and TOC and that between acute toxicity and COD are shown in Figure 4.63 and Figure 4.64, respectively. Toxicity data of the abietic acid solutions, runoffs samples and meltwater samples were incorporated into the plots. Both the figures show similar pattern. It is observed that the acute toxicity of the samples decreased linearly with the decrease of TOC and COD. High R^2 values of 0.81 and 0.85 were obtained for the linear correlation between acute toxicity and TOC and that between acute toxicity and COD, respectively.

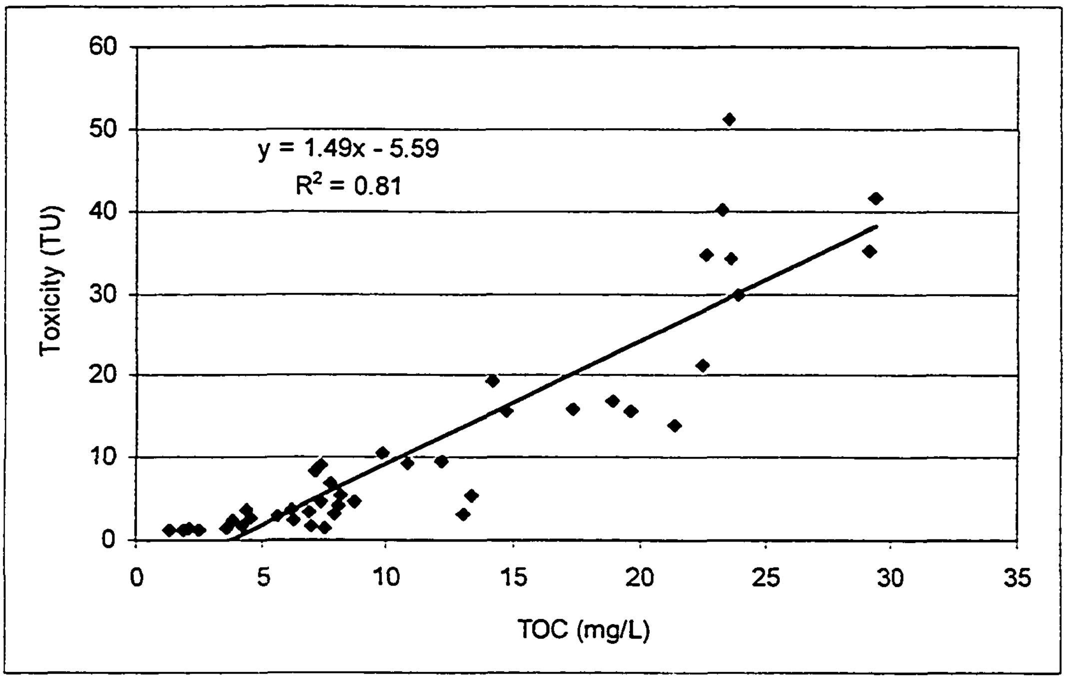


Figure 4.63: Correlation between acute toxicity and TOC of the samples obtained from the spray freezing experiments of abietic acid

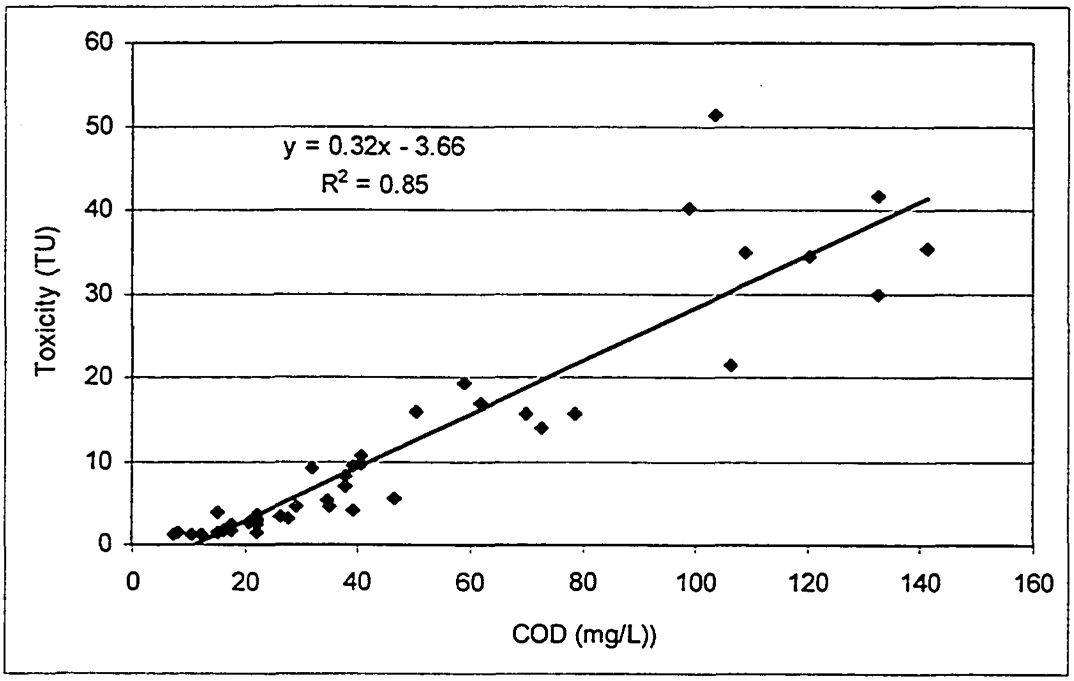


Figure 4.64: Correlation between acute toxicity and COD of the samples obtained from the spray freezing experiments of abietic acid

4.2.2.6. Statistical analysis of the meltwater impurity concentrations for linoleic acid and abietic acid solutions

A statistical analysis was performed on the TOC and COD concentration ratio data of the initial and final meltwater samples of the ice produced from the spray freezing of linoleic acid and abietic acid solutions to find out the significant factors for the impurity separation efficiency of initial meltwater and final meltwater.

Table 4.17 shows the p-values for the factors and interactions calculated from a 2^3 factorial experiment with 1 replicate and linoleic acid and abietic acid solutions were considered as 2 blocks. For 95% confidence level, the factors which have the p-values less than 0.05 are considered to be significant.

From the Table 4.17 it is observed that the spray temperature factor was not statistically significant at 95% confidence level. It was observed in the section 4.2.2.4 and section 4.2.2.5 that there was a slight effect of spray temperature on the meltwater impurity concentrations, where the warmer spray temperature caused higher impurity concentration in initial meltwater and lower impurity concentration in final meltwater, but statistically the effect was not enough to be significant.

The ice storage time factor was significant at 95% confidence level for TOC increase in initial meltwater (p-value = 0.0473). For COD increase in initial meltwater and for TOC and COD reduction in final meltwater, the effects of ice storage time were not enough to be statistically significant at 95% confidence level. It was observed in the section 4.2.2.4 and section 4.2.2.5. that ice storage time had an effect on the meltwater impurity concentrations. For longer storage time the impurity concentrations were higher in initial meltwaters and the impurity concentrations were lower in final meltwaters.

Table 4.17: p-values of the factors affecting the initial and final meltwater TOC and COD in linoleic acid and abietic acid ice melting experiments

Sources of variation	p-values			
	Initial meltwater		Final meltwater	
	TOC	COD	TOC	COD
Temperature (A)	0.9039	0.5084	0.4896	0.1450
Storage time (B)	0.0473	0.0888	0.0999	0.2317
Concentration (C)	0.5749	0.4505	0.2194	0.3865
Block (Linoleic/Abietic)	0.6354	0.6464	0.7661	0.9251
AB	0.7544	0.7725	0.8882	0.8629
AC	0.8189	0.6037	0.7525	0.7013
BC	0.8376	0.9067	0.5109	0.8838
ABC	0.7635	0.8389	0.8605	0.8629

Note: At 95% confidence level p-value = 0.05

The effect of the concentrations of acid solutions on impurity separation was not significant and the effect was also not clearly observed from the data in section 4.2.2.4 and section 4.2.2.5.

The block effect was also not significant at 95% confidence level as the p-values were higher than 0.05. So the impurity removal efficiency was not significantly different for linoleic acid and abietic acid solutions and it was observed from the data in the section 4.2.2.4 and section 4.2.2.5.

No two or three factor interaction was significant at 95% confidence interval.

4.3. Toxicity Reduction

Results of the beaker freezing experiments and the spray freezing and melting experiments were discussed in Section 4.1 and Section 4.2. Toxicity of the wastewaters was removed or reduced to an extent along with the reduction of impurities. Pulp mill effluent and refinery wastewater toxicity was based on EC_{20} and linoleic acid and abietic acid toxicity was based on EC_{50}. Toxicity results were calculated from the EC values using equation 1 and equation 2, in section 3.6.4.

The initial toxicity of the pulp mill effluent and refinery wastewater was measured to be 1.04 TU and 1.81 TU, respectively (Table 3.2). Initial toxicity of the linoleic acid was 4.44 TU for 5 mg/L solution and 27.6 TU for 20 mg/L solution. Initial toxicity of the abietic acid was 2.62 TU for 5 mg/L solution and 15.7 TU for 20 mg/L solution.

Diluted (1:10) pulp mill effluent and refinery wastewater was found to be non-toxic and all the ice samples produced from the beaker freezing experiments of diluted pulp mill effluent and refinery wastewater was also found to be non-toxic. Table 4.18 summarized the percent toxicity reduction data of the ice samples produced from the beaker freezing experiments of original pulp mill effluent and refinery wastewater. All the ice samples were found to be non-toxic, except two. Ice samples produced with the application of stirring were non-toxic. The minimum impurity reductions needed

Table 4.18: Percent reduction of toxicity in the ice samples produced from the beaker freezing tests of the wastewaters

Freezing Temperature	-10 °C		-25 °C	
Stirring	With	Without	With	Without
Pulp mill effluent (original)	Not toxic	Not toxic	Not toxic	Not toxic
Refinery wastewater (original)	Not toxic	47	Not toxic	18

to produce the non-toxic ice samples were 44% TOC, 51% COD and 44% color for pulp mill effluent (Table A-3, Appendix A) and 50% TOC and 48% COD for refinery wastewater (Table A-7, Appendix A). In beaker freezing experiments, toxicity reduction was believed to be caused by the reduction of impurities in ice samples. Correlations between toxicity and impurities (TOC and COD) showed a trend that the toxicity reduced with the reduction of impurities.

In spray freezing experiments, it was observed that the toxicity of the runoff increased significantly for all wastewaters (Section 4.2.1). The toxicity of the initial meltwater also increased significantly in ice melting experiments (Section 4.2.2). As the melting progressed, the toxicity in general was reduced. Table 4.19 presented the percent toxicity reduction in the final 50% of the meltwaters of the spray ice of wastewaters.

Table 4.19: Percent reduction of toxicity in the final 50% of the meltwaters of the spray ice produced from the wastewaters

Spray Temperature	-10 °C		-25 °C	
Storage Time	2 days	2 weeks	2 days	2 weeks
Pulp mill effluent	Not toxic	Not toxic	Not toxic	Not toxic
Refinery wastewater	59	69	48	73
Linoleic acid (5 mg/L)	59	70	21	54
Abietic acid (5 mg/L)	41	53	52	51

Final meltwater samples of the pulp mill effluent were only non-toxic. Others achieved minimum 21% to maximum 73% toxicity reduction. The minimum impurity reductions needed to produce the non-toxic samples of pulp mill effluent were 57% TOC, 61% COD and 65% color (Appendix A). Gao *et. al.* (2003) reported that higher than 80% treatment efficiency was required to produce a non-toxic oil sands tailing pond water.

The toxicity of the original pulp mill effluent was low. This might have caused the production of non-toxic final meltwater samples with impurity reduction efficiency lower than 80%. No final meltwater samples for linoleic acid and abietic acid solutions achieved more than 80% impurity reduction (Appendix-A). Only two final meltwater samples for refinery wastewater achieved more than 80% impurity reduction, but that did not produce any non-toxic final meltwater samples.

The main reason for toxicity reduction in spray freezing and ice melting experiments was the reduction of impurities in treated samples. Correlation of toxicity with TOC and COD showed that the toxicity reduced with the reduction of TOC and COD (Section 4.2). Toxicity reduction in spray freezing and ice melting experiments was believed to be achieved in several steps. When the wastewaters were sprayed through a nozzle and experienced a change from very high to low pressure, volatile toxic compounds had a chance to escape to the atmosphere. Production of very small water particles increased the specific surface area which might have facilitated the vaporization process of the volatile compounds. Vaporization might have also occurred when the water particles partially froze and the impurities concentrated in liquid phase. A portion of impurities was separated by the generation of runoffs, which reduced the toxicity of the produced ice samples. Escape of volatile compounds to the atmosphere also might have occurred when the ice samples were stored for a period. During melting experiments, initial meltwater washed away most of the impurities remained in the ice after runoff and leaved ice samples with lower toxicity.

4.4. Scanning Electron Microscopy

Scanning electron microscopy (SEM) images were taken for the ice samples produced by spray freezing of pulp mill effluent. The images were examined to observe the impurity distribution inside the ice samples and to find out the differences in impurity distribution among the ice samples which were produced and stored at different conditions. In most cases the images of the ice pores and the inside surface of the ice pores were taken. To expose the fractured ice surface the ice samples were subjected to the sublimation where the ice surfaces went down to a certain level leaving wafer-like (Facey *et. al.*, 2001) impurities on it.

Figure 4.65 to Figure 4.67 show the SEM images of a fractured ice specimen produced from spray freezing of pulp mill effluent at -10 °C and stored at the spray temperature for 2 days, at various magnifications. Figure 4.65 shows a cylindrical structure of impurities coming out of the pore, slightly above the ice surface, which was left after the sublimation. From the picture it can be assumed that the pore surface was covered with impurities and those contributed to the increase of impurity concentrations of the initial meltwater. Figure 4.66 shows the impurities inside a pore where the impurities look like a damaged dry leaf and Figure 4.67 shows the same impurities with higher magnification.

Figure 4.68 to Figure 4.71 show the SEM images of a fractured ice specimen produced from spray freezing of pulp mill effluent at -25 °C and stored at the spray temperature for 2 days, at various magnifications. Figure 4.68 shows an edge of a pore in the ice sample, where the surface of the edge was covered with impurities. These impurities would essentially be washed away with the meltwater when it would percolate

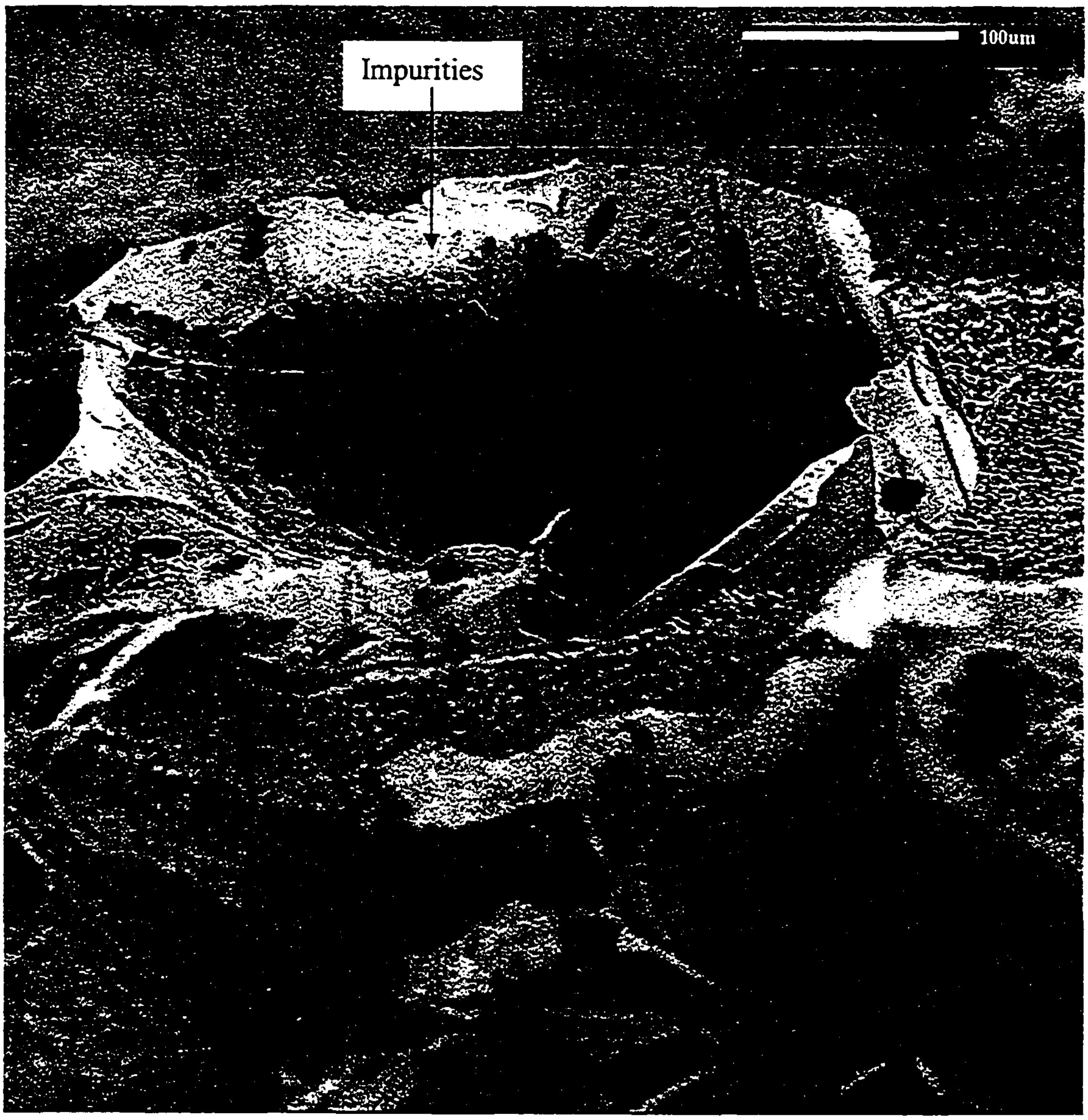


Figure 4.65: 180x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -10 °C and stored at the spray temperature for 2 days, showing a pore surrounded with wafer-like impurities.

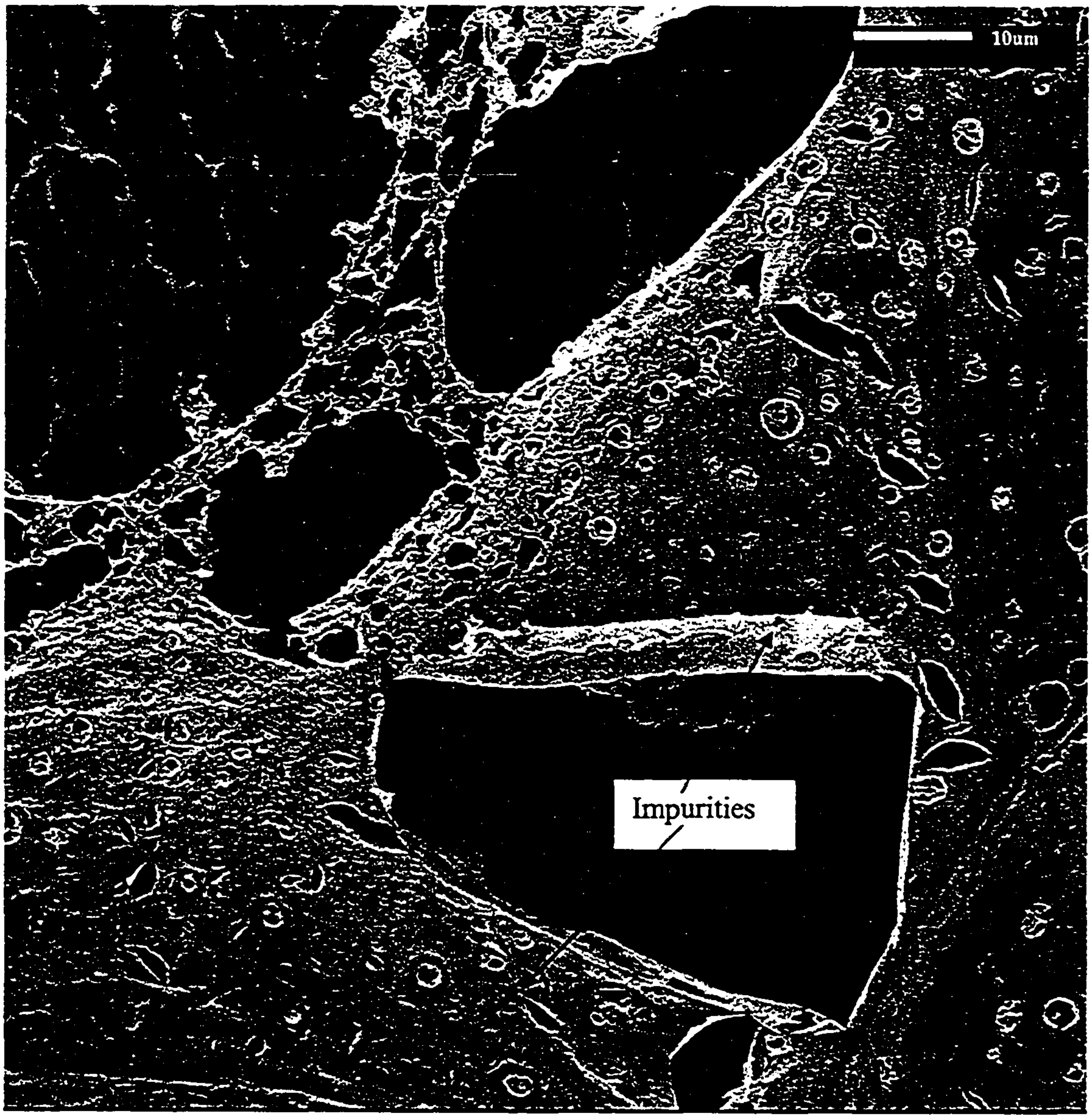


Figure 4.66: 1000x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -10 °C and stored at the spray temperature for 2 days, showing impurities inside a pore.

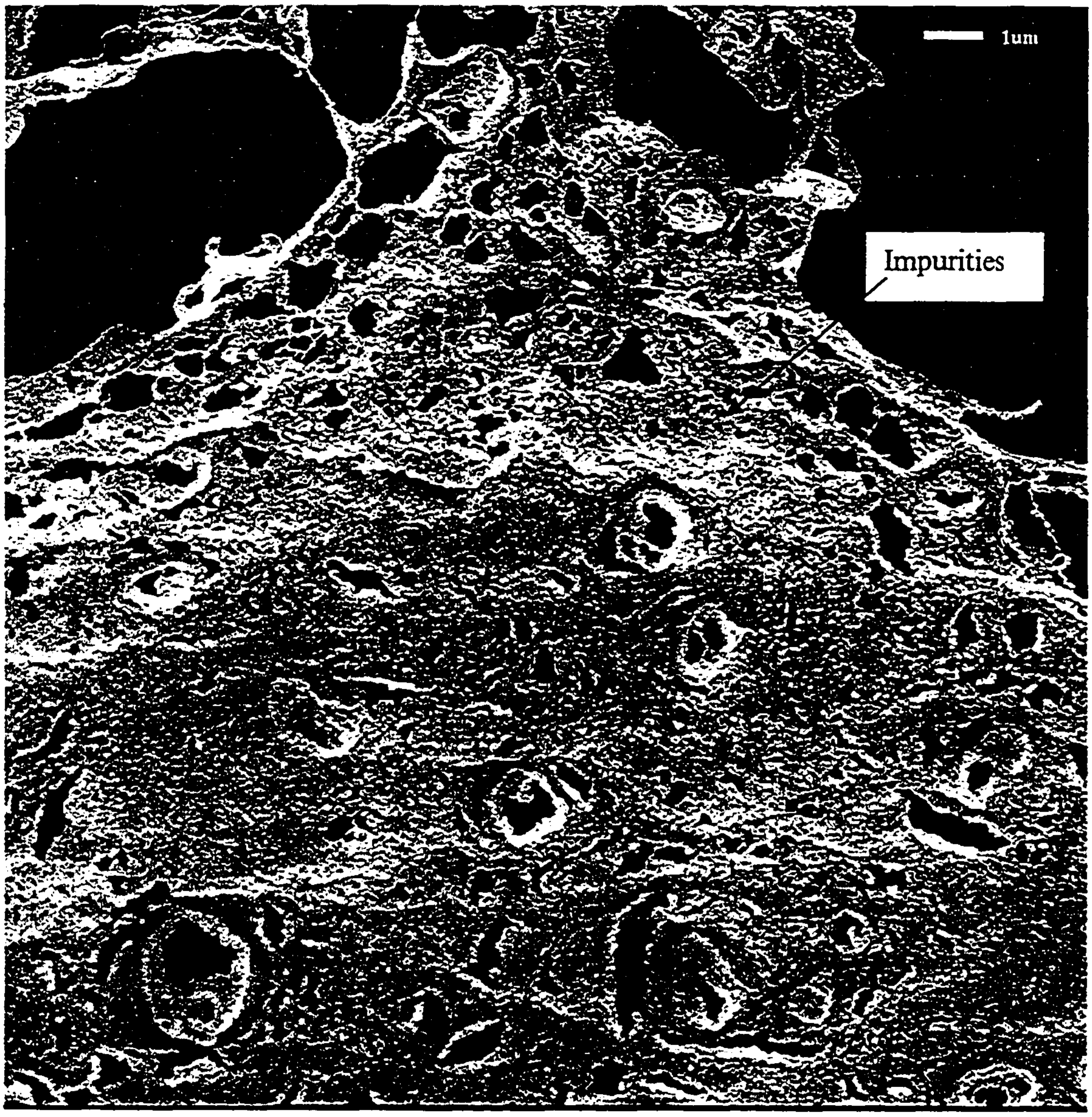


Figure 4.67: 5000x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -10 °C and stored at the spray temperature for 2 days, showing impurities inside a pore.

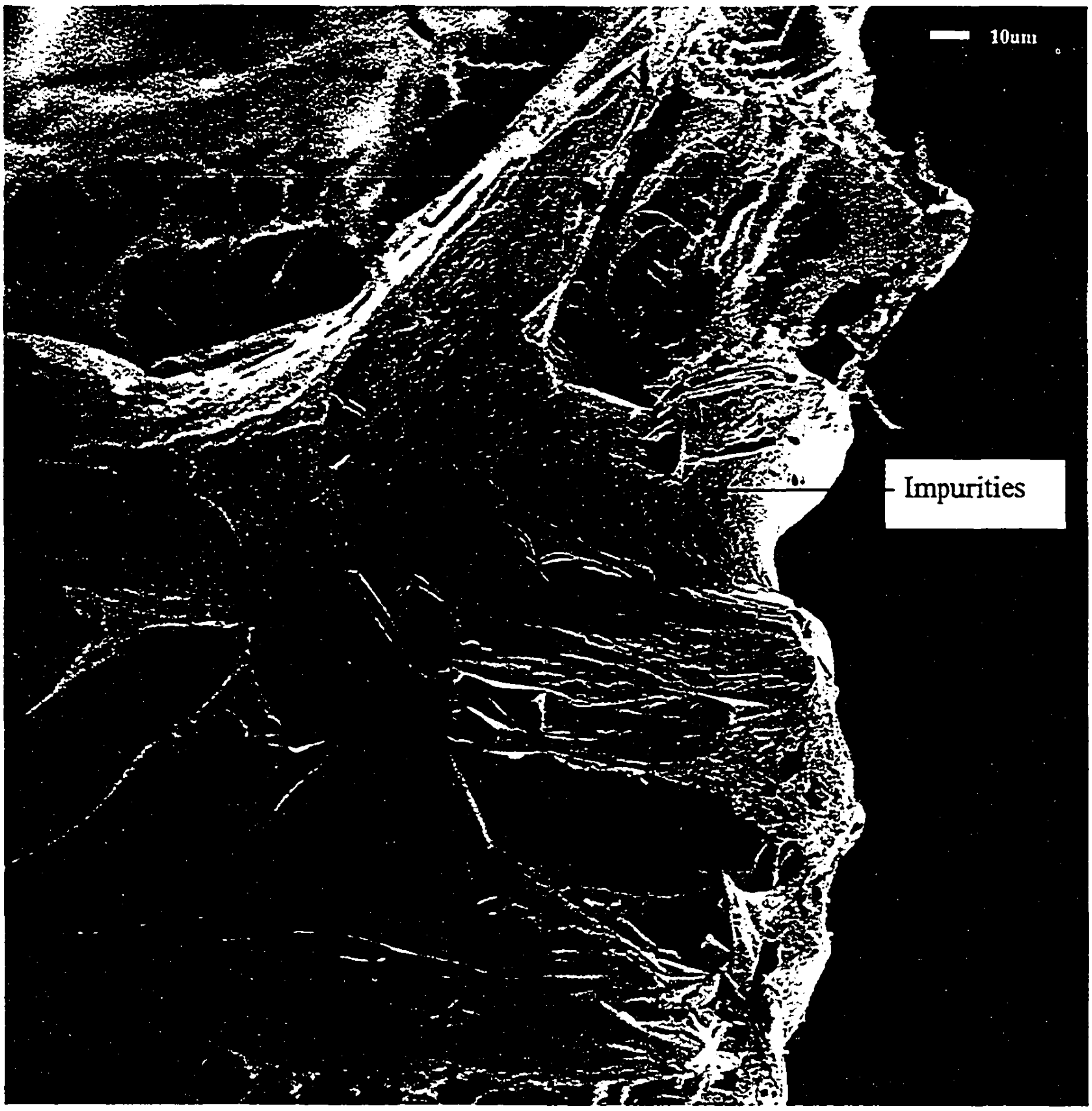


Figure 4.68: 350x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -25 °C and stored at the spray temperature for 2 days, showing impurities at the edge of a pore.

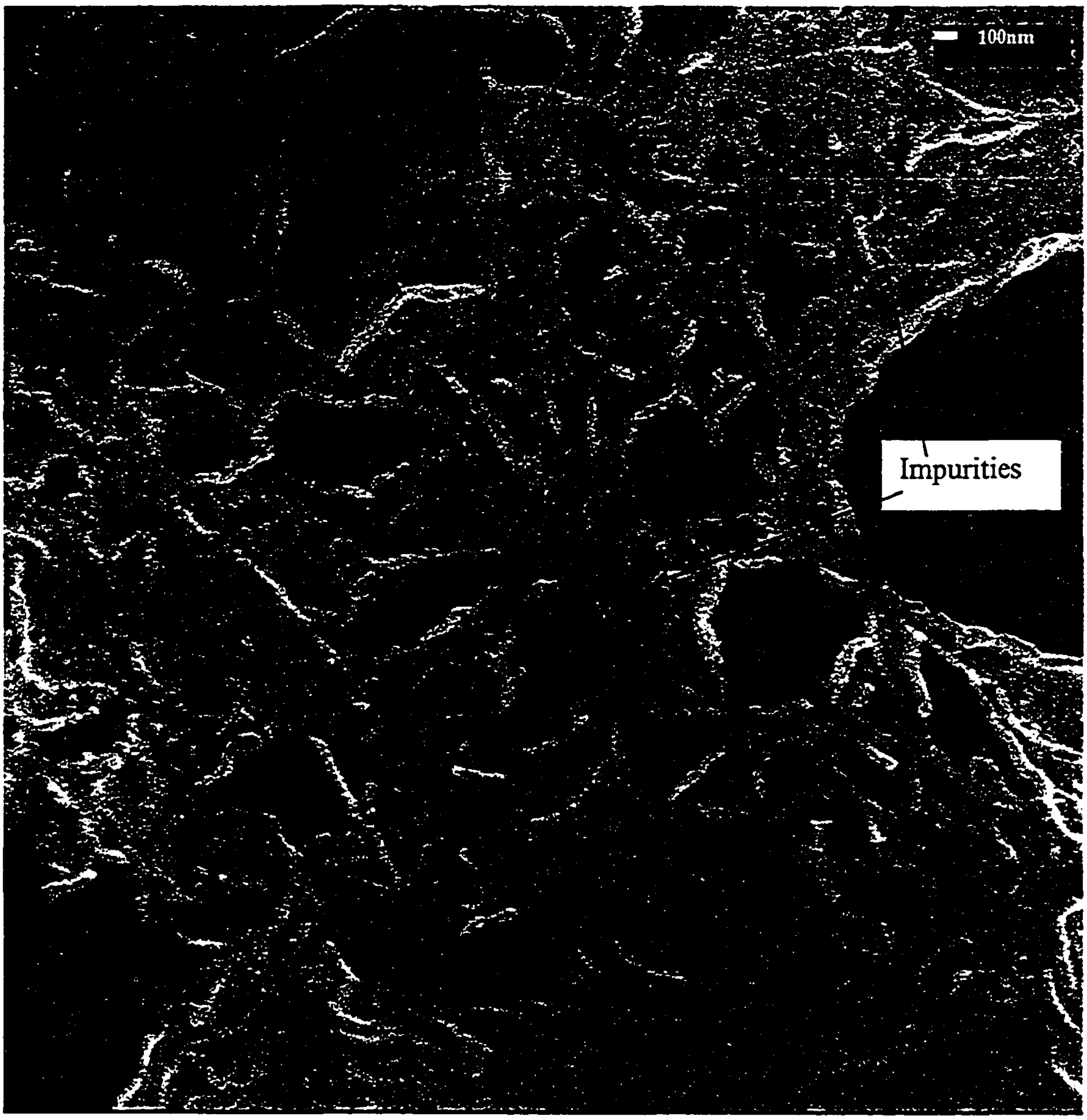


Figure 4.69: 20000x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -25 °C and stored at the spray temperature for 2 days, showing impurities inside a pore.

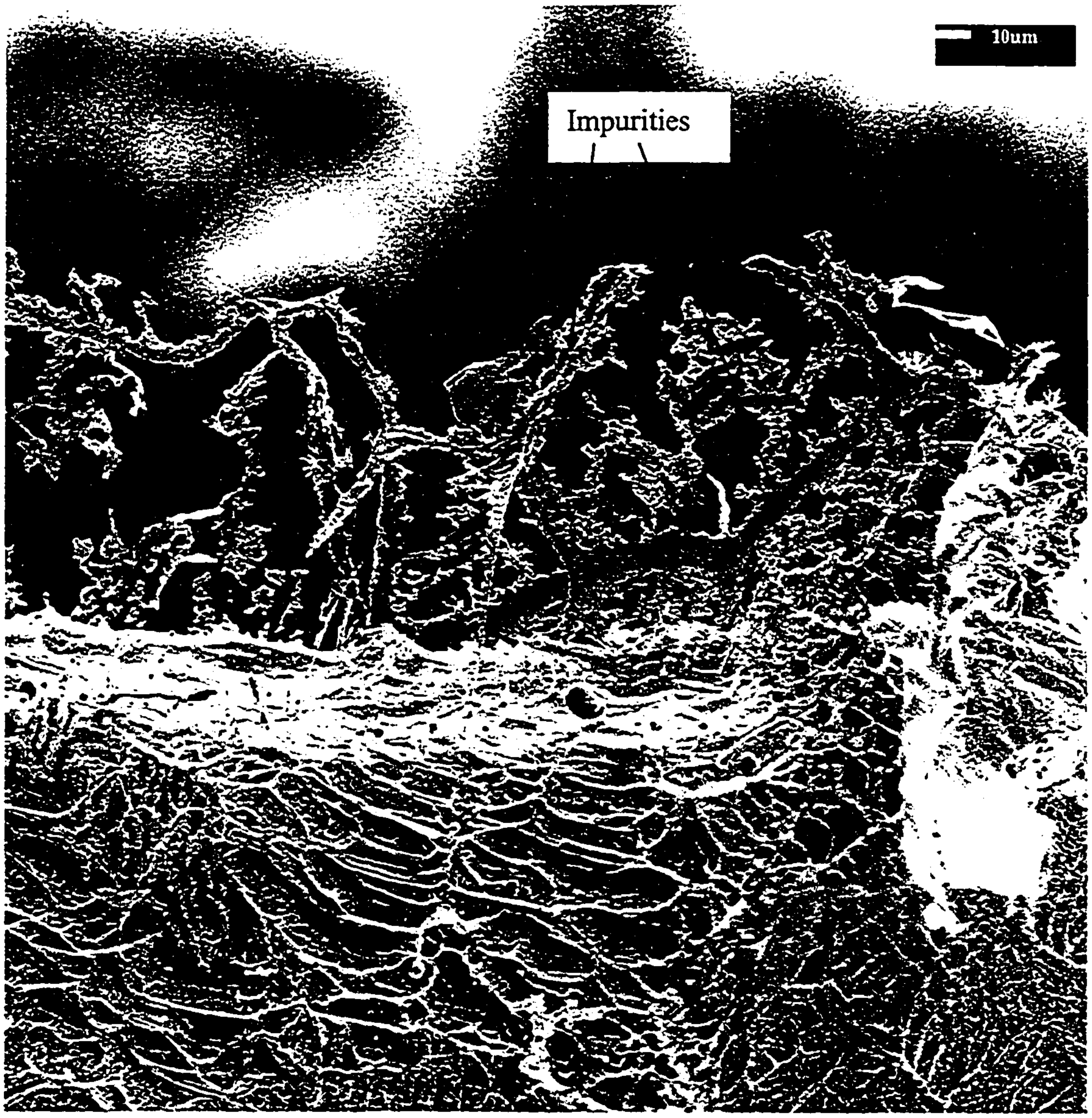


Figure 4.70: 300x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -25 °C and stored at the spray temperature for 2 days, showing dendritic effects inside a pore.

Figure 4.71: 2500x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -25 °C and stored at the spray temperature for 2 days, showing impurities in dendrite ice crystal inside a pore.

through the pore. Figure 4.69 shows a magnified image of the impurities on the surface inside the pore where impurities formed a web structure, which is different from the structure from by the impurities in the ice which was produced at -10 °C (Figure 4.66 and Figure 4.67). Figure 4.70 shows the dendrite ice with the impurities in it formed on the surface inside a pore. Figure 4.71 also shows the dendrite ice with the impurities, but with higher magnification. So the dendritic effect was only observed in the ice produced and stored at colder temperature (-25 °C). These dendrite ices with impurities in it should be readily removable by the meltwater when it passes through the pore.

Figure 4.72 to Figure 4.74 show the SEM images of a fractured ice specimen produced from spray freezing of pulp mill effluent at -10 °C and stored at the spray temperature for 14 days, at various magnifications. All three figures show the impurities on the surface inside a pore with gradually higher magnifications. It can be noticed that the structures of the impurities in theses images look more concentrated compared to that found in the images in Figure 4.65 to Figure 4.67. So it can be assumed that the impurity concentrations on the surface of the ice crystals are increased with the increase of the storage time, which eventually leads to the higher concentrations of the impurities in the early meltwater of the ice columns.

Figure 4.75 to Figure 4.78 show the SEM images of a fractured ice specimen produced from spray freezing of pulp mill effluent at -25 °C and stored at the spray temperature for 14 days, at various magnifications. Figure 4.75 shows the impurities on the surfaces of the ice pores and Figure 4.76 shows the same impurities with higher magnification. So, like any other pores, showed in the previous images, the pore surfaces are covered with impurities. Figure 4.77 also shows another pore whose surface is

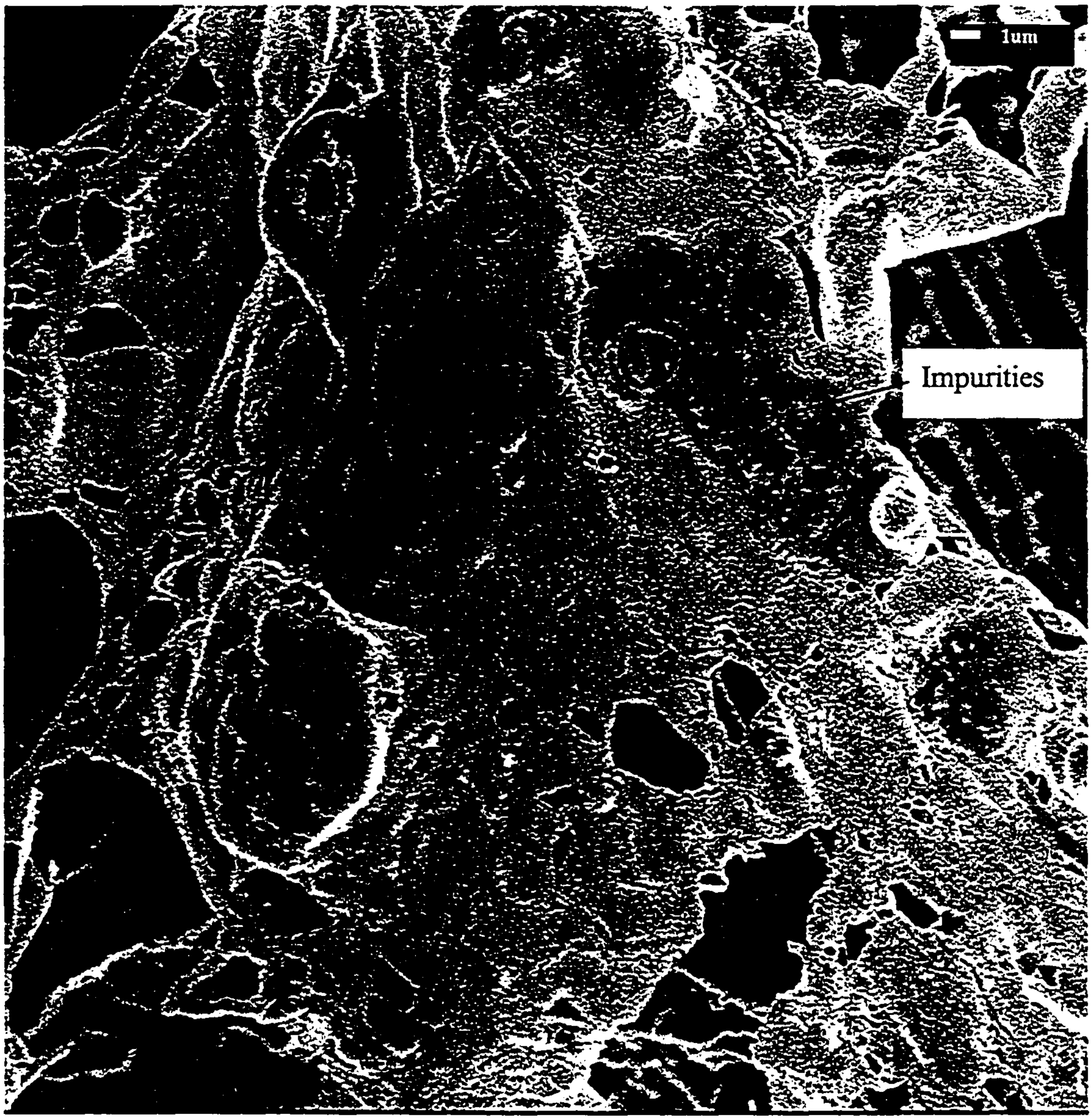


Figure 4.72: 2500x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -10 °C and stored at the spray temperature for 14 days, showing impurities inside a pore.

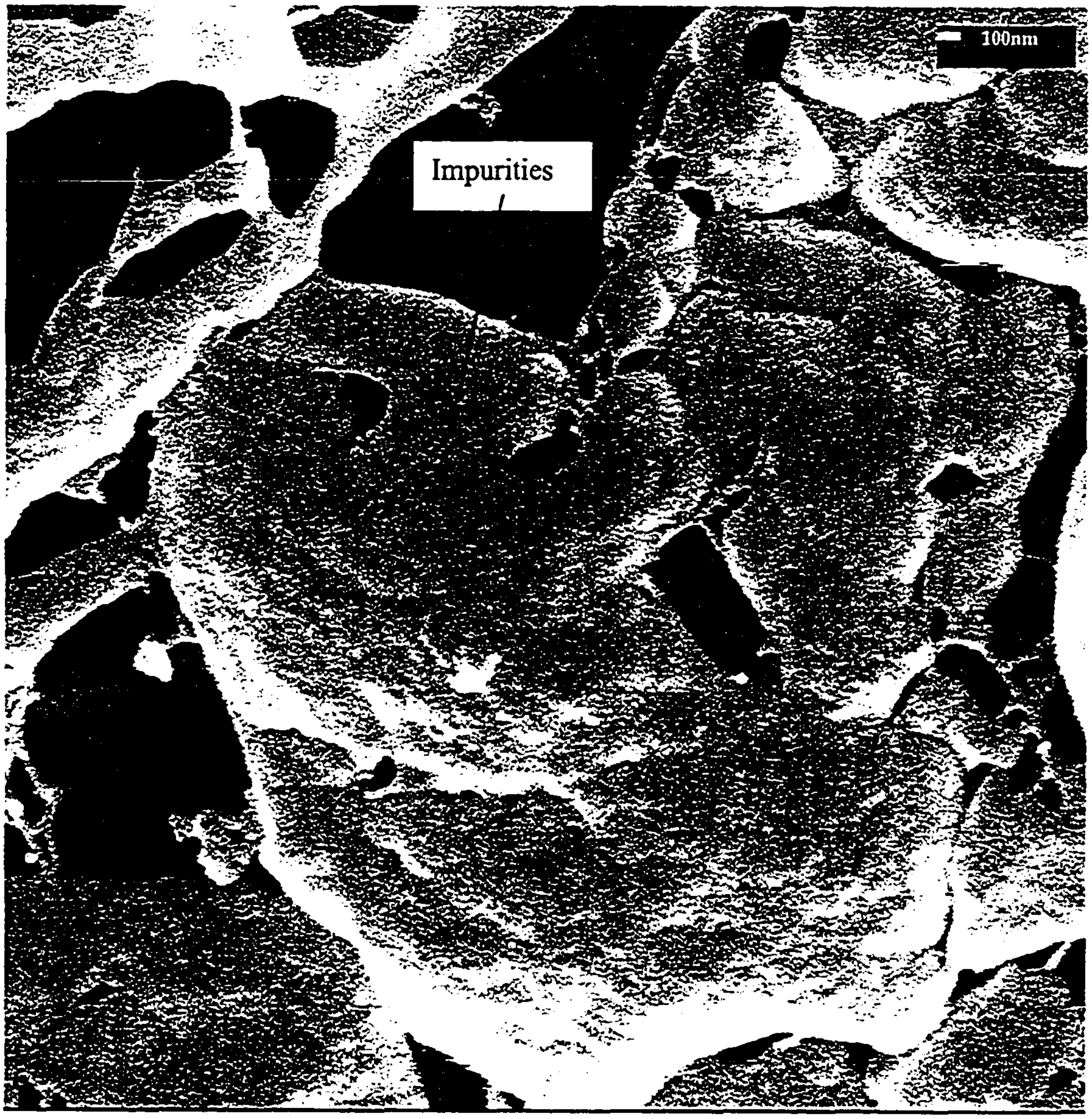


Figure 4.73: 20000x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -10 °C and stored at the spray temperature for 14 days, showing impurities inside a pore.

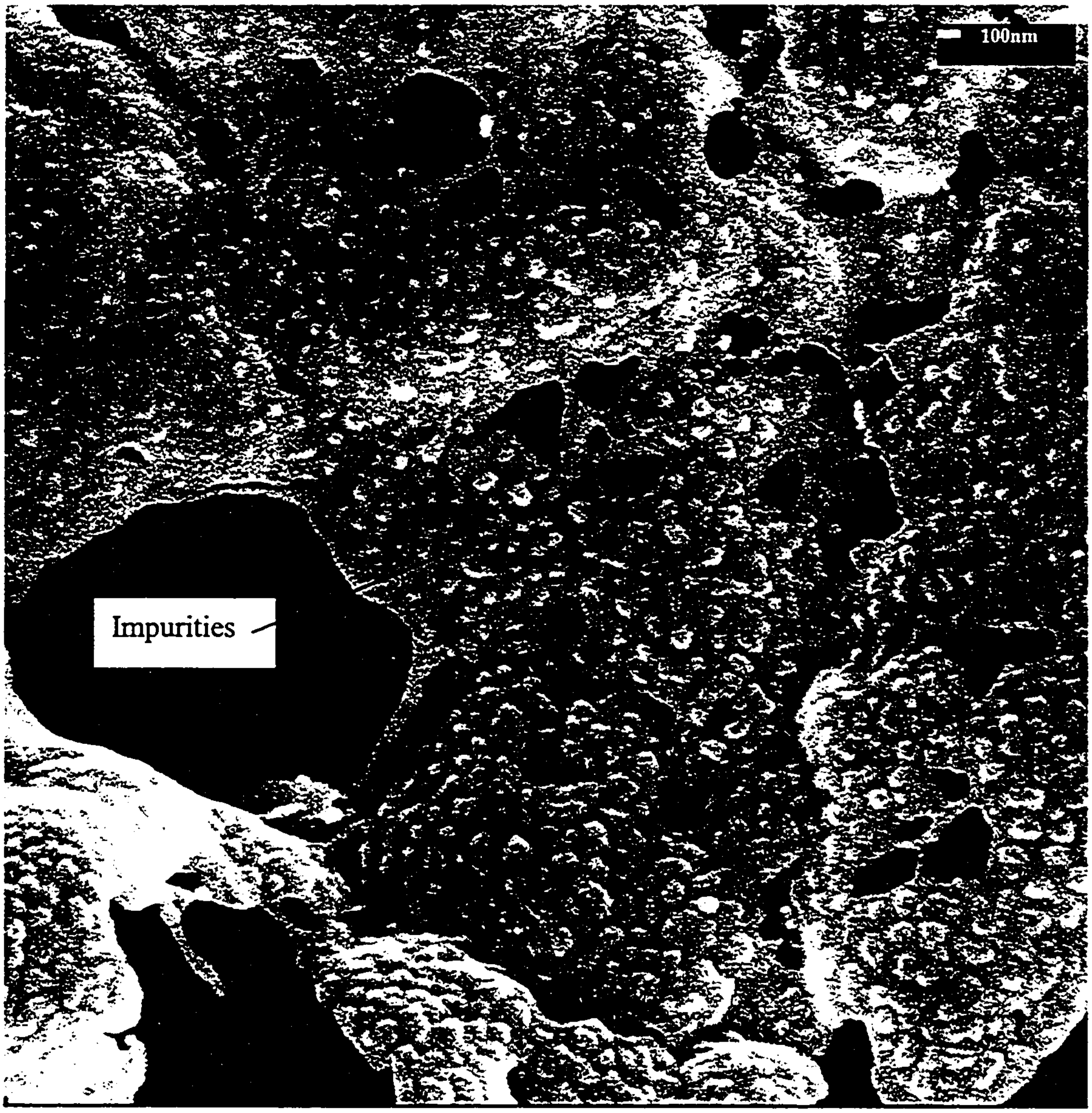


Figure 4.74: 20000x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -10 °C and stored at the spray temperature for 14 days, showing impurities inside a pore.

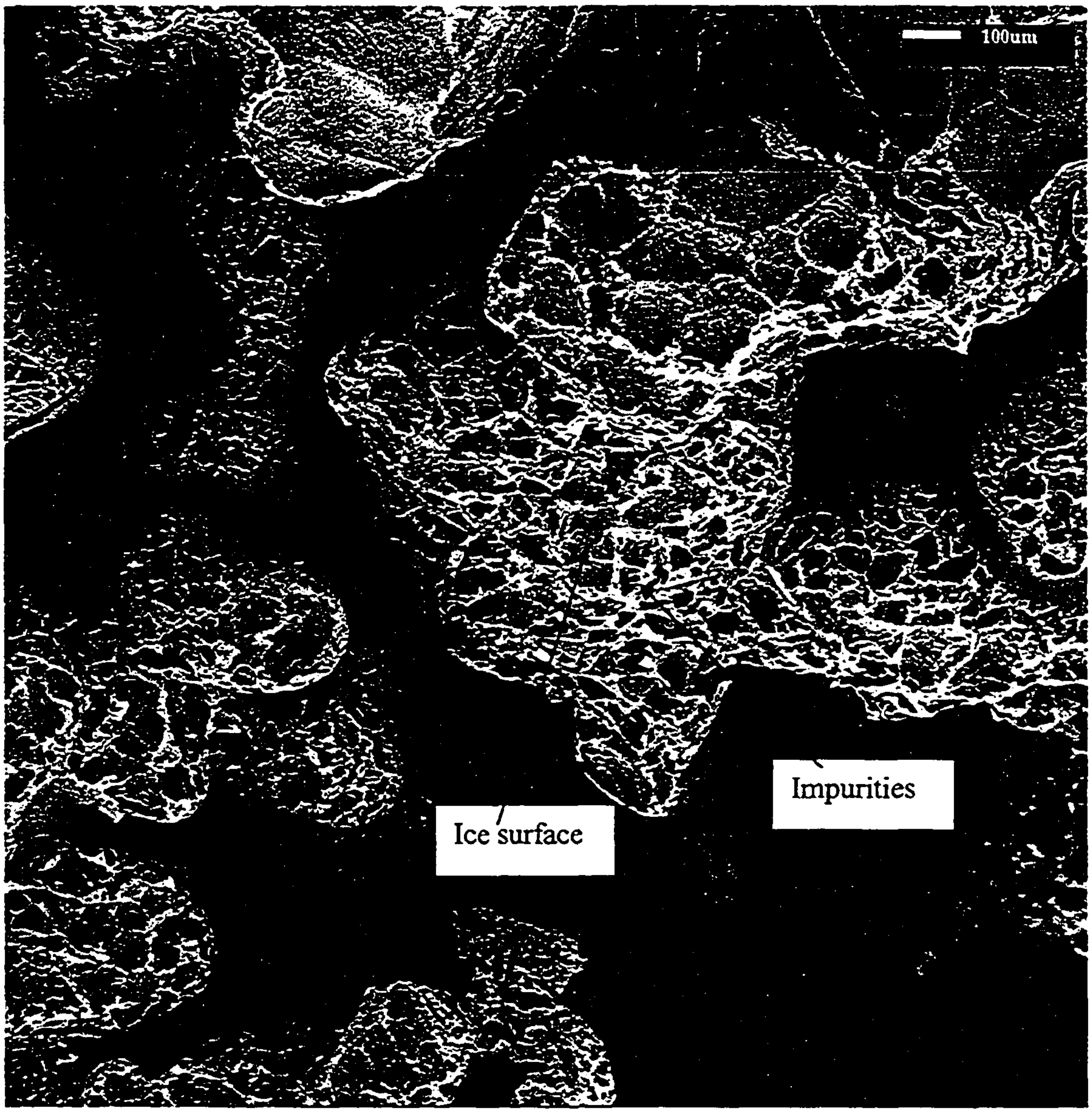


Figure 4.75: 50x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -25 °C and stored at the spray temperature for 14 days, showing impurities on the surface of the edges of a pore.

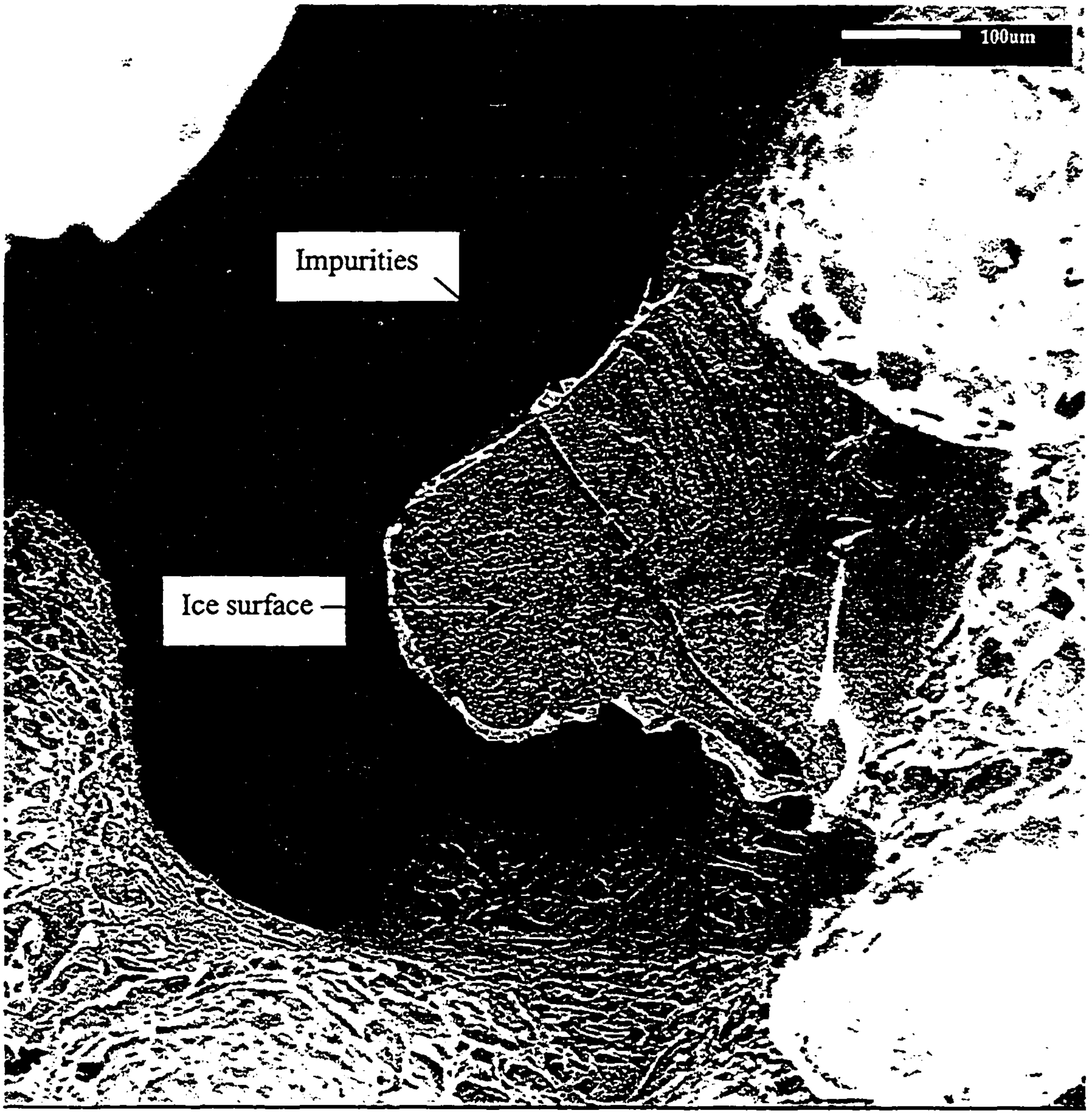


Figure 4.76: 100x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -25 °C and stored at the spray temperature for 14 days, showing impurities on the surface of the edges of a pore.

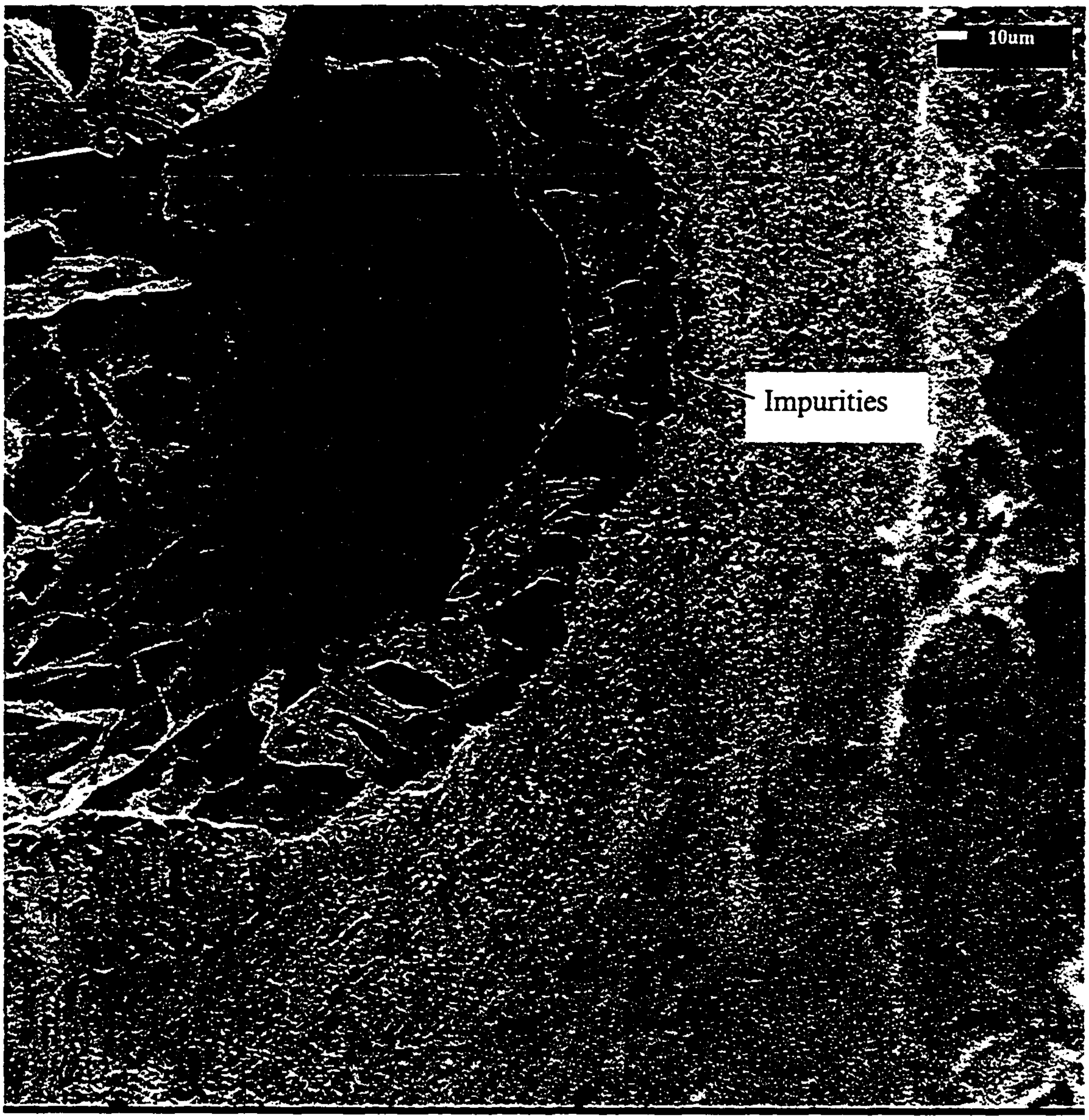


Figure 4.77: 270x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -25 °C and stored at the spray temperature for 14 days, showing wafer-like impurities surrounding the surface of a pore.

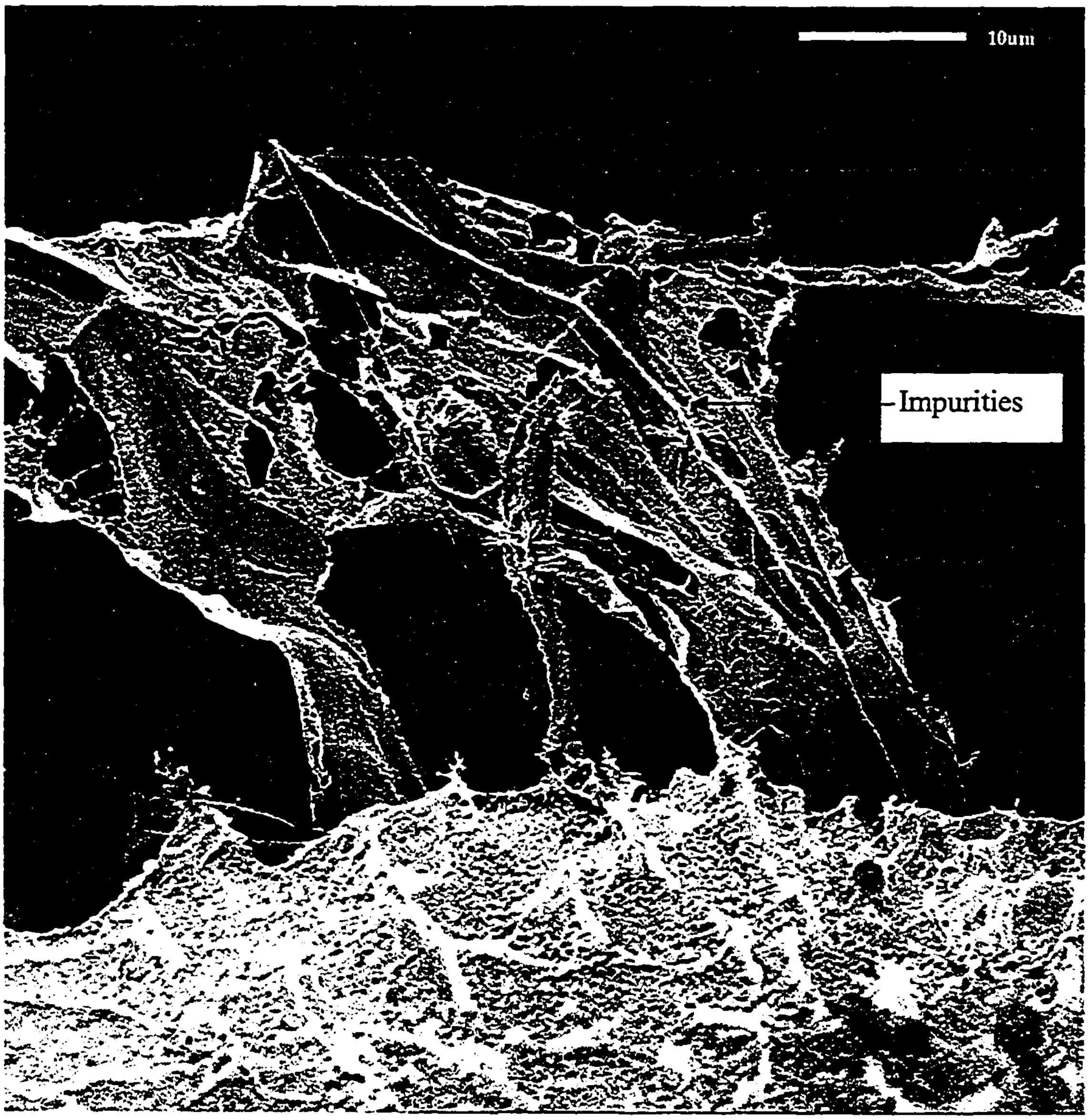


Figure 4.78: 1400x magnification scanning electron microscope image of a fractured ice specimen produced from spray freezing of pulp mill effluent at -25 °C and stored at the spray temperature for 14 days, showing impurities on the dendrite ice inside a pore.

covered with a layer of impurities which is similar to the image in Figure 4.65. But the image in Figure 4.77 is a bit different from the image in 4.65 when the structure of the impurity layer is observed. It can be noticed that the structure of the impurity layer found in the image in Figure 4.77 is more crisp, perforated and fragile, where the structure of the impurity layer found in the image in Figure 4.65 is smoother and stronger. The crisp and fragile structure of the impurity layer, formed in the ice produced at -25 °C and stored at the spray temperature for 2 weeks, can be attributed to the dendritic effect on ice which was profound at colder temperature. Figure 4.78 shows the dendrite ice structure with impurities on the surface inside a pore. This ice was stored for longer time (2 weeks) and a growth of dendrite ice structure can be noticed if the dendrite ice structure images in Figure 4.70 and Figure 4.71 are compared which was stored only for 2 days. It can also be noticed in the images in Figure 4.78 that the dendrite ice structure looks more concentrated with impurities. So the growth of dendrite ice structure with the ice storage time and the increase of impurity concentrations in it should lead to a higher impurity concentration in the initial meltwater. From all the SEM images, it can be observed that the dendritic effect of ice crystal was only noticed in the ice samples which were produced at the colder temperature and stored at the spray temperature.

5. CONCLUSIONS

This research project was carried out to fine the achievable toxicity and other impurity reduction efficiency and the factors affecting the efficiency. The experimental results obtained from this research study has shown that the impurities, as well as toxic compounds, in wastewaters can be effectively reduced by partial and spray freezing technique, which can be an alternative for cold region industries.

Partial freezing experiments conducted in beakers showed that as much as 97% impurities can be removed and the toxicity can be removed as well. Stirring was the most significant factor for removing impurities. The frozen portion obtained from the partial freezing with the application of stirring was found to be non toxic for both pulp mill effluent and refinery wastewater. It was also found that the higher impurity reduction could be achieved at warmer temperature, as -10 °C was more effective than -25 °C. Impurity concentration effect was also noticed. Impurity reduction efficiency was higher for wastewater with lower impurities, but with the application of stirring the impurity concentration effect can be minimized. Without stirring, 41% more TOC reduction was achieved for diluted (1:10) pulp mill effluent at -10 °C. With the application of stirring, the impurity reduction efficiency for both original and diluted pulp mill effluent was increased and the separation of impurities of original pulp mill effluent was about 5 % less than that of its diluted samples at -10 °C. Toxicity of the pulp mill effluent and refinery wastewater were reduced with the reduction of the impurities. For both wastewaters the correlation between toxicity and TOC and between toxicity and COD was positive where toxicity decreased with the reduction of impurities from the wastewaters. Impurity reduction efficiency can be different for different wastewaters, as it was also found that the impurity reduction was slightly better achieved for refinery wastewater than pulp mill effluent.

The results obtained from the spray freezing were also promising as an effective reduction of impurities from the spray ice was achieved by runoff impurity separation and initial meltwater impurity separation. As much as 90% and 80% impurity separation from the final 50% melt water was achieved for refinery wastewater and pulp mill effluent, respectively. The final 50% of the meltwater for pulp mill effluent was non-toxic and for refinery wastewater, linoleic acid and abietic acid solutions up to a certain level of toxicity reduction was achieved. It was found that a portion of impurities can be removed from the ice by runoff generated during spray freezing of wastewaters, which leaves an ice column with reduced impurity concentrations. So it is recommended to generate runoffs during spray freezing to achieve some impurity separation from the ice. The toxicity was also high as the impurity concentrations of the runoffs were high. It was noticed that the warmer spray temperature caused higher impurity concentrations in the runoffs, hence a purer ice.

When the ice melted, it was noticed that the initial meltwater had the higher impurity concentrations and the impurity concentrations reduced gradually with the sequential meltwater. It was found that the ice which was stored for more days (2 weeks) had higher concentration of impurities in the initial meltwater, which could be the result of the change in impurity distribution in the ice crystals with the ice storage time. For most of the cases it was found that the final 50% of the melt water achieved the higher impurity concentration reduction when the ice was produced at a warmer spray freezing temperature (-10 °C) and stored at spray temperature for longer period (2 weeks). This is believed to have happened for two higher impurity reduction steps; higher impurity reduction by runoff at -10 °C and higher impurity reduction by initial meltwater for longer ice storage time (2 weeks). Ice columns produced at -25 °C with shorter storage time (2 days) showed lower efficiency in impurity reduction of the final 50% meltwater than the ice columns which were produced at -10 °C and had shorter storage time (2 days). But the effect of spray temperature, at which the ice was produced, was reduced by the ice storage time. It was observed that the impurity reduction efficiency of the ice produced at colder temperatures but stored for longer period was close to the impurity reduction efficiency of the ice produced at warmer temperature with longer storage time. The impurity reduction efficiency for pulp mill effluent was significantly different from that for refinery wastewater, which was believed to happen because of the different nature and the concentration of impurities in the wastewaters. Correlation between toxicity and TCO and that between toxicity and COD were investigated and found to be strong. Toxicity reduced with the reduction of TOC and COD.

From the scanning electron microscopy images of the ice produced from the pulp mill effluent, it was found that the impurities were distributed and concentrated surrounding the pore surface of the ice which are believed to be washed away when meltwater percolates though the pores from top to bottom during melting. The wafer-like impurities looked more concentrated for the ice samples stored for longer period (2 weeks). Dendrite effect was only observed for the ice samples which were produced and stored at the colder temperature (-25 °C).

6. RECOMMENDATIONS

A greater difference in concentration of linoleic acid and abietic acid solutions can be used to carry out the spray freezing experiment, one with a very high and another with a very low concentration. Solution with low impurity concentration has a greater chance of erroneous result and can lead to wrong conclusion.

Optimum runoff generation rate can be determined for the spray freezing operation. Various amounts of runoff can be generated to see which removes the maximum amount of impurities and produce highest quality product water.

Effect of the height of the ice column on runoff generation and melt water impurity removal efficiency can be investigated. Runoff generation helps removes a portion of impurities. But with the increase of the height of the ice column runoff generation may reduce or stop. During ice melting operation, impurity separation by melt water may be affected by the height of the ice column.

Solubility of the impurities in water may have an effect in treatment efficiency. Spray freezing experiments can be conducted with synthetic wastewaters, one made with very soluble impurities and another with least soluble. Runoff and melt water results of the two synthetic wastewaters then can be compared.

A large scale filed study of spray freezing under natural condition can be carried out to investigate the impurity and toxicity reduction efficiency of wastewater. Laboratory results can be compared with field study results.

7. REFERENCES

1. Ali, M. and Sreekrishnan, T. R. 2001. Aquatic toxicity from pulp and paper mill effluents: a review. *Advances in Environmental Research*, V. 5, pp. 175-196.

2. American Public Health Association, American Water Works Association and American Environment Federation. 1998. Standard Methods for the Examination of Water and Wastewater. Edited by: Eaton, A.D., Clesceri, L.S. and Greenberg, A.E. American Public Health Association, Washington, DC.

3. Azouni, M. A., Casses, P., and Sergiani, B. 1997. Capture or repulsion of treated nylon particles by an ice water interface. *Colloids Surf. A: Physicochem Eng Aspects*, V.122, pp. 199-205.

4. Baker, R. A. 1967a. Trace organic contaminant concentration by freezing – I: Low inorganic aqueous solutions. *Water Research*, V.4, pp. 559-573.

5. Baker, R. A. 1967b. Trace organic contaminant concentration by freezing – II: Inorganic aqueous solutions. *Water Research*, V.4, pp. 559-573.

6. Baker, R. A. 1969. Trace organic contaminant concentration by freezing – III: Ice washing. *Water Research*, V.4, pp. 559-573.

7. Baker, R. A. 1970. Trace organic contaminant concentration by freezing – IV: Ionic effects. *Water Research*, V.4, pp. 559-573.

8. Bales, R. C., Davis, R. E. and Stanley, D. A. 1989. Ion elution through shallow homogeneous snow. *Water Resources Research*, V. 25, No. 8, pp. 1869-1877.

9. Brimblecombe, P., Clegg, S. L., Davies, T. D., Shooter, D. and Tranter, M. 1987. Observation of the preferential loss of major ions from melting snow and laboratory ice. *Water Research*, V. 21, No. 10, pp. 1279-1286.

10. Burton, J. A., Prim, R. C. and Slichter W. P. 1953. Distribution of solutes in crystals grown from the melt. *Journal of Chemistry & Physics*, V. 21, pp. 1987-1996.

11. Chalmers, B. 1959. How water freezes. *Scient. Am.*, V.200, pp. 114-122.

12. Chou, S. F. and Tsern, I. P. 2000. Treatment of low level liquid waste by an in-situ freezing-melting process. *Journal of the Chinese Institute of Engineers*, V. 23, No. 2, pp. 161-170.

13. Chowdhury, J. 1988. CPI warm up to freeze concentration. *Chem. Eng.*, V.95, pp. 24-31.

14. De Bruyn, A. M. H. and Rasmussen, J. B. 2001. Freeze concentration of ambient waters for toxicity testing. *Environmental Toxicology and Chemistry*, V. 20, No. 8, pp. 1733-1739.

15. Facey, R.M. and Smith, D.W. 2001. Freeze-Thaw Treatment of Membrane Concentrates Derived From Kraft Pulp Mill Operations. *Journal of Cold Regions Engineering*, Am. Soc. of Civil Engineers, V. 14, No. 2, pp. 69-90.

16. Fahraeus-Van Ree, G. E. and Payne, J. F. 1999. Enzyme cytochemical responses of mussels to resin acid constituents of pulp mill effluents. *Bulletin of Environmental Contaminant Toxicology*, V. 63, No. 4, pp. 430-437.

17. Gamal El-Din, M. and D.W. Smith. 2002. Comparing different designs and scales of bubble columns for their effectiveness in treating kraft pulp mill effluents. *Ozone: Science & Engineering*, V. 24, No. 5 pp. 307-320.

18. Gao, W., Sego, D. and Smith, D. W. 1996. Spray freezing to treat oil sands tailings pond water. In: Proceedings of 8th International Cold Regions Engineering Conference, Fairbanks, Alaska, August 12-17, 1996, pp. 60-70.

19. Gao, W. 1998. Partial freezing by spraying as a treatment alternative of selected industrial wastes. PhD Dissertation, University of Alberta, Edmonton, Alberta, Canada.

20. Gao, W., Smith, D. W., and Sego, D. C. 2003. Spray freezing treatment of water from oil sands tailing ponds. *Journal of Environmental Engineering and Science*, V. 2, No. 5, pp. 325-334.

21. Gao, W., Smith, D. W., and Sego, D. C. 2004a. Treatment of pulp mill and oil sands industrial wastewaters by the partial spray freezing process. *Water Research*, V. 38, pp. 579-584.

22. Gao, W., Smith, D. W., and Sego, D. C. 2004b. Release of contaminant from melting spray ice of industrial wastewater. *Journal of Cold Regions Engineering*, V. 18, No. 1, pp. 325-334.

23. Gay, G., Lorain, O., Azouni, A. and Aurelle, Y. 2003. Wastewater treatment by radial freezing with stirring effects. *Water Research*, V. 37, No. 10, pp. 2520.

24. Ham, F. van der, Witcamp, G. J., Graauw, J. de, and Rosmalen, G. M. van. 1998. Eutectic freeze crystallization: Application of process stream and wastewater purification. *Chemical Engineering and Processing*, V.37, pp. 207-213.

25. Hoekstra, P. and Miller, R. D. 1967. On the mobility of water molecules in the transition layer between ice and solid surface. *J. Colloid Interface Sci.*, V.25, pp. 166-173.

26. Huber, D. and Palmateer, G. 1985. Snowfluent: A joint experimental project between southwest regions of the Ministry of Environment and group Delta in the storage and renovation of sewage effluent by conversion to snow. Ontario Ministry of the Environment, 126 pp.

27. Islam S. and Hemond H. F. 1991. Evaluation of freeze-concentration technique for enrichment of natural organic substances in water. *Analytical Letters*, V. 24, No. 6, pp. 1035-1045.

28. Iwai, Y., Arai, Y., Itahara, H. and Ito, N. 1999. Effect of electric field on the normal freezing process of 3, 5-xylenol + naphthalene system. *Industrial and Engineering Chemistry Research*, V. 38, No. 12, pp. 4857-4859.

29. James, H.F. and Johnson, W.E. 1972. The role of freezing processes in wastewater treatment. Avco System Division, Willington, Massachusetts. Application of New Concepts of Physical-Chemical Wastewater Treatment, September, pp. 18-22.

30. Johannessen, M. and Henriksen, A. 1978. Chemistry of snow meltwater: changes in concentration during melting. *Water Resources Research*, 14, pp. 615-619

31. Krepchin, I. P. 1985. Fresh water from the sea. *High Techno.*, Sept. pp. 64-65.

32. Liss, S. N., Bicho, P. A., Saddler, J. N. 1997. Microbiology and biodegradation of resin acids in pulp mill effluents: a minireview. *Canadian Journal of Microbiology*, V. 43, pp. 599-611

33. Lorain, O., Thiebaud, P., Badorc, E. and Aurelle, Y. 2001. Potential of freezing in wastewater treatment: soluble pollutant applications. *Water Research*, V. 35, No. 2, pp. 541-547.

34. Martel, C. J. 1998. Cold weather clean; how freezing temperatures can be used for wastewater treatment. *Water Environment and Technology*, V. 10, No. 8, pp. 50-53.

35. McMinn, W. A. M., Keown, J., Allen, S. J. and Burnett, M. G. 2003. Effect of freeze-thaw process on partitioning of contaminants in ferric precipitate. *Water Research*, V. 37, No. 20, pp. 4815-4822.

36. Mohammed, A. and Smith, D. W. 1992. Effect of ozone on kraft process pulp mill effluent. *Ozone: Science & Engineering*, V. 14, pp. 461-485.

37. Murphy, J. K., Hulsey, R. A., Long, B. W. and Amarnath, R. K. 1993. Use of ozone and advanced oxidation processes to remove color from pulp and paper mill effluents. *Ozone in Water and Wastewater Treatment*, V. 2 Proceeding 11th, Ozone World Congress, San Francisco, S-10-24-37.

38. Murphy, P. 2000. Wastewater gets the cold treatment. *The Engineer*, V. 289, No. 7486, p. 26.

39. Peng, G. and Roberts, J. C. 2000. Solubility and toxicity of rasin acids. *Water Research*, V. 34, No. 10, pp. 2779-2785.

40. Poole, N. J., Wildish, D. J. and Kristmanson, D. D. 1978. The effects of the pulp and paper industry on the aquatic Environment. *Critical Review: Environment Control*, V. 8, No. 2, pp. 153-185.

41. Rodriguez, M., Luque, M., Alvarez, J. R. and Coca, J. 2000. A comparative study of reverse osmosis and freeze concentration for the removal of valeric acid from wastewaters. *Desalination*, V. 127, No. 1, pp. 1-11.

42. Roy-Arcand, L. and Archibald, F. 1996. Selective removal of resin and fatty acids from mechanical pulp effluents by ozone. *Water Research*, V. 30, No. 5, pp. 1269-1279.

43. Ruemekorf, R. 1994. Freeze concentration: its application in hazardous wastewater treatment. *J. Environmental Science and Pollution Control Ser*, V.7, pp. 513-524.

44. Sapach, R. and Viraraghavan, T. 1997. An introduction to the use of hydrogen peroxide and ultraviolet radiation: An advanced oxidation process. *Journal of Environmental Science & Health*. V. A32, No. 8, pp. 2355-2366.

45. Seip, H. M., Abrahamsen, G., Christophersen, N., Gjessing, E. T. and Staunes, A. O. 1980. Snow and meltwater chemistry in Minicatchments. SNSF-projec IR 53/80, Norwegian Forest Research Institute, Aas, Norway, 51 pp.

46. Shapiro, J. 1961. Freezing out, a safe technique for concentration of dilute solutions. *Science*, N.Y., V. 133, pp. 2063-2064.

47. Shirai, Y., Wakisaka, M., Miyawaki, O. and Sakashita, S. 1998. Condition for producing an ice layer with high purity for freeze wastewater treatment. *Journal of Food Processing*, V. 38, No. 38, pp. 297-308.

48. Sinclair, W. F. 1990. Controlling pollution from Canadian pulp and paper manufacturers: A federal perspective. *Ministry of Supply and Services Canada*, Ottawa.

49. Tsiouris, S., Vincent, C.E., Davies, T.D. and Brimblecombe, P. 1985. The elution of ions through field and laboratory snowpacks. *Annals of Glaciology*, V. 7.

50. Werker, A. G. and Hall, E. R. 1999. The influence of pH on the growth-linked biodegradation kinetics of selected resin acids found in pulp mill effluent. *Tappi Journal*, V. 82, No. 7, pp 169-177.

51. White, J.A. and Frere, D. 1994. *Snowfluentä* Wastewater Treatment through Atomizing Freeze-Crystallization. Delta Engineering, 2301 St. Laurent Blvd., Ottawa, Ontario, Canada K1G 4J7, pp 29.

52. Wiegandt, H. F. and Berg, R. L. von. 1980. Myths about freeze desalting. *Desalination*, V.33, pp. 287-297.

53. Workman E. J. and Reynolds S. E. 1949. Electrical phenomena occurring during the freezing of dilute aqueous solutions and their possible relationship to thunderstorm electricity. *Physical Review*, V. 3, No. 5, pp. 254-259.

54. Wright, G., Gamal El-Din, M. and Smith, D.W. 2002. Advanced oxidation processes for the removal of toxic chemicals from pulp mill effluents. International Ozone Association, Pan American Group Annual Conf., Raleigh, No. Carolina, 19-22 May, 13 p.

55. Wuite, J. J., MacAlpine, N. D., and Cook, S. 1997b. Snowfluent^{TM} treatment of liquid hog manure. Alberta Agriculture, Food, and Rural Development. 33 pp.

56. Wuite, J. J., MacAlpine, N. D., and Johnson, C. I. 1999. The use of Snowfluent^{TM} as an alternative method for treatment of liquid hog manure. Alberta Agriculture, Food, and Rural Development. 33 pp.

57. Yu, Z. and Mohn, W. W. 2002. Bio-augmentation with the resin acid-degrading bacterium *Zoogloea Resiniphila* DhA-35 to counteract pH stress in an aerated lagoon treating pulp and paper mill effluent. *Water Research*, V. 36, pp. 2793-2801.

APPENDIX A: Raw and Calculated Data

Beaker Freezing Experiments: Pulp Mill Effluent

Table A-1: TOC, COD, Color and Toxicity of frozen section for pulp mill effluent in beaker tests

Parameters		Freezing temperature = -10 °C				Freezing temperature = -25 °C			
		Dilution = 1:1		Dilution = 1:10		Dilution = 1:1		Dilution = 1:10	
		Stirring		Stirring		Stirring		Stirring	
		With	Without	With	Without	With	Without	With	Without
TOC (mg/L)	Replicate 1	27.01	139.34	1.26	3.87	50.37	135.33	0.84	4.94
	Replicate 2	29.34	126.67	2.33	3.73	47.76	135.90	1.19	4.37
	Average	28.18	133.01	1.79	3.80	49.07	135.62	1.01	4.65
COD (mg/L)	Replicate 1	131.11	385.62	11.77	18.96	165.62	187.06	13.20	24.71
	Replicate 2	144.05	346.80	13.20	23.27	169.94	369.80	17.52	26.15
	Average	137.58	366.21	12.49	21.11	167.78	378.43	15.36	25.43
Color (CU)	Replicate 1	69.18	480.76	3.77	11.47	159.59	484.61	3.77	21.09
	Replicate 2	59.56	438.44	3.77	13.39	196.14	511.54	3.77	26.86
	Average	64.37	459.60	3.77	12.43	177.86	498.08	3.77	23.97
Toxicity (TU)	Replicate 1	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic
	Replicate 2	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic
	Average	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic

Table A-2: TOC, COD, Color and Toxicity of unfrozen section for pulp mill effluent in beaker tests

Parameters		Freezing temperature = -10 °C				Freezing temperature = -25 °C			
		Dilution = 1:1		Dilution = 1:10		Dilution = 1:1		Dilution = 1:10	
		Stirring		Stirring		Stirring		Stirring	
		With	Without	With	Without	With	Without	With	Without
TOC (mg/L)	Replicate 1	574.00	402.40	70.80	53.84	503.2	396.2	66.57	52.64
	Replicate 2	524.20	382.30	69.76	51.46	459	403.5	61.09	53.61
	Average	549.10	392.35	70.28	52.65	481.1	399.85	63.83	53.13
COD (mg/L)	Replicate 1	1615.0	1223.9	236.08	201.57	1449.67	1221.04	234.64	194.38
	Replicate 2	1689.8	1294.3	218.82	213.07	1504.31	1169.28	223.14	184.31
	Average	1652.4	1259.2	227.45	207.32	1476.99	1195.16	228.89	189.35
Color (CU)	Replicate 1	2315.8	1523.3	236.53	198.06	2077.25	1696.44	207.68	201.91
	Replicate 2	2400.4	1661.8	217.30	184.6	1915.66	1569.48	215.37	182.67
	Average	2358.1	1592.6	226.92	191.33	1996.45	1632.96	211.53	192.29
Toxicity (TU)	Replicate 1	2.51	1.40	Not toxic	Not toxic	2.28	1.66	Not toxic	Not toxic
	Replicate 2	1.77	1.33	Not toxic	Not toxic	3.67	2.29	Not toxic	Not toxic
	Average	2.14	1.37	Not toxic	Not toxic	2.97	1.97	Not toxic	Not toxic

Table A-3: Normalized TOC, COD, color and toxicity in frozen section for pulp mill effluent in beaker tests

Parameters		Freezing temperature = -10 °C				Freezing temperature = -25 °C			
		Dilution = 1:1		Dilution = 1:10		Dilution = 1:1		Dilution = 1:10	
		Stirring		Stirring		Stirring		Stirring	
		With	Without	With	Without	With	Without	With	Without
TOC (C/C_o)	Replicate 1	0.11	0.58	0.05	0.14	0.21	0.56	0.03	0.18
	Replicate 2	0.12	0.53	0.09	0.14	0.2	0.56	0.04	0.16
	Average	0.12	0.55	0.07	0.14	0.2	0.56	0.04	0.17
COD (C/C_o)	Replicate 1	0.17	0.5	0.14	0.23	0.22	0.5	0.16	0.3
	Replicate 2	0.19	0.45	0.16	0.28	0.22	0.48	0.21	0.31
	Average	0.18	0.48	0.15	0.25	0.22	0.49	0.18	0.3
Color (C/C_o)	Replicate 1	0.08	0.54	0.04	0.12	0.18	0.55	0.04	0.23
	Replicate 2	0.07	0.49	0.04	0.15	0.22	0.58	0.04	0.29
	Average	0.07	0.52	0.04	0.13	0.2	0.56	0.04	0.26
Toxicity (TU/TU_o)	Replicate 1	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic
	Replicate 2	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic
	Average	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic	Not toxic

Table A-4: Normalized TOC, COD, color and toxicity in unfrozen section for pulp mill effluent in beaker tests

Parameters		Freezing temperature = -10 °C				Freezing temperature = -25 °C			
		Dilution = 1:1		Dilution = 1:10		Dilution = 1:1		Dilution = 1:10	
		Stirring		Stirring		Stirring		Stirring	
		With	Without	With	Without	With	Without	With	Without
TOC (C/C_o)	Replicate 1	2.39	1.67	2.63	2	2.09	1.65	2.47	1.95
	Replicate 2	2.18	1.59	2.59	1.91	1.91	1.68	2.27	1.99
	Average	2.28	1.63	2.61	1.95	2	1.66	2.37	1.97
COD (C/C_o)	Replicate 1	2.11	1.6	2.82	2.41	1.89	1.59	2.8	2.32
	Replicate 2	2.2	1.69	2.62	2.55	1.96	1.53	2.67	2.2
	Average	2.16	1.64	2.72	2.48	1.93	1.56	2.74	2.26
Color (C/C_o)	Replicate 1	2.61	1.71	2.56	2.15	2.34	1.91	2.25	2.19
	Replicate 2	2.7	1.87	2.36	2	2.16	1.77	2.33	1.98
	Average	2.65	1.79	2.46	2.07	2.25	1.84	2.29	2.08
Toxicity (TU/TU_o)	Replicate 1	2.42	1.35	Not toxic	Not toxic	2.20	1.60	Not toxic	Not toxic
	Replicate 2	1.71	1.28	Not toxic	Not toxic	3.54	2.21	Not toxic	Not toxic
	Average	2.06	1.32	Not toxic	Not toxic	2.87	1.90	Not toxic	Not toxic

Table A-5: TOC, COD and toxicity of frozen section for refinery wastewater in beaker tests

Parameters		Freezing temperature = -10 °C				Freezing temperature = -25 °C			
		Dilution = 1:1		Dilution = 1:10		Dilution = 1:1		Dilution = 1:10	
		Stirring		Stirring		Stirring		Stirring	
		With	Without	With	Without	With	Without	With	Without
TOC (mg/L)	Replicate 1	0.64	5.10	0.08	0.39	1.47	7.36	0.17	0.54
	Replicate 2	0.47	4.6	0.11	0.31	1.31	6.86	0.26	0.59
	Average	0.55	4.85	0.09	0.35	1.39	7.11	0.21	0.56
COD (mg/L)	Replicate 1	5.50	29.69	1.23	2.65	6.92	35.39	1.23	2.65
	Replicate 2	5.50	25.42	0	2.65	5.50	36.81	1.23	2.65
	Average	5.50	27.56	0.61	2.65	6.21	36.1	1.23	2.65
Toxicity (TU)	Replicate 1	Not toxic	0.90	Not toxic	Not toxic	Not toxic	1.67	Not toxic	Not toxic
	Replicate 2	Not toxic	1.02	Not toxic	Not toxic	Not toxic	1.30	Not toxic	Not toxic
	Average	Not toxic	0.96	Not toxic	Not toxic	Not toxic	1.49	Not toxic	Not toxic

Table A-6: TOC, COD and toxicity of unfrozen section for refinery wastewater in beaker tests

Parameters		Freezing temperature = -10 °C				Freezing temperature = -25 °C			
		Dilution = 1:1		Dilution = 1:10		Dilution = 1:1		Dilution = 1:10	
		Stirring		Stirring		Stirring		Stirring	
		With	Without	With	Without	With	Without	With	Without
TOC (mg/L)	Replicate 1	44.42	25.81	5.88	4.37	43.5	25.06	5.69	3.88
	Replicate 2	41.12	25.44	5.72	4.66	43.75	26.91	5.36	4.1
	Average	42.77	25.62	5.8	4.51	43.62	25.99	5.52	3.99
COD (mg/L)	Replicate 1	190.53	140.72	24	18.31	176.3	132.18	22.58	16.88
	Replicate 2	183.42	144.99	22.58	16.88	177.72	139.29	21.15	19.73
	Average	186.97	142.85	23.29	17.6	177.01	135.73	21.87	18.31
Toxicity (TU)	Replicate 1	8.89	6.46	Not toxic	Not toxic	9.87	10.5	Not toxic	Not toxic
	Replicate 2	13.76	4.97	Not toxic	Not toxic	7.64	5.34	Not toxic	Not toxic
	Average	11.32	5.72	Not toxic	Not toxic	8.76	7.92	Not toxic	Not toxic

Table A-7: Normalized TOC, COD and toxicity in frozen section for refinery wastewater in beaker tests

Parameters		Freezing temperature = -10 °C				Freezing temperature = -25 °C			
		Dilution = 1:1		Dilution = 1:10		Dilution = 1:1		Dilution = 1:10	
		Stirring		Stirring		Stirring		Stirring	
		With	Without	With	Without	With	Without	With	Without
TOC (C/C_o)		0.04	0.36	0.04	0.21	0.1	0.52	0.09	0.29
		0.03	0.32	0.06	0.17	0.09	0.48	0.14	0.32
		0.04	0.34	0.05	0.19	0.1	0.5	0.11	0.3
COD (C/C_o)	Replicate 1	0.08	0.43	0.15	0.32	0.1	0.51	0.15	0.32
	Replicate 2	0.08	0.37	0	0.32	0.08	0.53	0.15	0.32
	Average	0.08	0.4	0.07	0.32	0.09	0.52	0.15	0.32
Toxicity (TU/TU_o)	Replicate 1	Not toxic	0.5	Not toxic	Not toxic	Not toxic	0.92	Not toxic	Not toxic
	Replicate 2	Not toxic	0.56	Not toxic	Not toxic	Not toxic	0.72	Not toxic	Not toxic
	Average	Not toxic	0.53	Not toxic	Not toxic	Not toxic	0.82	Not toxic	Not toxic

Table A-8: Normalized TOC, COD and toxicity in unfrozen section for refinery wastewater in beaker tests

Parameters		Freezing temperature = -10 °C				Freezing temperature = -25 °C			
		Dilution = 1:1		Dilution = 1:10		Dilution = 1:1		Dilution = 1:10	
		Stirring		Stirring		Stirring		Stirring	
		With	Without	With	Without	With	Without	With	Without
TOC (C/C$_o$)		3.12	1.81	3.13	2.32	3.06	1.76	3.03	2.07
		2.89	1.79	3.04	2.48	3.08	1.89	2.85	2.18
		3.01	1.8	3.09	2.4	3.07	1.83	2.94	2.12
COD (C/C$_o$)	Replicate 1	2.74	2.02	2.88	2.19	2.53	1.9	2.71	2.02
	Replicate 2	2.64	2.08	2.71	2.02	2.56	2	2.54	2.36
	Average	2.69	2.05	2.79	2.11	2.55	1.95	2.62	2.19
Toxicity (TU/TU$_o$)	Replicate 1	4.91	3.57	Not toxic	Not toxic	5.45	5.8	Not toxic	Not toxic
	Replicate 2	7.59	2.75	Not toxic	Not toxic	4.22	2.95	Not toxic	Not toxic
	Average	6.25	3.16	Not toxic	Not toxic	4.83	4.37	Not toxic	Not toxic

Table A-9: TOC, COD, color and toxicity for runoff at -10 °C and -25 °C for pulp mill effluent

	Spray unit temperature = -10 ^{o}C					Spray unit temperature = -25 ^{o}C				
Parameters	Rep 1	Rep 2	Rep 3	Rep 4	Average	Rep 1	Rep 2	Rep 3	Rep 4	Average
TOC (mg/L)	501.9	499.1	503.3	495.2	499.9	433.4	439.6	442.7	454.7	442.6
COD (mg/L)	1493	14678	1458	1515	1483	1347	1331	1283	1322	1320.8
Color (CU)	1870	1783	1812	1754	1805	1610	1645	1575	1598	1607.0
Toxicity (TU)	2.54	2.18	-	-	2.36	1.60	2.12	-	-	1.86

Table A-10: Normalized TOC, COD, color and toxicity for runoff at -10 °C and -25 °C for pulp mill effluent

	Spray unit temperature = -10 ^{o}C					Spray unit temperature = -25 ^{o}C				
Parameters	Rep 1	Rep 2	Rep 3	Rep 4	Average	Rep 1	Rep 2	Rep 3	Rep 4	Average
TOC (C/C_o)	1.98	1.96	1.98	1.95	1.97	1.71	1.73	1.74	1.79	1.74
COD (C/C_o)	1.94	1.91	1.90	1.97	1.93	1.75	1.73	1.67	1.72	1.72
Color (C/C_o)	2.05	1.96	1.99	1.92	1.98	1.77	1.80	1.73	1.75	1.76
Toxicity (TU/TU_o)	2.00	1.73	-	-	1.86	1.27	1.67	-	-	1.47

Table A-11: TOC (mg/L) in melt water for pulp mill effluent

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	413.25	434.45	423.85	593.7	604.6	599.15	416	402.35	409.18	624.65	616.1	620.38
21.43	305.93	314.9	310.41	398.28	393.47	395.87	309.29	301.11	305.2	371.88	368.7	370.29
50	142.34	135.04	138.69	136.27	128.98	132.62	150.38	139.91	145.14	144.52	125.6	135.06
100	93.53	88.05	90.79	63.32	53.6	58.46	107.51	111.53	109.52	80.28	75.1	77.69

Table A-12: COD (mg/L) in melt water for pulp mill effluent

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	1325.2	1409.0	1367.1	1732.3	1785.3	1758.8	1204.7	1270.8	1237.8	1804.4	1792.6	1798.5
21.43	831.4	979.8	905.6	1013.6	894.6	954.1	918.1	937.2	927.7	1037.2	987.2	1012.2
50	389.0	346.4	367.7	362.5	334.6	348.6	384.6	419.9	402.2	336.1	365.5	350.8
100	227.3	221.4	224.4	161.2	171.5	166.3	290.5	303.8	297.1	218.5	211.2	214.8

Table A-13: Color (CU) in melt water for pulp mill effluent

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	1534.9	1609.9	1572.4	2544.8	2360.1	2452.4	1396.3	1523.3	1459.8	2279.3	2337.0	2308.2
21.43	1229.0	1292.5	1260.7	1309.8	1534.9	1422.3	1136.7	1194.4	1165.5	1211.7	1361.7	1286.7
50	526.9	576.9	551.9	492.3	534.6	513.5	530.8	569.3	550.0	426.9	380.7	403.8
100	313.5	280.8	297.1	226.9	190.4	208.6	338.5	303.9	321.2	250.0	234.6	242.3

Table A-14: Toxicity (TU) in melt water for pulp mill effluent

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	2.79	-	-	3.73	-	-	2.36	-	-	4.55	-	-
21.43	1.45	-	-	2.35	-	-	1.16	-	-	1.29	-	-
50	0.85	-	-	0.55	-	-	0.64	-	-	0.71	-	-
100	Not toxic	-	-	Not toxic	-	-	Not toxic	-	-	Not toxic	-	-

Table A-15: Normalized TOC concentration in the sequential meltwater samples of the spray ice made from pulp mill effluent

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	1.63	1.71	1.67	2.34	2.38	2.36	1.64	1.58	1.61	2.46	2.43	2.44
21.43	1.20	1.24	1.22	1.57	1.55	1.56	1.22	1.19	1.20	1.46	1.45	1.46
50	0.56	0.53	0.55	0.54	0.51	0.52	0.59	0.55	0.57	0.57	0.49	0.53
100	0.37	0.35	0.36	0.25	0.21	0.23	0.42	0.44	0.43	0.32	0.30	0.31

Table A-16: Normalized COD concentration in the sequential meltwater samples of the spray ice made from pulp mill effluent

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	1.73	1.83	1.78	2.26	2.32	2.29	1.57	1.65	1.61	2.35	2.33	2.34
21.43	1.08	1.28	1.18	1.32	1.16	1.24	1.20	1.22	1.21	1.35	1.29	1.32
50	0.51	0.45	0.48	0.47	0.44	0.45	0.50	0.55	0.52	0.44	0.48	0.46
100	0.30	0.29	0.29	0.21	0.22	0.22	0.38	0.40	0.39	0.28	0.27	0.28

Table A-17: Normalized color concentration in the sequential meltwater samples of the spray ice made from pulp mill effluent

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	1.68	1.77	1.72	2.79	2.59	2.69	1.53	1.67	1.60	2.50	2.56	2.53
21.43	1.35	1.42	1.38	1.44	1.68	1.56	1.25	1.31	1.28	1.33	1.49	1.41
50	0.58	0.63	0.61	0.54	0.59	0.56	0.58	0.62	0.60	0.47	0.42	0.44
100	0.34	0.31	0.33	0.25	0.21	0.23	0.37	0.33	0.35	0.27	0.26	0.27

Table A-18: Normalized toxicity in the sequential meltwater samples of the spray ice made from pulp mill effluent

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	2.20	-	-	2.95	-	-	1.87	-	-	3.59	-	-
21.43	1.14	-	-	1.85	-	-	0.91	-	-	1.02	-	-
50	0.67	-	-	0.43	-	-	0.50	-	-	0.56	-	-
100	Not toxic	-	-	Not toxic	-	-	Not toxic	-	-	Not toxic	-	-

Table A-19: TOC, COD and toxicity for runoff at -10 °C and -25 °C for refinery wastewater

	Spray unit temperature = -10 °C					Spray unit temperature = -25 °C				
Parameters	Rep 1	Rep 2	Rep 3	Rep 4	Average	Rep 1	Rep 2	Rep 3	Rep 4	Average
TOC (mg/L)	28.76	29.51	28.85	31.04	29.54	24.82	25.12	25.92	24.83	25.17
COD (mg/L)	157.41	148.61	151.54	160.35	154.48	129.54	133.94	132.47	126.6	130.64
Toxicity (TU)	4.65	7.32	-	-	5.99	8.88	4.87	-	-	6.87

Table A-20: Normalized TOC, COD and toxicity for runoff at -10 °C and -25 °C for refinery wastewater

	Spray unit temperature = -10 °C					Spray unit temperature = -25 °C				
Parameters	Rep 1	Rep 2	Rep 3	Rep 4	Average	Rep 1	Rep 2	Rep 3	Rep 4	Average
TOC (C/C_o)	1.91	1.96	1.91	2.06	1.96	1.65	1.67	1.72	1.65	1.67
COD (C/C_o)	2.18	2.05	2.10	2.22	2.14	1.79	1.85	1.83	1.75	1.81
Toxicity (TU/TU_o)	1.95	3.07	-	-	2.51	3.72	2.04	-	-	2.88

Table A-21: TOC (mg/L) of the melt water for refinery wastewater

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	24.66	23.74	24.2	42.48	45.78	44.13	22.93	24.32	23.62	44.29	38.8	41.54
21.43	18.9	17.48	18.19	28.69	25.08	26.88	16.35	18.62	17.49	32.87	34.73	33.8
50	8.85	9.88	9.36	7.74	7.05	7.39	10.69	11.91	11.3	8.09	8.53	8.31
100	5.91	6.67	6.29	1.01	1.58	1.29	6.88	5.29	6.08	1.08	2.34	1.71

Table A-22: COD (mg/L) of the melt water for refinery wastewater

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	136.87	147.14	142.01	205.82	192.62	199.22	123.67	128.07	125.87	198.49	210.22	204.36
21.43	88.46	97.26	92.86	133.94	119.27	126.6	87	98.73	92.86	117.8	123.67	120.74
50	41.52	38.58	40.05	40.05	34.18	37.12	54.72	51.79	53.25	45.92	44.45	45.19
100	22.45	20.98	21.71	13.65	12.18	12.91	26.85	25.38	26.11	16.58	13.65	15.11

Table A-23: Toxicity (TU) of the melt water for refinery wastewater

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	5.96	-	5.96	18.58	-	18.58	4.26	-	4.26	14.64	-	14.64
21.43	2.32	-	2.32	3.24	-	3.24	4.05	-	4.05	6.46	-	6.46
50	1.18	-	1.18	1.33	-	1.33	1.12	-	1.12	1.25	-	1.25
100	0.98	-	0.98	0.73	-	0.73	1.23	-	1.23	0.65	-	0.65

Table A-24: Normalized TOC concentration in the meltwater samples of the spray ice made from refinery wastewater

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	1.64	1.57	1.6	2.82	3.04	2.93	1.52	1.61	1.57	2.94	2.57	2.76
21.43	1.25	1.16	1.21	1.9	1.66	1.78	1.08	1.24	1.16	2.18	2.3	2.24
50	0.59	0.66	0.62	0.51	0.47	0.49	0.71	0.79	0.75	0.54	0.57	0.55
100	0.39	0.44	0.42	0.07	0.1	0.09	0.46	0.35	0.4	0.07	0.15	0.11

Table A-25: Normalized COD concentration in the meltwater samples of the spray ice made from refinery wastewater

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	1.89	2.03	1.96	2.85	2.66	2.75	1.71	1.77	1.74	2.74	2.91	2.83
21.43	1.22	1.34	1.28	1.85	1.65	1.75	1.2	1.37	1.28	1.63	1.71	1.67
50	0.57	0.53	0.55	0.55	0.47	0.51	0.76	0.72	0.74	0.63	0.61	0.62
100	0.31	0.29	0.3	0.19	0.17	0.18	0.37	0.35	0.36	0.23	0.19	0.21

Table A-26: Normalized toxicity in the samples of the spray ice made from refinery wastewater

% melt water	Spray unit temperature = -10 °C						Spray unit temperature = -25 °C					
	2 day-storage			2 week-storage			2 day-storage			2 week-storage		
	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average	Rep 1	Rep 2	Average
7.14	2.5	-	2.5	7.78	-	7.78	1.78	-	1.78	6.13	-	6.13
21.43	0.97	-	0.97	1.35	-	1.35	1.7	-	1.7	2.71	-	2.71
50	0.49	-	0.49	0.56	-	0.56	0.47	-	0.47	0.52	-	0.52
100	0.41	-	0.41	0.31	-	0.31	0.52	-	0.52	0.27	-	0.27

Spray Freezing and Melting Experiment: Linoleic Acid

Table A-27: TOC, COD and toxicity of runoff at -10 °C and -25 °C for linoleic acid

Parameters	Spraying unit temperature							
	-10 °C				-25 °C			
	5 mg/L	5 mg/L	20 mg/L	20 mg/L	5 mg/L	5 mg/L	20 mg/L	20 mg/L
TOC (mg/L)	8.47	8.91	21.06	20.96	8.60	8.34	19.63	20.57
COD (mg/L)	49.19	52.56	87.55	91.81	43.51	42.39	80.45	86.00
Toxicity (TU)	29.33	21.51	51.02	45.45	11.95	14.62	33.90	63.29

Table A-28: Normalized TOC, COD and toxicity of runoff -10 °C and -25 °C for linoleic acid

Parameters	Spraying unit temperature							
	-10 °C				-25 °C			
	5 mg/L	5 mg/L	20 mg/L	20 mg/L	5 mg/L	5 mg/L	20 mg/L	20 mg/L
TOC (C/C_o)	1.65	1.73	1.66	1.65	1.67	1.62	1.55	1.62
COD (C/C_o)	1.86	1.99	1.62	1.70	1.65	1.61	1.49	1.59
Toxicity (TU/TU_o)	6.60	4.84	1.85	1.65	2.69	3.29	1.23	2.29

Table A-29: TOC (mg/L) of the melt water for linoleic acid

% melt water	Spraying unit temperature							
	-10 °C				-25 °C			
	Ice storage Time				Ice storage Time			
	2 days		2 weeks		2 days		2 weeks	
	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L
7.14	8.48	19.45	10.64	24.69	7.76	20.47	10.65	26.41
21.43	6.15	16.29	7.60	18.20	6.86	15.84	7.75	19.85
50.00	3.83	13.89	4.07	12.52	4.05	14.71	4.53	12.44
100.00	2.54	6.75	1.59	5.92	2.84	7.42	1.77	5.69

Table A-30: COD (mg/L) of the melt water for linoleic acid

% melt water	Spraying unit temperature							
	-10 °C				-25 °C			
	Ice storage Time				Ice storage Time			
	2 days		2 weeks		2 days		2 weeks	
	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L
7.14	50.61	87.55	61.29	93.27	40.66	79.03	51.11	107.80
21.43	39.24	52.03	36.57	70.01	32.14	46.35	38.03	59.83
50.00	15.09	46.35	13.32	52.56	20.77	39.24	22.04	45.30
100.00	10.83	20.77	6.05	13.32	15.09	30.72	11.86	19.13

Table A-31: Toxicity (TU) of the melt water for linoleic acid

% melt water	Spraying unit temperature							
	-10 °C				-25 °C			
	Ice storage Time				Ice storage Time			
	2 days		2 weeks		2 days		2 weeks	
	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L
7.14	23.47	49.50	31.25	51.02	18.21	48.31	9.03	57.14
21.43	24.33	24.69	12.66	33.67	8.69	23.64	10.86	32.36
50.00	4.87	25.71	2.22	24.33	5.36	16.53	4.25	23.58
100.00	1.84	5.46	1.33	1.99	3.50	9.42	2.03	4.64

Table A-32: Normalized TOC concentration in the meltwater samples of the spray ice made from linoleic acid

% melt water	Spraying unit temperature							
	-10 °C				-25 °C			
	Ice storage Time				Ice storage Time			
	2 days		2 weeks		2 days		2 weeks	
	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L
7.14	1.65	1.53	2.07	1.94	1.51	1.61	2.07	2.08
21.43	1.20	1.28	1.48	1.43	1.33	1.25	1.51	1.56
50.00	0.74	1.09	0.79	0.99	0.79	1.16	0.88	0.98
100.00	0.49	0.53	0.31	0.47	0.55	0.58	0.34	0.45

Table A-33: Normalized COD concentration in the meltwater samples of the spray ice made from linoleic acid

% melt water	Spraying unit temperature							
	-10 °C				-25 °C			
	Ice storage Time				Ice storage Time			
	2 days		2 weeks		2 days		2 weeks	
	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L
7.14	1.92	1.62	2.32	1.73	1.54	1.46	1.94	2.00
21.43	1.49	0.96	1.39	1.30	1.22	0.86	1.44	1.11
50.00	0.57	0.86	0.50	0.97	0.79	0.73	0.83	0.84
100.00	0.41	0.38	0.23	0.25	0.57	0.57	0.45	0.35

Table A-34: Normalized toxicity in the meltwater samples of the spray ice made from linoleic acid

% melt water	Spraying unit temperature							
	-10 °C				-25 °C			
	Ice storage Time				Ice storage Time			
	2 days		2 weeks		2 days		2 weeks	
	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L
7.14	5.28	1.79	7.03	1.85	4.10	1.75	2.03	2.07
21.43	5.47	0.89	2.85	1.22	1.95	0.86	2.44	1.17
50.00	1.10	0.93	0.50	0.88	1.21	0.60	0.96	0.85
100.00	0.41	0.20	0.30	0.07	0.79	0.34	0.46	0.17

Spray Freezing and Melting Experiment: Abietic Acid:

Table A-35: TOC, COD and toxicity of runoff at -10 °C and -25 °C for abietic acid

Parameters	Spray unit temperature							
	-10 °C				-25 °C			
	5 mg/L	5 mg/L	20 mg/L	20 mg/L	5 mg/L	5 mg/L	20 mg/L	20 mg/L
TOC (mg/L)	8.06	7.77	23.63	23.94	7.10	7.35	22.63	23.54
COD (mg/L)	39.24	38.03	120.23	132.51	37.82	35.12	108.87	103.44
Toxicity (TU)	4.11	6.88	34.36	29.94	8.23	4.66	34.84	51.28

Table A-36: Normalized TOC, COD and toxicity of runoff at -10 °C and -25 °C for abietic acid

Parameters	Spray unit temperature							
	-10 °C				-25 °C			
	5 mg/L	5 mg/L	20 mg/L	20 mg/L	5 mg/L	5 mg/L	20 mg/L	20 mg/L
TOC (C/C_o)	1.76	1.70	1.61	1.63	1.55	1.61	1.54	1.61
COD (C/C_o)	1.91	1.85	1.72	1.89	1.84	1.71	1.56	1.48
Toxicity (TU/TU_o)	1.57	2.62	2.19	1.91	3.14	1.78	2.22	3.27

Table A-37: TOC (mg/L) of the melt water for abietic acid

% melt water	Spray unit temperature							
	-10 °C				-25 °C			
	Ice storage Time				Ice storage Time			
	2 days		2 weeks		2 days		2 weeks	
	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L
7.14	8.12	22.43	9.81	29.12	7.40	23.25	10.80	29.35
21.43	5.64	17.34	6.25	19.60	6.20	18.89	6.91	21.33
50.00	3.57	12.14	4.24	13.04	4.41	14.13	3.87	13.36
100.00	2.15	7.92	1.32	7.00	2.51	8.69	1.87	7.54

Table A-38: COD (mg/L) of the melt water for abietic acid

% melt water	Spray unit temperature							
	-10 °C				-25 °C			
	Ice storage Time				Ice storage Time			
	2 days		2 weeks		2 days		2 weeks	
	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L
7.14	34.98	106.02	40.93	141.24	32.14	98.92	39.48	132.51
21.43	22.19	50.61	22.04	78.73	22.19	61.98	26.40	72.91
50.00	15.09	40.66	16.22	27.85	15.09	59.14	17.68	46.75
100.00	7.98	22.19	7.50	17.68	12.25	29.30	10.41	22.04

Table A-39: Toxicity (TU) of the melt water for abietic acid

% melt water	Spray unit temperature							
	-10 °C				-25 °C			
	Ice storage Time				Ice storage Time			
	2 days		**2 weeks**		**2 days**		**2 weeks**	
	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L
7.14	5.33	21.41	10.63	35.34	9.06	40.16	9.30	41.67
21.43	2.86	16.00	2.42	15.60	3.65	16.89	3.32	14.01
50.00	1.47	9.53	1.62	3.20	3.78	19.38	2.42	5.46
100.00	1.53	3.24	1.23	1.67	1.26	4.65	1.29	1.53

Table A-40: Normalized TOC concentration in the meltwater samples of the spray ice made from abietic acid

% melt water	Spray unit temperature							
	-10 °C				-25 °C			
	Ice storage Time				Ice storage Time			
	2 days		2 weeks		2 days		2 weeks	
	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L
7.14	1.78	1.53	2.15	1.99	1.62	1.59	2.36	2.00
21.43	1.23	1.18	1.37	1.34	1.36	1.29	1.51	1.46
50.00	0.78	0.83	0.93	0.89	0.96	0.96	0.85	0.91
100.00	0.47	0.54	0.29	0.48	0.55	0.59	0.41	0.51

Table A-41: Normalized COD concentration in the meltwater samples of the spray ice made from abietic acid

% melt water	Spraying unit temperature							
	-10 °C				-25 °C			
	Ice storage Time				Ice storage Time			
	2 days		2 weeks		2 days		2 weeks	
	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L
7.14	1.70	1.51	1.99	2.02	1.56	1.41	1.92	1.89
21.43	1.08	0.72	1.07	1.12	1.08	0.89	1.28	1.04
50.00	0.73	0.58	0.79	0.40	0.73	0.84	0.86	0.67
100.00	0.39	0.32	0.36	0.25	0.60	0.42	0.51	0.31

Table A-42: Normalized toxicity in the meltwater samples of the spray ice made from abietic acid

% melt water	Spraying unit temperature							
	-10 °C				-25 °C			
	Ice storage Time				Ice storage Time			
	2 days		2 weeks		2 days		2 weeks	
	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L	5 mg/L	20 mg/L
7.14	2.03	1.37	4.05	2.25	3.45	2.56	3.55	2.66
21.43	1.09	1.02	0.92	1.00	1.39	1.08	1.27	0.89
50.00	0.56	0.61	0.62	0.20	1.44	1.24	0.92	0.35
100.00	0.59	0.21	0.47	0.11	0.48	0.30	0.49	0.10

APPENDIX B: Statistical Data

Beaker Freezing Experiment

Table B-1: Analysis of variance for concentration ratio of TOC of frozen section in the beaker test of pulp mill effluent and refinery wastewater

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F_0	p-value
Temperature (A)	0.03	1	0.03	7.15	0.0136
Dilution (B)	0.22	1	0.22	52.65	0.0000
Stirring (C)	0.52	1	0.52	123.86	0.0000
Block (Pulp/Refinery)	0.01	1	0.01	1.44	0.2423
AB	0.00	1	0.00	0.58	0.4528
AC	0.00	1	0.00	0.50	0.4853
BC	0.12	1	0.12	28.00	0.0000
ABC	0.00	1	0.00	0.30	0.5906
Error	0.10	23	0.00		
Total	1.00	31			

Table B-2: Analysis of variance for concentration ratio of TOC of unfrozen section in the beaker test of pulp mill effluent and refinery wastewater

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F_0	p-value
Temperature (A)	0.08	1	0.08	2.17	0.1547
Dilution (B)	0.59	1	0.59	15.81	0.0006
Stirring (C)	4.49	1	4.49	120.09	0.0000
Block (Pulp/Refinery)	1.77	1	1.77	47.36	0.0000
AB	0.03	1	0.03	0.79	0.3845
AC	0.02	1	0.02	0.55	0.4666
BC	0.10	1	0.10	2.62	0.1194
ABC	0.00	1	0.00	0.08	0.7795
Error	0.86	23	0.04		
Total	7.95	31			

Table B-3: Analysis of variance for concentration ratio of COD of frozen section in the beaker test of pulp mill effluent and refinery wastewater

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F_0	p-value
Temperature (A)	0.01	1	0.01	6.72	0.0163
Dilution (B)	0.06	1	0.06	27.26	0.0000
Stirring (C)	0.48	1	0.48	215.68	0.0000
Block (Pulp/Refinery)	0.01	1	0.01	5.25	0.0314
AB	0.00	1	0.00	0.04	0.8527
AC	0.00	1	0.00	0.04	0.8527
BC	0.06	1	0.06	25.71	0.0000
ABC	0.00	1	0.00	1.19	0.2873
Error	0.05	23	0.00		
Total	0.68	31			

Table B-4: Analysis of variance for concentration ratio of COD of unfrozen section in the beaker test of pulp mill effluent and refinery wastewater

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F_0	p-value
Temperature (A)	0.09	1	0.09	1.98	0.1732
Dilution (B)	1.44	1	1.44	31.43	0.0000
Stirring (C)	1.95	1	1.95	42.68	0.0000
Block (Pulp/Refinery)	0.27	1	0.27	5.91	0.0233
AB	0.01	1	0.01	0.20	0.6594
AC	0.01	1	0.01	0.12	0.7315
BC	0.01	1	0.01	0.20	0.6594
ABC	0.00	1	0.00	0.08	0.7811
Error	1.05	23	0.05		
Total	4.83	31			

Spray Freezing Experiment

Pulp Mill Effluent and Refinery Wastewater

Table B-5: Analysis of variance for concentration ratio of TOC of initial melt water in the spray freezing experiment of pulp mill effluent and refinery wastewater

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F_0	p-value
Block (Pulp/Refinery)	0.15	1	0.15	4.24	0.0639
Temperature (A)	0.01	1	0.01	0.26	0.6214
Storage Time (B)	4.08	1	4.08	116.76	0.0000
AB	0.00	1	0.00	0.00	0.9791
Error	0.38	11	0.03		
Total	4.47	15			

Table B-6: Analysis of variance for concentration ratio of TOC of final melt water in the spray freezing experiment of pulp mill effluent and refinery wastewater

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F_0	p-value
Block (Pulp/Refinery)	0.02	1	0.02	5.23	0.0431
Temperature (A)	0.01	1	0.01	1.43	0.2563
Storage Time (B)	0.19	1	0.19	40.32	0.0001
AB	0.00	1	0.00	0.11	0.7501
Error	0.05	11	0.00		
Total	0.25	15			

Linoleic Acid and Abietic Acid

Table B-7: Analysis of variance for concentration ratio of TOC of initial melt water in the spray test of linoleic acid and abietic acid solution

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F_0	p-value
Temperature (A)	0.00	1	0.00	0.02	0.9039
Storage time (B)	0.46	1	0.46	5.77	0.0473
Concentration (C)	0.03	1	0.03	0.35	0.5749
Block (Lino/abietic)	0.02	1	0.02	0.25	0.6354
AB	0.01	1	0.01	0.11	0.7544
AC	0.00	1	0.00	0.06	0.8189
BC	0.00	1	0.00	0.05	0.8376
ABC	0.01	1	0.01	0.10	0.7635
Error	0.56	7	0.08		
Total	1.09	15			

Table B-8: Analysis of variance for concentration ratio of TOC of final melt water in the spray test of linoleic acid and abietic acid solution

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F_0	p-value
Temperature (A)	0.01	1	0.01	0.53	0.4896
Storage time (B)	0.03	1	0.03	3.59	0.0999
Concentration (C)	0.02	1	0.02	1.82	0.2194
Block (Lino/abietic)	0.00	1	0.00	0.10	0.7661
AB	0.00	1	0.00	0.02	0.8882
AC	0.00	1	0.00	0.11	0.7525
BC	0.00	1	0.00	0.48	0.5109
ABC	0.00	1	0.00	0.03	0.8605
Error	0.07	7	0.01		
Total	0.13	15			

Table B-9: Analysis of variance for concentration ratio of COD of initial melt water in the spray test of linoleic acid and abietic acid solution

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F_0	p-value
Temperature (A)	0.04	1	0.04	0.49	0.5084
Storage time (B)	0.30	1	0.30	3.90	0.0888
Concentration (C)	0.05	1	0.05	0.64	0.4505
Block (Lino/abietic)	0.02	1	0.02	0.23	0.6464
AB	0.01	1	0.01	0.09	0.7725
AC	0.02	1	0.02	0.30	0.6037
BC	0.00	1	0.00	0.01	0.9067
ABC	0.00	1	0.00	0.04	0.8389
Error	0.54	7	0.08		
Total	0.97	15			

Table B-10: Analysis of variance for concentration ratio of COD of final melt water in the spray test of linoleic acid and abietic acid solution

Sources of variation	Sum of squares	Degrees of freedom	Mean square	F_0	p-value
Temperature (A)	0.04	1	0.04	2.69	0.1450
Storage time (B)	0.03	1	0.03	1.71	0.2317
Concentration (C)	0.01	1	0.01	0.85	0.3865
Block (Lino/abietic)	0.00	1	0.00	0.01	0.9251
AB	0.00	1	0.00	0.03	0.8629
AC	0.00	1	0.00	0.16	0.7013
BC	0.00	1	0.00	0.02	0.8838
ABC	0.00	1	0.00	0.03	0.8629
Error	0.12	7	0.02		
Total	0.21	15			

APPENDIX C: Pictures of the experiments

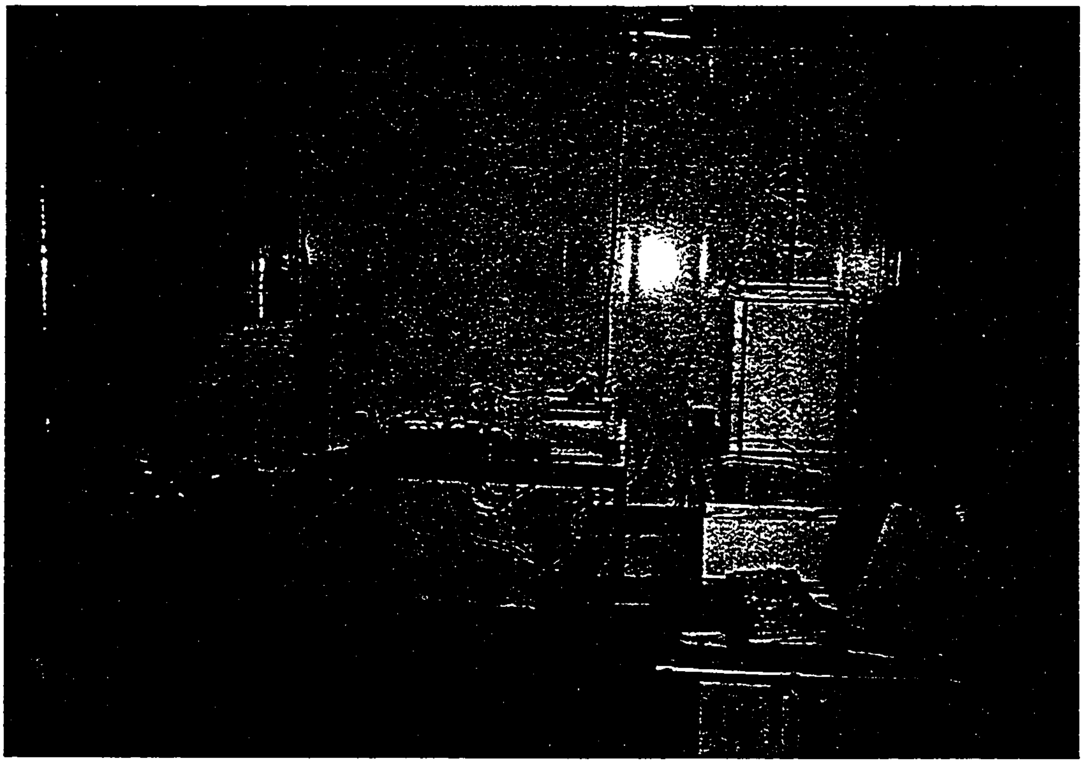


Figure C-1: Experimental setup inside the cold room

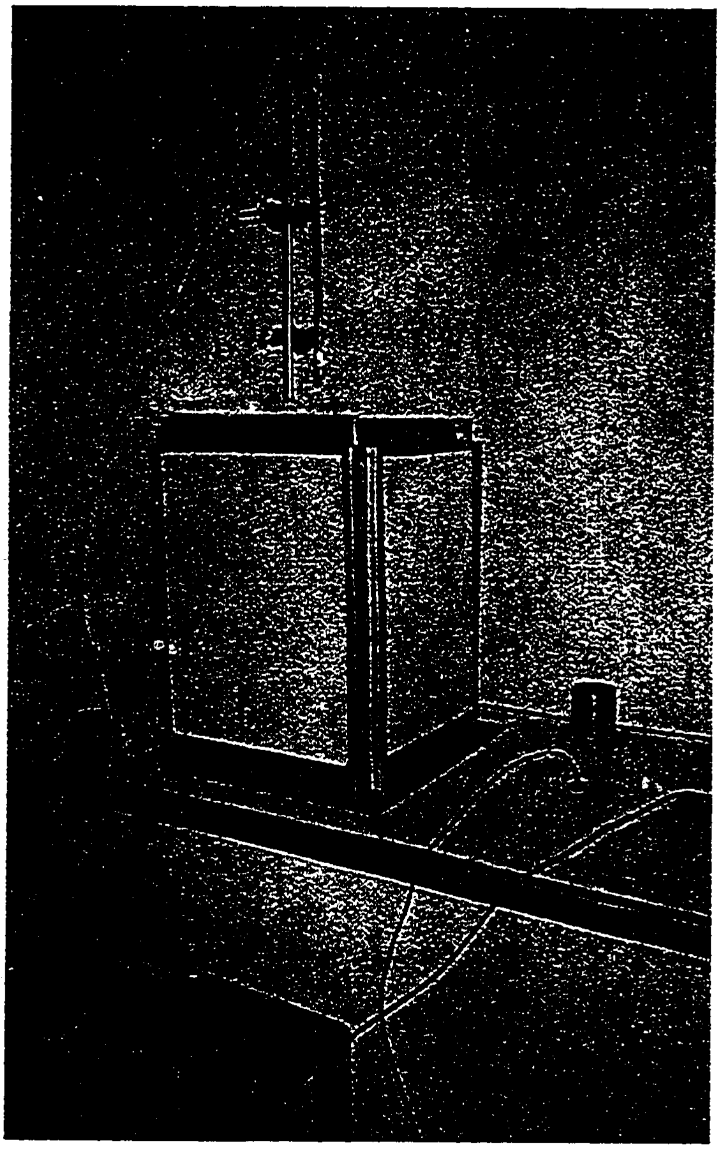


Figure C-2: Spray freezing experimental setup

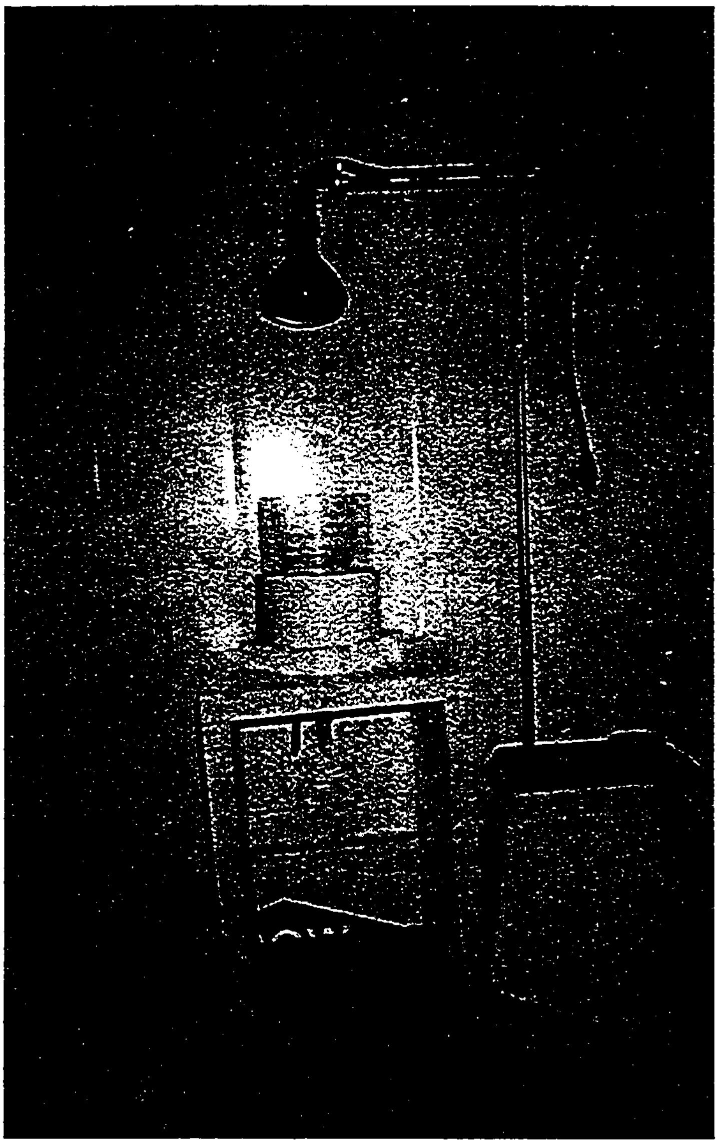


Figure C-3: Melting experimental setup

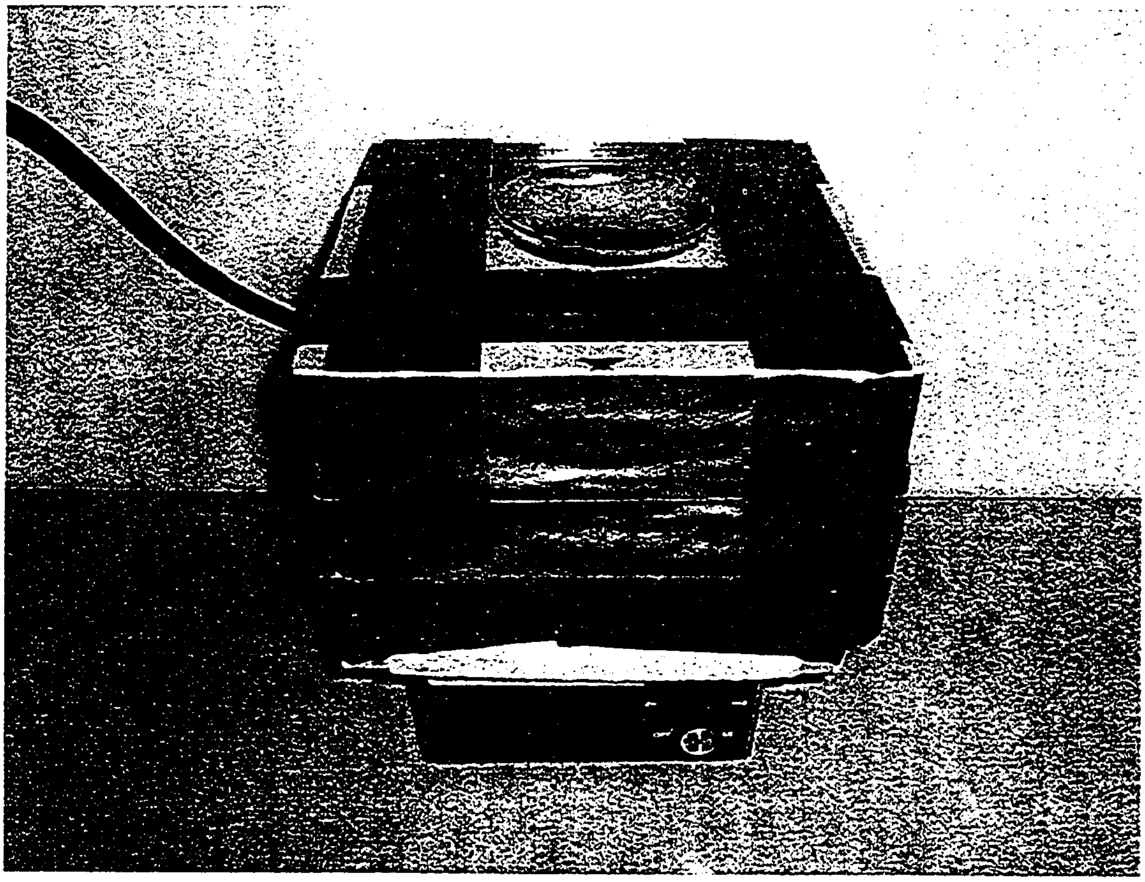


Figure C-4: Beaker freezing experimental setup (front view)

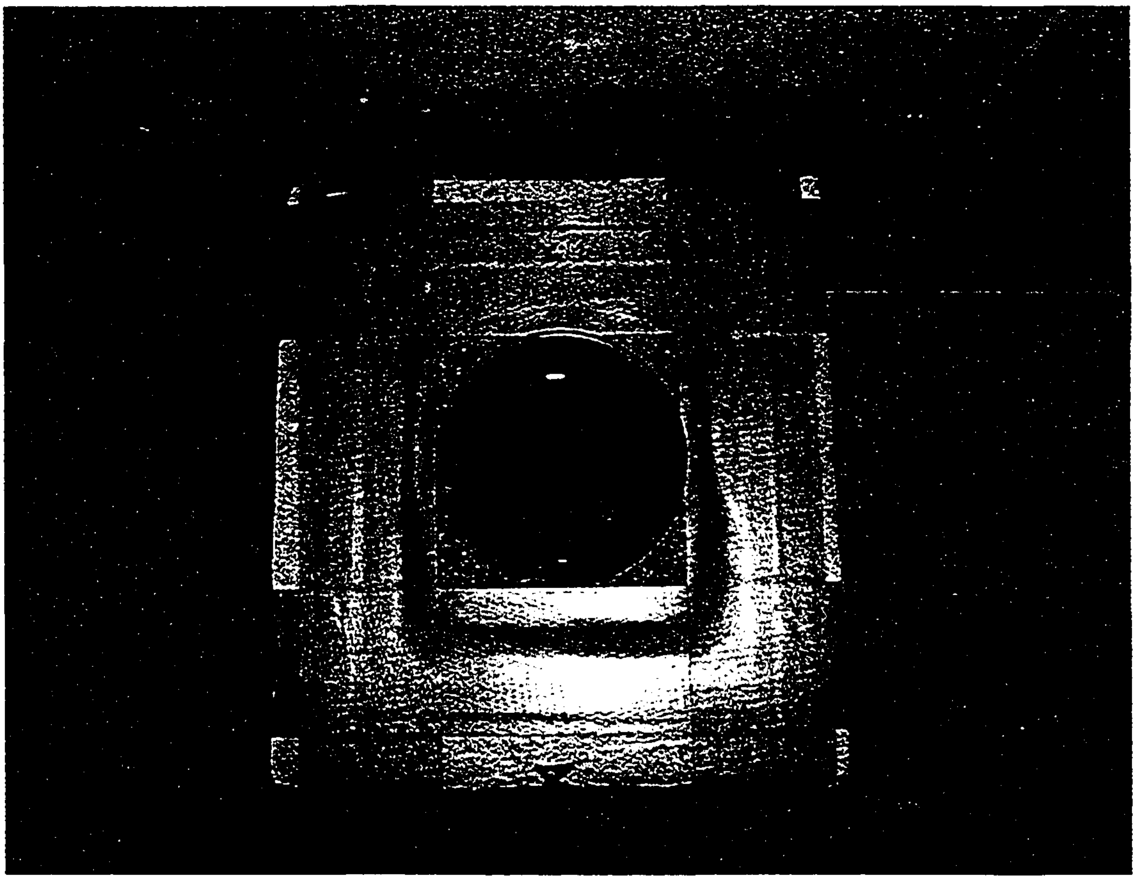
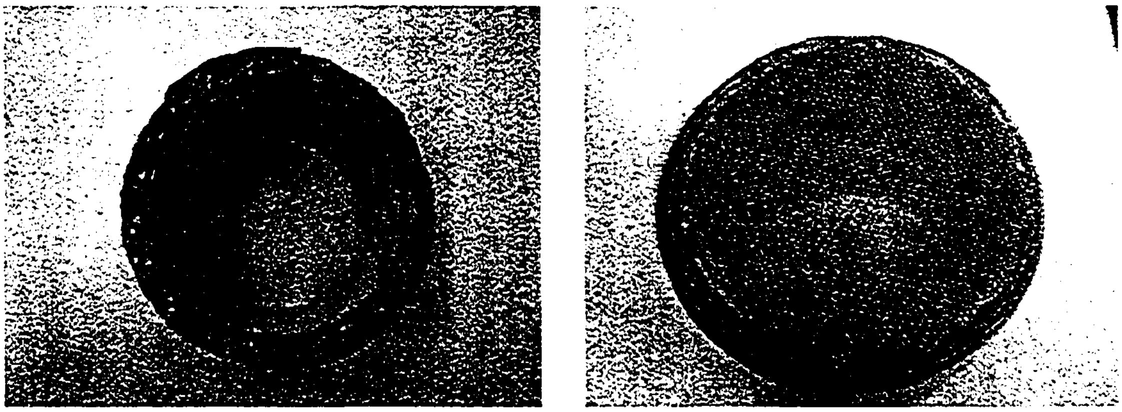


Figure C-5: Beaker freezing experimental setup (top view)



Top view

Bottom view

Figure C-6: Plexiglas ice storage column