TREATMENT OF THERMOMECHANICAL (TMP) WHITE WATER WITH ORGANICALLY-TAILORED SYNTHETIC ZEOLITES

by

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B.A.Sc., The University of British Columbia, 1998

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Date JANUARY 18, 2002
ABSTRACT

In an effort to reduce fresh water usage and wastewater discharge, white water process streams in pulp and paper mills can be targeted for recycling. However, accumulations of dissolved and colloidal substances (DCS) in a closed white water system are detrimental to mill operations, machine runnability, and product quality.

This study determined the technical feasibility of using organically-tailored synthetic zeolites, whose cation exchange capacities (CEC) and external CEC (ECEC) values ranged from approximately 80 to 240 meq/100g and 20 to 160 meq/100g, respectively, for treatments of synthetic process water (SPW) and thermomechanical (TMP) white water (WW) samples. The SPW contained only dehydroabietic acid (DHA) at a concentration of approximately 30 mg/L.

Treatment of SPW with untailored synthetic zeolites at 20 g/L mineral dose resulted in removal of 19-45% of DHA. Complete uptakes of DHA were also achieved when water-soluble organic cations (C15 and C17) were used to tailor the zeolites. Lower DHA uptake capacities (9-71% removal efficiencies) were observed when alcohol- (methanol and ethanol) soluble organic surfactants (C20-C40) were used for tailoring the zeolites. Mineral doses of TDTMA-tailored synthetic zeolite as low as 5 g/L removed 90% of the DHA from SPW, and complete DHA removal was obtained at doses of 10 g/L and higher. Also, the uptake of DHA from SPW by TDTMA-tailored synthetic zeolite occurred within minutes of contact, where the maximum removal efficiency was achieved after 3 minutes of treatment. DHA removals at low pH (4-7.25) values ranged from 40 to 100%, as compared to the 20-27% removals observed at pH 10-12. In addition, the removal of DHA from SPW was not affected by the nature of the buffering system used (unbuffered, acetate, and phosphate).

Treatment of white waters (pH 7.25) using TDTMA-tailored zeolites at 1 g/L mineral dose resulted in 51% reduction of resin and fatty acids (RFA), 10% removals of soluble biochemical and chemical oxygen demands, 85% removal of acute toxicity, and 24% uptake of sterols. Higher (20 g/L) mineral doses resulted in more complete
removals of the compounds of concern: RFA (100%), soluble biochemical oxygen demand (SBOD) (36%), soluble chemical oxygen demand (SCOD) (38%), acute toxicity (91%), and sterols (100%).
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<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>AB</td>
<td>Alberta</td>
</tr>
<tr>
<td>BC</td>
<td>British Columbia</td>
</tr>
<tr>
<td>BCTMP</td>
<td>Bleached chemi-thermomechanical pulp</td>
</tr>
<tr>
<td>BOD</td>
<td>Biochemical oxygen demand</td>
</tr>
<tr>
<td>BSTFA</td>
<td>Bis-(trimethylsilyl)-trifluoro-acetamide</td>
</tr>
<tr>
<td>CEC</td>
<td>Cation exchange capacity</td>
</tr>
<tr>
<td>CI</td>
<td>Confidence interval</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
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<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
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<tr>
<td>CPPA</td>
<td>Canadian Pulp and Paper Association</td>
</tr>
<tr>
<td>CTMP</td>
<td>Chemi-thermomechanical pulp</td>
</tr>
<tr>
<td>DAF</td>
<td>Dissolved air flotation</td>
</tr>
<tr>
<td>DCS</td>
<td>Dissolved and colloidal substances</td>
</tr>
<tr>
<td>DDTMA</td>
<td>Dodecytrimethylammonium</td>
</tr>
<tr>
<td>DHA</td>
<td>Dehydroabietic acid</td>
</tr>
<tr>
<td>ECEC</td>
<td>External cation exchange capacity</td>
</tr>
<tr>
<td>EDC</td>
<td>Endocrine disrupting chemicals</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
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<tr>
<td>FA</td>
<td>Fatty acids</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
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<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatography mass spectrometry</td>
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<tr>
<td>HDTMA</td>
<td>Hexadecyltrimethylammonium</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>ICEC</td>
<td>Internal cation exchange capacity</td>
</tr>
<tr>
<td>IS</td>
<td>Internal standard</td>
</tr>
<tr>
<td>MTBE</td>
<td>Methyl tert-butyl ether</td>
</tr>
<tr>
<td>NCASI</td>
<td>National Council of the Paper Industry for Air and Stream Improvement</td>
</tr>
<tr>
<td>NCE</td>
<td>Networks of Centres of Excellence</td>
</tr>
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NSERC  Natural Science and Engineering Research Council of Canada
O-MPCA  O-methylpodocarpic acid
PA     Pennsylvania
QUAT   Quaternary ammonium cations
RA     Resin acids
RFA    Resin and fatty acids
RS     Recovery Standard
RT     Retention time
SBOD   Soluble biochemical oxygen demand
SCOD   Soluble chemical oxygen demand
SEM    Scanning electron microscopy
SFM    Sustainable Forest Management
SPW    Synthetic process water
SS     Suspended solids
TDS    Total dissolved solids
TDFS   Total dissolved fixed solids
TDTMA  Tetradecyltrimethylammonium
T(D)A  Tetra(decyl)ammonium
TEA    Tetraethylammonium
TFS    Total fixed solids
TFSS   Total fixed suspended solids
THA    Tetraheptylammonium
TMP    Thermomechanical pulp
TOA    Tetraoctylammonium
TPA    Tetrabutylammonium
TS     Total solids
TSS    Total suspended solids
TVS    Total volatile solids
TVDS   Total volatile dissolved solids
TVSS   Total volatile suspended solids
WW     White water
### LIST OF UNITS

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<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>adt, t</td>
<td>Air dried ton, ton</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celcius</td>
</tr>
<tr>
<td>g, mg, µg</td>
<td>Grams, milligram, microgram</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>kV</td>
<td>Kilovolts</td>
</tr>
<tr>
<td>L, mL, µL</td>
<td>Litre, millilitre, microlitre</td>
</tr>
<tr>
<td>M, mM</td>
<td>Molar, millimolar</td>
</tr>
<tr>
<td>m²</td>
<td>Meter square</td>
</tr>
<tr>
<td>m³</td>
<td>Cubic meter</td>
</tr>
<tr>
<td>meq</td>
<td>milliequivalent</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>mm, µm, nm</td>
<td>Millimeter, micrometer, nanometer</td>
</tr>
<tr>
<td>mmHg</td>
<td>Millimeter mercury</td>
</tr>
<tr>
<td>N</td>
<td>Normal</td>
</tr>
<tr>
<td>psi</td>
<td>Pound per square inch</td>
</tr>
<tr>
<td>rpm</td>
<td>Revolution (rotation) per minute</td>
</tr>
<tr>
<td>w/w</td>
<td>Weight by weight</td>
</tr>
<tr>
<td>%v/v</td>
<td>Percent volume by volume</td>
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Network / Networks of Centres of Excellence (NCE). Laboratory and office space were provided by the UBC Pulp and Paper Centre.
To: P & M, ABA, FA, AWA, BBS, DCBA, EBM, FBH, FA

"There are two things I've learned: There is a God. And, I'm not Him."

-Anonymous-
CHAPTER 1:
INTRODUCTION

1.1 Research Motivation

Large fresh water usage in pulp and paper mills results in a significant amount of wastewater disposal into the environment. In an effort to reduce, if not eliminate, both water consumption and effluent discharge, pulp and paper mills have looked towards water circuit closure as an innovative solution. Process water streams, such as the white water system, can be targeted for recycling. Many research papers and other publications in recent years, such as those written by Bessonoff et al. (2000), Kahmark and Unwin (1999), and Ramamurthy and Wearing (1998), discuss the issue of mill closure. Although definitely beneficial, these papers and others also review the challenges presented by the idea. As attractively interesting and easy as it may sound, closing the water systems in pulp and paper mills can be problematic to plant operations.

White water contains dissolved, colloidal, and suspended contaminants, such as resin and fatty acids, sterols, lignins, lignans, and steryl esters. Increased recycling will, without a doubt, alter the balance of these contaminants in the white water system. Not only do dissolved and colloidal substances (DCS) have negative effects on the runnability of the paper machine and on many paper qualities (Bessonoff et al., 2000), they also affect the effluent toxicity. Resin and fatty acids (RFA) are detrimental constituents of DCS that, for example, have been found to reduce the wet web strength properties (Zhang et al., 1999).

Methods currently used to partially purify white water include evaporation, filtration, clarification, and membrane filtration (Young, 1994; Carlyle et al., 1996; Pietschker, 1996; Webb, 1997; Nuortila-Jokinen et al., 1998). However, in the face of reduced fresh water input and increased recycling, these technologies may not be able to achieve acceptable DCS concentrations. Consequently, there is a need for the development of a polishing treatment technology that can cope with such closure and can maintain the DCS concentration at a desirable level. An emerging alternative for white
water treatment is the use of minerals to remove or reduce DCS within white water systems (Bouffard, 1998; Bouffard and Duff, 1999; Bouffard and Duff, 2000).

Pulp and paper mills are no strangers to mineral usage in their operations. Minerals, such as bentonite and zeolite have been used in many areas, for instance, as retention aids, fillers, and flocculants (Tarasevich, 1994; Tsitsishvili \textit{et al.}, 1992; Tsitsishvili, 1985; Lengyel \textit{et al.}, 1973; Libor and Szenbanyak, 1972). In addition, Kuntz (1997), and Vinje and Kuntz (1998) found that minerals were able to remove the RFA contained in kraft and chemi-thermomechanical pulp (CTMP) effluent samples. Furthermore, Bouffard (1998), Bouffard and Duff (1999), and Bouffard and Duff (2000) have shown promising results with organically-tailored minerals for the removal of RFA, particularly dehydroabietic acid (DHA).

Consequently, this research focuses more on the application of organically-tailored zeolites for the treatment of pulp and/or paper mill white water to remove DCS, especially RFA. The viability of exploiting such minerals depends mainly on their uptake capabilities.

1.2 Thesis Outline

Chapter two presents a general review on the motivation for and challenges faced by pulp and paper mills as they move toward white water system closure. The chapter also reviews the basic structure and properties of zeolites, adsorption of tailoring cations onto zeolite surfaces, and methods of removal of organic solutes by organically-tailored zeolites.

Chapter three outlines the research objectives, while the methodologies and materials used in the study to achieve the research objectives are described in chapter four.

Chapter five presents and discusses all of the results obtained from the treatment tests. The conclusions from all of the experimental work are presented in chapter six. Chapter seven provides a list of recommendations for future work.
Appendix A presents the results of resin and fatty acids (RFA) removals by centrifugation of the white water (WW) samples. The gas chromatography (GC) conditions used for the sterols analysis are outlined in Appendix B. In addition, supplementary graphical results obtained from the pore analysis of zeolites are shown in Appendix C.
CHAPTER 2:
LITERATURE REVIEW

Pulp and paper is one of the oldest and most significant industries in the world. In Canada, and certainly in British Columbia (BC), it is one of the largest areas of commerce (Canadian Pulp and Paper Association-CPPA, 2001). The industry generates billions of dollars in revenue ($16.7 billion in Canada as of 1999) and employs large number of people (1,016,700) directly and indirectly (Canadian Pulp and Paper Association-CPPA, 2001). The pulp and paper industry, however, has long been labelled as an industrial sector that highly pollutes the environment. The massive consumption (10-120 m$^3$/ton pulp) of fresh water results in an enormous discharge of wastewater into the environment. In recent years, more stringent regulations have been imposed on pulp and paper mills in an effort to solve their pollution problems. The issue of water circuit closure in pulp and paper mills has become one of the attractive propositions among the ways of reducing, if not eliminating, wastewater discharge. Consequently, progressive closure of process streams in most mills is emerging (McCubbin, 1992).

2.1 Motivation Towards System Closure in Pulp and Paper Mills

Depending on the type of paper produced, about 1000 m$^3$ of fresh water is required for the manufacture of 1 ton of paper in the classical kraft pulping or papermaking process (Mobius, 1980). The large consumption of fresh water, which is used for pulp dilution, sheet formation, and machine showers, results in a significant amount of wastewater discharge into the environment, especially by older mills. To reduce fresh water usage and, hence, wastewater disposal, many mills have considered implementing the concept of system closure. This study defines system closure as a closed-cycle design that results in zero liquid effluent discharge.

An example of closed-cycle design is shown in Figure 2.1, which depicts a schematic of a closed-cycle bleached kraft mill (Smook, 1992).
Figure 2.1. A closed-cycled design of bleached kraft mill (Smook, 1992)

One of the main incentives that drives pulp and paper mills toward implementation of system closure is economics. Other incentives include (Panchapakesan, 1992; Pietschker, 1996; Wohlgemuth et al., 1996; Webb, 1997):

1. stringent discharge regulations;
2. increasing cost of end-of-pipe wastewater treatment;
3. expensive waste disposal costs;
4. limited available quantities of high quality fresh water;
5. increasing cost of raw water;
6. recovery of fibers, fines, chemicals, and energy; and
7. environmental consciousness.
There are several measures that can be applied in pulp and paper mills to progressively accomplish the objective of zero water discharge (Thurley et al., 1996; Wiseman and Ogden, 1996; Woodward, 1996; Blanco et al., 1997; Houle et al., 1998). One way to reduce fresh water consumption and, hence, wastewater disposal is by recycling process water streams.

The benefits from recycling are reductions in: (1) raw water, chemical, and energy consumption, (2) fibers, fines, and chemical losses, and (3) effluent treatment and waste disposal costs (Panchapakesan, 1992; Pietschker, 1996).

One of the mill process streams that can be targeted for recycling is the white water system. White water refers to the water that drains from wet stock in pulping and papermaking operations, regardless of color (Smook, 1992). The objectives of managing or recycling white water are to reduce raw water uptake and heat loses, recover raw materials and/or chemicals, supply a consistent quality water and prevent foreign materials to the manufacturing process, and minimize the load on the treatment system and environment (McCubbin, 1992). However, white water contains many organic and inorganic contaminants as well as fibers and fines that must be removed before extensive recycling can be implemented.

Figure 2.2 shows a closed white water system in pulp and paper mills (Smook, 1992).
2.2 Contaminants in White Water

White water contains many different organic and inorganic dissolved and colloidal substances (DCS). Some of the contaminants, such as alkaline earth salts and humic acids, enter into the system by the uptake of raw water, but most are added with, or as raw materials and auxiliary agents. When the system is closed, these contaminants can cause numerous problems to the mill operations, and consequently, some of the white water has to be purged. To replace the loss due to purging, large quantities of fresh water are needed and thus fresh water consumption accounts for a significant fraction of the total water intake volume.

The low-molecular-weight constituents of the DCS in white water are mainly comprised of lipophilic extractives, such as resin and fatty acids (RFA), terpenes, sterols, glycerides, and semi-lipophilic phenolic extractives (lignans) (Ekman et al., 1990; Hoel and Aarsand, 1995). The high-molecular-weight fractions of the DCS consist of lignin.
fragments, neutral polysaccharides (cellulose and hemicellulose), and negatively-charged hydrophilic polysaccharides (Sjostrom, 1990; Orsa and Holmbom, 1994; Thornton, 1994; Garver et al., 1998). Figure 2.3 shows the structures of some of the DCS contaminants that can be found in white water.

![Figure 2.3. Structures of some of DCS contaminants found in white water (Stebbing et al., 2001)](image)

In the current study, RFA, and dehydroabietic acid (DHA) in particular, were used as model DCS compounds. RFA have been shown to be one of the main contaminants that are responsible for machine runnability problems in closed white water systems. The structures of some of the RFA commonly found in softwood are shown in Figure 2.4.
2.3 Problems of White Water System Closure in Pulp and Paper Mills

A detailed review on the problems encountered with system closure and methods for white water treatment in pulp and paper mills can be found in Bouffard (1998). Closing the white water system in pulp and paper mills presents numerous problems to the mills' operations. These problems include (Geller and Gottsching, 1982; McCubbin, 1992; Noel et al., 1992; Barton et al., 1996; Barnett and Grier, 1996; Francis et al., 1998):

1. build up of suspended, and dissolved and colloidal substances (DCS);
2. accumulation of dissolved inorganic contaminants;
3. increase in system temperature; and
4. increased growth of biological activity, especially thermophilic bacteria.
The consequences of these problems on the papermaking operations are (Melzer, 1974; Auhorn and Melzer, 1979; Springer and Peterson, 1980; Wenzl, 1981; Jarvinen et al., 1985; Panchapakesan, 1992; McCubbin, 1992; Baker and Howard, 1995; Barton et al., 1996; Woodward, 1996; Habets et al., 1996; Robertson and Schwingel, 1996; Edwards, 1996; Gudlauski, 1996; Barnett and Grier, 1996; Blanco et al., 1997; Jaycock, 1997):

(1) loss of retention (meaning that increasing amount of fibers and fillers are not retained);
(2) reduced dewatering velocity or sheet drainage rate in paper or pulp machine;
(3) increased plugging of shower nozzles, headbox, filters, screens, wires, and forming fabrics;
(4) reduced performance of vacuum pumps;
(5) increased slime and pitch deposits, and biological growth;
(6) increased wear;
(7) reduced equipment life span, caused by pitch and deposits formation; and
(8) increased corrosion, foaming, and scaling.

The build up of contaminants in the system due to closure also affects paper qualities. They include (Horn and Melzer, 1975; Lindstrom and Soremark, 1977; Dobbins and Alexander, 1977; Lindstrom et al., 1977; Geller and Gottsching, 1982; Jarvinen et al., 1985; McCubbin, 1992; Edwards, 1996; Gudlauski, 1996; Habets et al., 1996; Francis and Ouchi, 1997; Zhang et al., 1999; Bessonoff et al., 2000; Serreqi et al., 2000; Tay, 2001; Francis and Ouchi, 2001):

(1) loss of brightness;
(2) internal sizing and opacity problems;
(3) discoloration;
(4) reduced paper/tensile strength;
(5) reduced burst index and breaking lengths;
(6) formation of specks and holes;
(7) reduced bulk, smoothness, and porosity; and
(8) fiber degradation.
In summary, machine runnability, production, and product qualities are affected when a closed-cycle system is implemented due to the accumulation of undesirable substances.

2.4 Treatment of White Water

Technologies (listed below in the order of decreasing capital and operating costs) that are considered in laboratory, pilot, and full-scale applications for treatment of white water include (Lengyel et al., 1973; Gaarder, 1993; Gerbasi et al., 1993; Young, 1994; Nuortila-Jokinen et al., 1995; Elefsiniotis et al., 1995; Carlyle et al., 1996; Meadows, 1996; Pietschker, 1996; Lagace et al., 1996; Webb, 1997; Ramamurthy and Wearing, 1998; Nuortila-Jokinen et al., 1998):

1. freeze crystallization;
2. evaporation;
3. membrane filtration;
4. biological treatment; and
5. physico-chemical treatments, where flocculation by coagulants, dissolved air flotation (DAF), and clarification are used.

Each of these treatment technologies has its advantages. Freeze crystallization and evaporation offer the potential for further volume reduction of fresh water intake down to about 2-5 m$^3$/adt pulp. In addition, membrane filtration helps eliminate the use of a clarification technology. Biological treatment, which has been around and widely used for more than 30 years in pulp and paper mills for treatment of wastewater effluents, also offers a low operating cost.

The drawbacks of freeze crystallization and evaporation include high capital and operating costs, attachment of contaminants to ice crystals, corrosion, and scale formation. Furthermore, membrane filtration results in high pumping costs, cleaning problems due to accumulation of contaminants on the membrane surface, expensive membrane replacement costs, and formation of scale. Also, poor settleability in
biological processes can affect paper qualities due to carry-over of flocs and microorganisms.

Ideally, a simple treatment for white water should be employed in order to minimize interference with the pulping and papermaking operations. Not only are physico-chemical treatments reasonably inexpensive, they also meet this requirement. Consequently, a physico-chemical process provides the basis of the current study.

2.5 Applications of Organically-Tailored Zeolites

Natural minerals, for example mordenites, bentonites, clinoptilolites, kaolinites, heulandites, chabazites, and zeolites, have been widely used in many applications, including in gas separation, agriculture, desiccation, energy storage and heat pumps, as well as treatment of contaminated water containing heavy metals, aromatics, radioactive substances, and ions (Keller and Jones, 1980; Minato, 1985; Takasaka and Matsuda, 1986; Ulku, 1986; Haderlein and Schwarzenbach, 1993; Al-Sabri et al., 1993; Smith and Galan, 1995; Zhao et al., 2000).

In addition, organically-tailored zeolites have been employed for the removal of phenols, chlorinated organics, and aromatics from contaminated water (Kruglitskaya et al., 1985; Huddleston, 1990; Gao et al., 1991; Neel, 1992; Rustamov et al., 1992; Garcia et al., 1993; Smith and Galan, 1995). Moreover, hexadecyltrimethylammonium (HDTMA)-tailored zeolites have been shown to be able to uptake chromate and perchloroethylene (Haggerty and Bowman, 1994; Li and Bowman, 1997; Li and Bowman, 1998a; Li and Bowman, 1998b; Li et al., 1999).

Interestingly, pulp and paper mills are no strangers to mineral usage in their operations. Minerals, such as bentonite and zeolite have been employed in many areas, for example, as retention aids, fillers, and flocculants (Libor and Szenbanyak, 1972; Lengyel, et al., 1973; Tsitsishvili, 1985; Tsitsishvili et al., 1992; Tarasevich, 1994). Not much research, however, has concentrated on the use of organically-tailored zeolites for treatment of white water. Nevertheless, the results from work by Bouffard (1998), Bouffard and Duff (1999), and Bouffard and Duff (2000) showed promise for the use of
organically-tailored minerals as a polishing technology in pulp and paper mills to treat white water.

2.5.1 Properties of Zeolites

A comprehensive review on the structures, chemistry, synthesis, and properties of zeolites can be found in Breck (1974). Gates (1991) also presented a chapter in his book on zeolite structure, and ion exchange and catalytic reactions involving zeolites. There is a wealth of literature discussing the synthesis, occurrence, properties, utilization, development, adsorption and ion exchange processes, and photocatalytic reactions of zeolites, such as those compiled and edited by Anpo (2000), Misaelides et al. (1999), Occelli and Robson (1992), Kallo and Sherry (1988), Murakami et al. (1986), and Flank (1980). This section outlines a brief summary of the basic structures and properties of zeolites.

Zeolites belong to a class of minerals called tectosilicates (Marcus and Cormier, 1999). They are microporous, crystalline, and hydrated aluminosilicates of groups I and II elements, particularly sodium, potassium, magnesium, calcium, strontium, and barium. Zeolites have high internal surface areas, and have well-defined three-dimensional aluminosilicate framework structures, which are open and contain aluminum, silicon, and oxygen. The frameworks are based on an infinitely extending three-dimensional web of AlO₄ and SiO₄ tetrahedra, which are connected to each other through sharing of the oxygen atoms (Breck, 1974). The SiO₄ tetrahedron in a crystalline network can be represented as in Figure 2.5.

![Tetrahedral structure of SiO₄ (Gates, 1991)](image)
The second structure (a space-filling model), which is based on close-packed spheres, is the most accurate representation. In the third model, the Si and O atoms are represented as a point and as a line, respectively. The SiO$_4$ unit is a building block (Figure 2.6(a)), and its assemblage defines the structure of the crystalline zeolite particles. A chain of building blocks is assembled as a single unit is connected to one after another (Figure 2.6(b)). Figure 2.7 shows two- and three-dimensional layers that are formed by linked chains of building blocks. Other examples of basic building units that can compose the zeolite structure are shown in Figure 2.8.

Figure 2.6. Building block of zeolite structure: (a) single unit, (b) chain formation
(Gates, 1991)
The structure of zeolites can be visualized by taking a neutral SiO$_2$ framework and substituting AlO$_2^-$ for one of the SiO$_2$ unit. Since the SiO$_4$ units are neutral and the AlO$_4^-$ has a net negative charge, the resulting structure exhibits a net negative charge on the aluminum framework. The net negative charge is balanced by cations (for instance: Na$^+$, K$^+$, Ca$^{2+}$, or NH$_4^+$) that reside in the framework. These cations are highly mobile and can...
be exchanged for other cations. This ion-exchange property accounts for the greatest volume use of zeolites today (Zeolyst International, 1999). The type of cation present is also a factor in the zeolite adsorptive and catalytic properties. Synthetic zeolites of high purity display uniform pore sizes that can be further modified to specific molecular dimensions by changing the nature of the cation after synthesis.

The unit cell structural formula of a zeolite is usually expressed as:

$$M \frac{x}{n}\left(\text{AlO}_2\right)_x\left(\text{SiO}_2\right)_y\cdot w\text{H}_2\text{O},$$

where $M$ is the cation of valence $n$, $w$ is the number of water molecules, and the $y$ to $x$ ratio ($y/x$) usually has a value between 1 and 5, depending upon the structure. The sum $(x + y)$ is the total number of tetrahedra in the unit cell (Breck, 1974).

Some zeolites contain interconnected voids (cavities or channels) that can host cations, water, or other molecules. The zeolite pore is a two-dimensional aperture, the size of which is determined by the number of interconnected tetrahedral units. The void structure builds up as the tetrahedral units join together in a three-dimensional array. This array can lead to a larger inner cavities linked by the pore openings (Figure 2.9). Some other zeolites, however, may not have any cavities, but a series of two-, or three-dimensional channels through the structure.
Figure 2.9. Sodalite cages of zeolites showing internal cavities (Gates, 1991)

There are approximately 40 known naturally-occurring zeolites. Most commercial zeolites, however, are produced synthetically, which accounts for more than 150 synthetic zeolites presently available (Marcus and Cormier, 1999; Zeolyst International, 1999). During synthesis, some zeolite properties that need to be considered include: (1) structure, (2) silica-to-alumina ratio (Si/Al), (3) pore size, and (4) framework density (atoms per unit cell).

Because of their regular and reproducible structure, zeolites behave in a predictable manner. If used to adsorb solutes, zeolites can be regenerated using relatively easy methods, such as heating, ion exchanging with sodium to remove cations, or pressure swing to remove adsorbed gases (Kuntz, 1997; Deng et al., 1998; Li and Bowman, 2001).

2.5.2 Tailoring of Zeolites with Quaternary Ammonium Cations (QUAT)

Quaternary ammonium cations (QUAT) are organic surfactants that possess positively-charged head groups attached to the aromatic or aliphatic hydrocarbon chain (Alther et al., 1988). Tailoring a zeolite with organic cations is simply a process of binding the QUAT to the zeolite surfaces through an ion-exchange process, where the QUAT are exchanged with the naturally-present inorganic cations, such as Na\(^+\), Ca\(^{2+}\), or Mg\(^{2+}\), of the zeolite. Depending on the chain length of the tailoring cation, the hydrophobicity of the zeolite is enhanced.
The ion-exchange process of the inorganic cation ($M^+$) of the zeolite with the protonated organic tailoring cations ($RNH_3^+$) can be described as follows:

$$RNH_3^+ + M^+ - Zeolite \leftrightarrow RNH_3^+ + Zeolite + M^+$$

The exact locations of the inorganic cations in the zeolite are important to the success of the ion-exchange process (for example, as shown in Figure 2.10). Type I sites are positioned at the centers of the hexagonal prisms, type I' sites reside in the sodalite cages across the hexagonal faces from type I sites, type II sites are positioned in the supercages near the unjoined hexagonal faces, and type II' sites reside in the supercages, farther from the hexagonal faces than the type II sites. Inorganic cations in type II and II' sites are readily accessible to the tailoring cations, while those in type I and I' sites are less exchangeable.

![Figure 2.10. Locations of inorganic cations ($M^+$) in zeolite (Gates, 1991)](image)

Adsorption of tailoring cations, such as hexadecyltrimethylammonium (HDTMA), onto mineral surfaces has previously been studied (Haggerty and Bowman, 1994; Xu and Boyd, 1995; Li and Bowman, 1997; Sullivan et al., 1998a; Sullivan et al., 1998b; Li et al., 1998). In their work, Li and Bowman (1997) determined the effects of counterions
(Cl\textsuperscript{-}, Br\textsuperscript{-}, and HSO\textsubscript{4}\textsuperscript{-}) on the sorption of HDTMA on clinoptilolite zeolite. In addition, Li \textit{et al.} (1998) studied the chemical and biological stability of HDTMA-tailored zeolites in laboratory batch and column experiments.

Below its critical micelle concentration (CMC), the organic tailoring surfactant exists as monomers in solution (Israelachvili, 1991). Spherical micelles are formed by the joined monomers when the surfactant concentration is above its CMC.

Adsorption of tailoring cation monomers occurs through coulombic (cation exchange), dipole-dipole, and hydrophobic interactions to the inorganic cations exchange sites available in the zeolite (Chen \textit{et al.}, 1992; Xu and Boyd, 1995). The organic tailoring cation monomers then form a monolayer or “hemimicelle” on the zeolite surface by adopting different orientations (monomer, dimer, or flat) (Figure 2.11A).

![Figure 2.11](image)

\textbf{Figure 2.11.} Formations of (A) monolayer or “hemimicelle” and (B) bilayer or “admicelle” by organic tailoring cations on zeolite surface (Haggerty and Bowman, 1994)
Above the CMC, the organic tailoring surfactant forms a bilayer ("admicelle") or multilayers on the zeolite surface (Figure 2.11B). The stability of the organic layers is dependent upon hydrophobic tail-to-tail interactions between the surfactant molecules.

**2.5.3 Removal of Dissolved and Colloidal Contaminants Using Organically-Tailored Zeolites**

Bouffard (1998) has provided an extensive review on the mechanisms of removal of organic solutes by organically-tailored minerals.

Minerals that have been tailored with short chain organic surfactants, such as tetraethylammonium (TEA) and tetrapropylammonium (TPA), remove organic solutes through discrete adsorption. The adsorption process occurs through van der Waals, and electrostatic and hydrogen bonding interactions (Cowan and White, 1962; Jaynes and Boyd, 1991b; Lagaly, 1994).

Removals of organic solutes by minerals, which have been tailored with long chain organic surfactants (QUAT), such as hexadecyltrimethylammonium (HDTMA), occur mainly by solute partitioning or dissolution due to the formation of organic layers on mineral surfaces (Smith and Galan, 1995; Bouffard, 1998; Li and Bowman, 1998b; Alther, 2000; Li et al., 2000). Solvation of hydrocarbon chains, ammonium head groups, and mineral surfaces have also been observed to enhance the uptake of organic solutes by organically-tailored minerals (Sheng et al., 1996a).
CHAPTER 3:
RESEARCH OBJECTIVES

This research was an extension of the work by Bouffard (1998), Bouffard and Duff (1999), and Bouffard and Duff (2000). The main objective of this research was to determine the technical feasibility of using organically-tailored synthetic zeolites to treat white water in mechanical pulp and paper mills. This study mainly focused on the removal of resin and fatty acids (RFA), sterols, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and acute toxicity.

Preliminary runs with synthetic process water (SPW) were conducted prior to investigations with white water (WW) samples. The synthetic process water contained only dehydroabietic acid (DHA), which has been found to be present in the highest amount in pulp mill effluents and to be the least degradable of resin acids (Patoine et al., 1997; Volkman et al., 1993; Bisaillon et al., 1991).

Consequently, the following research objectives were established:

Using synthetic process water:
(1) characterize the synthetic zeolites;
(2) compare the effectiveness for uptake of DHA of untailored synthetic zeolites to that of the same synthetic zeolites that had been organically tailored;
(3) determine the effects on DHA removal of using different organic cations to tailor the synthetic zeolites;
(4) determine the minimum mineral loading that could be applied to eliminate DHA;
(5) determine the contact time required for organically-tailored zeolites to treat the process water; and
(6) determine the effects of pH on the treatment efficiency.

Using white water samples, the objective was to assess the technical feasibility of using organically-tailored synthetic zeolites for the removal of RFA, sterols, BOD, COD, and acute toxicity.
CHAPTER 4:
METHODS AND MATERIALS

This chapter describes all the experimental methods and materials employed in this research. The first section (4.1) outlines the analyses involved in the characterization of the synthetic zeolites. The procedure for the tailoring of the zeolites with the organic cations is presented in the next section (4.2). The next section (4.3) deals with the preparation of the synthetic process water (SPW) and white water (WW) samples, prior to being treated with the tailored zeolites. This is followed in section 4.4 by the detailed protocols for all the batch treatment tests of the SPW and the WW samples. Section 4.5 then describes the analytical methods used to obtain the results from the treatment tests. Lastly, section 4.6 outlines the methods used for analysis of the experimental data.

4.1 Characterization of Synthetic Zeolites

This study investigated the technical feasibility of using organically-tailored minerals to treat pulp and paper mill white water. The minerals of choice were synthetic zeolites due to their large and uniform pores (Breck, 1974; Gates, 1991; Marcus and Cormier, 1999).

This investigation examined five synthetic zeolites of four different kinds, namely: (A) β-type (CP814E), (B) Y-type (CBV100), (C) Y-type (CBV780), (D) Mordenite (CBV10A), and (E) ZSM-5 (CBV3024E). These minerals will hereafter be referred to as zeolites A, B, C, D, and E, respectively. All of the zeolite samples were in the form of fine white powders and were purchased from Zeolyst International (Valley Forge, PA).

In previous work, Bouffard (1998) found that the highest treatment efficiency was attained with small mineral particle size (less than 0.180 mm). Above 0.5 mm, however, the aggregate size did not affect the removal efficiency. This finding was in agreement with the work of Crocker et al. (1995), who showed that increased desorption rate of naphthalene bound to HDTMA-tailored smectite was obtained with aggregates smaller
than 0.5 mm. Bouffard and Duff (2000) also revealed that aggregate size had marginal (9%) effect on the partitioning of DHA into the hydrophobic HDTMA layer.

In the current study, mineral sieving was not conducted with these zeolites since they already existed in fine powder form. Nevertheless, prior to use, each zeolite was further ground with a mortar and a pestle to break up any mineral clusters. The zeolites were stored in the originally-supplied polyethylene containers.

Unfortunately, due to its academic policy and confidentiality concerning its manufactured products, Zeolyst International could only reveal limited information about the minerals. The characteristics of each zeolite as provided are shown in Table 4.1.

Table 4.1. Characteristics of the studied zeolites (Zeolyst International, 1999)

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>Nominal Cation Form</th>
<th>SiO₂/Al₂O₃ Mole Ratio</th>
<th>Surface Area (m²/g)</th>
<th>pH in H₂O Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ammonium (NH₄⁺)</td>
<td>25</td>
<td>680</td>
<td>5-7</td>
</tr>
<tr>
<td>B</td>
<td>Sodium (Na⁺)</td>
<td>5.1</td>
<td>900</td>
<td>9-11</td>
</tr>
<tr>
<td>C</td>
<td>Hydrogen (H⁺)</td>
<td>80</td>
<td>780</td>
<td>3-5</td>
</tr>
<tr>
<td>D</td>
<td>Sodium (Na⁺)</td>
<td>13</td>
<td>425</td>
<td>8-10</td>
</tr>
<tr>
<td>E</td>
<td>Ammonium (NH₄⁺)</td>
<td>30</td>
<td>400</td>
<td>5-7</td>
</tr>
</tbody>
</table>

Although the information tabulated above was useful, it was incomplete. It was therefore important to determine other characteristics of the zeolites, such as pore and particle size distributions, and their exchange capacities (total, external, and internal), which were used in the screening process of the zeolite samples. The procedures for determining such characteristics are outlined in the following sections.

4.1.1 Analysis of Zeolite Particle Sizes

The particle size distribution of each zeolite sample was determined using a Malvern Particle Sizer Instrument (model: Master Sizer 2000), which was equipped with Hydro 2000 MU(A) accessory.

Each zeolite sample of known amount (approximately 1.5 g) was suspended in the sampling beaker that had been filled with deionized water. The beaker with the zeolite suspension was then seated in the sampling port. Next, the mixing-suction arm was fully
lowered to provide stirring as the sample was being withdrawn through a circulating tube from the beaker to the analysis compartment. Upon clicking the "start" icon on the computer screen, a laser beam was directed through the crystal glass case. The zeolite sample diverted some of the beam, and the intensities of its deflected rays were then compared and measured with respect to the initial strength. The size distribution of the zeolite was automatically determined by assuming the zeolite particles to be spherical. Prior to the next sample, the whole compartment was cleaned by passing deionized water through until the cloudiness in the circulating tube disappeared, which indicated that the zeolite sample had then been completely flushed out of the instrument. At the same time, one end of the circulating tube was detached from the suction arm so that the flush water could be wasted into another beaker.

4.1.2 Analysis of Zeolite Pore Sizes

The pore size distribution of each zeolite sample was determined utilizing a Micromeritics PoreSizer 9320 instrument. The poresizer instrument measured the volume of the pore fractions in each zeolite sample structure, with diameters ranging from the largest value (depending on how large the pore size was available in the sample) down to 0.006 μm. The underlying theory of the mercury porosimetry analysis is based on a cylindrical pore model (Webb and Orr, 1997).

This instrument makes use of liquid mercury, a non-wetting agent for most materials, to penetrate the pores of the zeolite. Extreme care was therefore necessary at all times when using the poresizer (Fisher Scientific, 1999). Each analytical method consisted of two parts, which were low- and high-pressure runs. Operating the instrument involved 6 basic steps: (1) Loading the penetrometer bulb with the zeolite sample and weighing them altogether, (2) Entering all the sample information and choosing the analysis and report parameters, (3) Installing the loaded penetrometer unit on the low pressure port, (4) Evacuating the gases and vapors from the zeolite sample in the penetrometer bulb, (5) Collecting the low-pressure run data, and (6) Transferring the mercury-filled penetrometer from the low to the high pressure port for the automatic data collection.
The operation of the poresizer closely followed the protocols described in the instruction manual supplied by the manufacturer (Micromeritics/Folio Corporation). The poresizer was initially run with the provided standard material. This served to ensure that the instrument was functioning well prior to analysis of the zeolite sample.

In the low-pressure run, only larger pores were intruded, while in the high-pressure case, the mercury was highly pressurized so that the smaller pores could be penetrated. Mercury, whose average molecular diameter is approximately 13.8 nm (Israel, 2001; Alcock, 1990; Greenwood, 1984), can theoretically penetrate pores as small as 0.0036 μm in diameter (Israel, 2001). The smallest pore size diameter that the poresizer model was able to measure was 0.006 μm.

Mercury intrusion, however, is rather unreliable at the theoretical lower limit of the pores being penetrated, as a result of a number of problems. First, mercury can lose its physical properties as higher pressure is applied (Israel, 2001). Second, compressing the mercury at high pressure can create a tremendous amount of heat, causing the mercury to expand out of the pores (Israel, 2001; Webb and Orr, 1997). Third, many materials, especially those that contain closed pores, cannot sustain their structures at high pressure, consequently leading to structural damage (Webb and Orr, 1997). Fourth, if the sample to be analyzed is in the form of tightly packed powder particles, there is a possibility that the mercury penetrating the voids between particles will be mistakenly classified as having entered the internal pores (Micromeritics/Folio Corporation). Although this analysis has many trade-offs, the results can provide valuable information about the zeolite porous structure.

On a personal note, mercury porosity was long and tedious, especially when the samples to be analyzed were fine powders. The intrusion process required that the system pressure be reduced down to 50 mm Hg, before filling the sample with mercury, to remove any gases or vapors that were presorbed in the zeolite structure. This system pressure reduction process was very time consuming. It was suggested that the zeolites first be dried in an oven prior to the analysis. However, there was a concern that drying
the zeolites might alter their structures and/or properties caused by structural decomposition. Tsitsishvili et al. (1992) found that heulandite was completely decomposed after heating for 3-4 hours at 350°C. In addition, when loading the zeolite sample into the penetrometer bulb, extra care was needed to make sure that none of the sample went into the stem. This could otherwise yield to erroneous results.

4.1.3 Scanning Electron Microscopy (SEM) of Zeolites

Microscopic photographs of each zeolite were obtained using a Hitachi S-2300 SEM, which was equipped with a Robinson Kevex Quantum vacuum detector. The SEM instrument was operated at a beam voltage of 20 kV.

First, the zeolite sample was suspended in ethanol in a small (10-mL) beaker. The use of ethanol as the solvent in this analysis was appropriate because of the negligible solubilities of the zeolite samples in ethanol. Ultrasound was used to facilitate the dispersion of the zeolite particles in the ethanol-filled beaker to break up any clustering of the mineral. Using a Pasteur pipette, a single drop of each zeolite suspension was then placed onto a carbon plate and allowed to dry for sufficient time to evaporate the ethanol. The sample was gold-plated using a Denton Gold Vacuum Desk II Sputter Coater prior to placing it into the analysis compartment. The small video monitor on the SEM provided a view of the sample under analysis, with the magnification factor and scale shown at the bottom right corner of the screen. To start the run, the on/off button on the machine was pressed after the vacuum condition had been set up. Photographs of each particle were captured by clicking the appropriate icon on the computer interface program. The qualities of the two-dimensional photographs of the zeolite samples, however, deteriorated at high magnification levels.

4.1.4 Energy Dispersive X-Ray (EDX) Diffusion of Zeolites

The purpose of this EDX analysis was to determine the elemental compositions of the zeolite samples.

The EDX analysis of each zeolite was performed using the same SEM equipment as above. The major difference was that instead of gold-plating, the sample was carbon-
plated, using a Balzers JEE-4B Vacuum Carbon Evaporator, prior to analysis. The different elemental spectra displayed on the computer screen corresponded to those present in each zeolite sample that could be determined from the database. Some elemental spectra, such as those of ammonium and hydrogen, however, could not be detected because of the sensitivity limits of the instrument's detector.

4.2 Procedure for Zeolite Tailoring

4.2.1 Pretreatment of Zeolites for Tailoring

All the zeolite samples had to undergo an initial treatment before being tailored with the organic cations. The pretreatment, which has been reported to improve the exchange capacity of the zeolite (Foldesova et al., 1998), prepared each zeolite to its homoionic form. The zeolite samples were first saturated with sodium ions to replace the nominal cations and had to be treated to remove free-iron oxides. This procedure closely followed that of Bouffard (1998).

Ten grams of each zeolite sample were initially dispensed into a 250-mL polyethylene container. The zeolite was then mixed with 200 mL of solution that contained 0.3 M tribasic sodium citrate (\(\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\cdot2\text{H}_2\text{O}\)), 1.0 M sodium bicarbonate (\(\text{NaHCO}_3\)), and 0.2 g sodium hydrosulphite (\(\text{Na}_2\text{S}_2\text{O}_3\))/g zeolite. The addition of the sodium hydrosulphite into the solution was to eliminate the free-iron oxides that could be present in the zeolite (Jackson, 1958). The mineral suspension was mixed on a magnetic stirring plate for 15 minutes. A water bath system was also used in order to maintain the temperature of the suspension at a constant level of 80°C. For health and safety purposes, this procedure was performed in fume hood due to the potential for the formation of carbon monoxide (CO), carbon dioxide (CO\(_2\)), and oxides of sulphur (SO\(_x\)) (Fisher Scientific, 1997). To avoid some mineral loss, the suspension was allowed to completely settle before the supernatant was decanted following the reaction period. The zeolite was then stirred for 4 hours in 200 mL of 1.0 N NaCl solution. This procedure was repeated three consecutive times, followed by another three successive rinses of the zeolite with 200 mL of deionized water. It was important to ensure that all the zeolite
suspensions were completely mixed during the reaction and rinsing. The zeolites were finally dried at 60°C overnight and stored in the same polyethylene containers.

4.2.2 Determination of Pretreated Zeolite Exchange Capacity

One of the key parameters for the ensuing tailoring process is the mineral cation exchange capacity. For each zeolite sample, the total, external, and internal cation exchange capacities can be determined. The procedures for determining these properties are outlined in the following subsections. All of the centrifugation processes were performed using an IEC-CU 5000 instrument at 2250 x g for 15 minutes. The use of an end-over-end rotator, which revolved at 8 rpm, enabled all of the mixing processes.

4.2.2.1 Determination of Total Cation Exchange Capacity (CEC)

The procedures of Hesse (1972) and the United States Environmental Protection Agency (USEPA, 1986) were adopted to determine each zeolite total cation exchange capacity (CEC). This method involves three basic steps: saturating all the exchange sites of the zeolite with sodium (Na\(^{+}\)) ions, extracting the Na\(^{+}\) ions with ammonium (NH\(_4\)\(^{+}\)) ions, and analyzing the extracted solutions for Na\(^{+}\) ions. Particle size has been found to have very little effect on the CEC determination process (Ming and Dixon, 1987).

The CEC determination of each zeolite was carried out in duplicate. First, each pretreated zeolite sample was ground to break up any particle clusters before being precisely (± 0.0001 g) weighed. The weighed sample was then dispensed into a 50-mL glass-pyrex centrifuge tube. The zeolite was exchanged through four successive 10-minute saturations with 33 mL of 1.0 N sodium acetate (NaCH\(_3\)COO) solution (pH 8.20). This initial step would replace all the nominal cations present in the exchange sites of each zeolite with Na\(^{+}\) ions. The mineral suspension was centrifuged, after which the clear supernatant was decanted.

The zeolite was then mixed through three consecutive 10-minute rinses with 33 mL of isopropyl alcohol (electronic grade) and centrifuged. To substitute the Na\(^{+}\) ions with NH\(_4\)\(^{+}\) ions, each Na\(^{+}\)-saturated zeolite sample was subjected to three successive 10-
minute extractions with 33 mL of 1 N ammonium acetate (NH₄CH₃COO) solution (pH 7).

After each centrifugation, the supernatant was transferred to a 100-mL volumetric flask. The total volume of the three collected supernatants was made to 100 mL with 1 N NH₄CH₃COO solution before being analyzed for the Na⁺ ions. The analysis of the sodium ion concentrations in the duplicate samples was carried out using inductively coupled plasma (ICP) emission by an external laboratory (International Plasma Laboratory Ltd., Vancouver, BC).

Using equation 4.1, the CEC of each zeolite was calculated (USEPA, 1986).

\[
\text{CEC (meq / 100g)} = \frac{[\text{Na}^+] \times \text{DF} \times \text{V} \times 100}{\text{m} \times \text{MW}}
\]

where:

- \([\text{Na}^+] = \text{Sodium concentration (mg/L)}
- \text{V} = \text{Extracted volume (L)}
- \text{DF} = \text{Dilution factor}
- \text{M} = \text{Weight of mineral (g), and}
- \text{MW} = \text{Molecular weight of sodium (23 g/mole = 23 mg/meq)}

4.2.2.2 Determinations of External (ECEC) and Internal (ICEC) Cation Exchange Capacities

The method for ECEC and ICEC determinations is based on the exclusion of large organic cations from the internal pores of the minerals. It is assumed that these cations are able to exchange with the external Na⁺ ions only.

The procedure outlined in this section emulates the method of Ming and Dixon (1987), which had also been employed by Haggerty and Bowman (1994) to determine the ECEC and ICEC of their clinoptilolite-dominated zeolite. In this study, tetradecyltrimethylammonium (TDTMA) as TDTMA-bromide (Sigma-Aldrich), instead
of t-butylammonium, was utilized for surface exchange with the external Na\(^+\) ions to measure the ECEC of each zeolite sample.

A single TDTMA amine (C\(_{17}\)H\(_{38}\)NBr) molecule has an average head group diameter of approximately 0.7 nm, a chain diameter of about 0.4 nm, and a chain length of approximately 3.3 nm (Israelachvili, 1991; Walz, 2001). The size of these C17 cations is much larger than that of a single Na\(^+\) ion, which has an average ionic head radius of approximately 0.1 nm (Israelachvili, 1991; Alcock, 1990; Greenwood, 1984).

The four stages involved in the determinations of the ECEC and ICEC of each zeolite sample are: (1) saturation of all the zeolite exchange sites with Na\(^+\) ions, (2) extraction of the external Na\(^+\) ions with the C17 cations, (3) extraction of the internal Na\(^+\) ions with NFL* ions, and (4) analysis of both the extracted solutions for Na\(^+\) ions.

The ECEC and ICEC determinations of each zeolite were carried out on duplicate samples. Each pretreated zeolite sample was first ground to break up any particle clusters before being precisely (± 0.0001 g) weighed. The weighed sample was then dispensed into a 50-mL glass-pyrex centrifuge tube. The zeolite was exchanged through four successive 10-minute saturations with 40 mL of 1.0 N sodium acetate (NaCH\(_3\)COO) solution (pH 5) to replace all the nominal cations present in the exchange sites of each zeolite with Na\(^+\) ions. The mineral suspension was centrifuged, after which the clear supernatant was decanted.

Excess interstitial Na\(^+\) ions were removed by one 10-minute rinse with 40 mL of deionized water. The zeolite was then mixed through three consecutive 10-minute rinses with 33 mL of isopropyl alcohol (electronic grade) and centrifuged.

To replace the external exchangeable Na\(^+\) ions (ECEC) with the C17 cations, each zeolite was subjected to one 24-hour extraction and two successive 15-minute extractions with 30 mL of 0.3 N TDTMA-Br (C\(_{17}\)H\(_{38}\)NBr) solution. After centrifuging the zeolite suspension, each supernatant was decanted to a 100-mL volumetric flask. The three collected supernatants were then diluted to 100 mL with 0.3 N C\(_{17}\)H\(_{38}\)NBr solution before being analyzed for the Na\(^+\) ions.
The internal exchangeable Na\(^+\) ions (ICEC) were dislodged by three successive 15-minute extractions with 30 mL of 1 N NH\(_4\)CH\(_3\)COO solution (pH 7). After centrifugation, the three supernatants were transferred to a 100-mL volumetric flask and diluted to volume with 1 N NH\(_4\)CH\(_3\)COO solution prior to the Na\(^+\)-ion analysis.

4.2.3 Organic Tailoring of Zeolites (Organo-Zeolite Preparation)

Tailoring the zeolite samples with organic cations is simply a process of exchanging the Na\(^+\) ions present in all of the exchange sites of the pretreated zeolites with the organic cations. Depending on the chain length of the tailoring cation, this surface modification would make the zeolites more hydrophobic (Popovici et al., 1997; Cadena and Cazares, 1995).

Resin and fatty acids (RFA), such as dehydroabietic acid (DHA), are colloidal contaminants that are present in pulp and paper mill white water as hydrophobic compounds. The hydrophobicity of the tailored zeolites increases the uptake capacities of the zeolites for these RFA compounds. The adsorption of the RFA contaminants from the white water occurred by dissolving the RFA molecules into the cation tails due to the “like dissolves like” principle (Bouffard, 1998; Alther, 2000). This removal process is known as partitioning, which has also been previously reported to be responsible for the sorption of perchloroethylene by HDTMA-tailored zeolite (Li and Bowman, 1998b).

A total of six organic cations were exploited in this study. They were: (1) dodecyltrimethylammonium (DDTMA) \((C_{15}H_{34}NBr)\), (2) TDTMA \((C_{17}H_{38}NBr)\), (3) tetrapentylammonium \((TPA) \(C_{20}H_{44}NBr)\), (4) tetraheptylammonium \((THA) \(C_{28}H_{60}NBr)\), (5) tetraoctylammonium \((TOA) \(C_{32}H_{68}NBr)\), and (6) tetra(decyl)ammonium \((T(D)A) \(C_{40}H_{84}NBr)\). All of these chemicals were purchased from Sigma-Aldrich Canada.

Two of these organic surfactants (C15 and C17) were water-soluble, while the others had to be dissolved in organic solvents, such as methanol (for C20 and C32) and
ethanol (for C28 and C40). Table 4.2 summarizes their properties, including their solubility limits.

Table 4.2. Properties of the organic surfactants used (Sigma-Aldrich, 1999)

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>MW (g/mole = mg/meq)</th>
<th>Solubility Limit</th>
<th>Solubility Media</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{15}H_{34}NBr</td>
<td>308.35</td>
<td>50 mg/mL</td>
<td>H_2O</td>
</tr>
<tr>
<td>C_{17}H_{38}NBr</td>
<td>336.41</td>
<td>100 mg/mL</td>
<td>H_2O</td>
</tr>
<tr>
<td>C_{19}H_{44}NBr</td>
<td>378.49</td>
<td>10% w/w</td>
<td>Methanol</td>
</tr>
<tr>
<td>C_{28}H_{60}NBr</td>
<td>490.71</td>
<td>100 mg/mL</td>
<td>Ethanol</td>
</tr>
<tr>
<td>C_{32}H_{68}NBr</td>
<td>546.82</td>
<td>10% w/w</td>
<td>Methanol</td>
</tr>
<tr>
<td>C_{40}H_{84}NBr</td>
<td>659.03</td>
<td>100 mg/mL</td>
<td>Ethanol</td>
</tr>
</tbody>
</table>

For the batch exchange experiments, each tailoring cation was added to the precisely (± 0.0001 g) weighed samples of pretreated zeolite in an amount equal to 100% of the zeolite CEC. The zeolite suspensions were then mixed using an end-over-end rotator, which revolved at 8 rpm, at 25°C for 24 hours and centrifuged using an IEC-CU 5000 instrument (2250 x g, 15 minutes) to separate the two phases. The 24-hour contact time had been shown to be sufficient for complete sorption of HDTMA and tetraethylammonium bromide (TEA) onto clinoptilolite (Sullivan et al., 1998a).

After the supernatants had been decanted, the zeolites were subjected to five successive 5-minute rinses with deionized water. The mineral suspensions were then centrifuged, and the supernatants were decanted. The tailored zeolites were dried at 60°C and were finally stored in polyethylene containers prior to use.

4.3 Preparations of Synthetic Process Water (SPW) and White Water (WW)

The two types of process water being treated in this study were synthetic and white water. The synthetic process water (SPW), which contained only dehydroabietic acid (DHA), was used to determine the effects of pH, different type of tailoring cations, different mineral loadings, various treatment times, and buffers.

The white water (WW) samples, which were obtained from two different pulp mills, were also treated to determine the technical feasibility of using organically-tailored zeolites to remove the RFA contaminants present in the WW samples.
4.3.1 Preparation of Synthetic Process Water (SPW)

Before synthetic process water (SPW) solutions were prepared, all the needed glassware was washed and fired at 520°C to eliminate any traces of organics. Since the solubility of DHA is pH dependent, the deionized water used to make up the stock solution of 1000 mg/L DHA (Helix Biotech, Richmond, BC) was first adjusted to pH 12 with 1 N NaOH before dissolving the appropriate amount of DHA crystals.

The synthetic process water (SPW) was prepared by diluting the proper amount from the stock solution in a volumetric flask, which contained enough preweighed mixtures of Na$_2$HPO$_4$ and NaH$_2$PO$_4$ or NaCH$_3$COO and CH$_3$COOH to yield a 50-mM buffer. The initial DHA concentration of the SPW was $(30 \pm 1)$ mg/L.

The stock solution and the buffered synthetic process water were then stored in a cold-room at 4°C. Prior to the batch treatment tests, the pH of the synthetic process water was adjusted to the desired pH value by addition of 1 N NaOH or H$_2$SO$_4$.

When preparing the SPW at pH 4, 5, and 6, white precipitates of DHA were observed. This was because the solubility of DHA is very low at those pH values. The DHA precipitates in the SPW were removed prior to the batch treatment test, which is outlined later in section 4.4.1, so that the DHA removal efficiency of the tailored zeolite would not be overestimated. The extent of DHA removal by the centrifugation process (2250 x g, 20 minutes) was determined and is shown in Figure 4.1.
Figure 4.1. Removal of DHA by centrifugation (2250 x g, 20 minutes) at pH 4, 5, and 6 in unbuffered (U), acetate (A), and phosphate (P) buffered environments.

It can be seen from the trend of the figure that the lower the pH, the more the DHA was removed. The DHA concentrations after centrifugation were determined to be approximately 0, 2.5, and 5.6 mg/L at pH 4, 5, and 6, respectively. These values corresponded to 100%-80% reduction of the DHA. Moreover, these concentrations, which indicated the solubilities of DHA at these pH values, were in good agreement with those values found by Nyren and Back (1958) and Peng and Roberts (2000).

4.3.2 Preparation of White Water (WW)

The white water (WW) samples were obtained from two different pulp mills, Millar Western Pulp Ltd. BCTMP mill in Whitecourt, AB and Quesnel River Pulp Company BCTMP/TMP mill in Quesnel, BC. The two white water samples were immediately stored in a cold-room at 4°C upon receiving.

The initial pH of the Millar WW sample was 5.4, while the Quesnel WW sample had an initial pH of 8.5. Prior to the batch treatment tests, the pH of each white water sample was adjusted to the desired pH value with 1 N NaOH or H₂SO₄.
By visual inspection, the Millar white water sample was cloudier and contained more suspended solids than the Quesnel white water sample. The solids content of each white water sample was determined according to the Standard Methods 2540 B – 2540 E (American Public Health Association, 1992).

The presence of suspended solids (SS) in both of these white water samples provided a problem in the separation method of the tailored zeolites from the white water. Solid particles, such as fibers and fines, could firmly bind or adsorb the extractives in a pulp suspension, as suggested by Ekman et al. (1990). The sedimentation of the suspended solids in the white water samples could result in a potential overestimation of the zeolite treatment efficiency due to loss of extractives (Alamo et al., 1989; Francis and Ouchi, 1997).

Consequently, to minimize the overestimation difficulty, the white water samples were first centrifuged (2250 x g, 20 minutes) to remove the suspended solids before being contacted with the tailored zeolites. The RFA concentrations before and after centrifugation as well as after the batch treatment test in each sample were determined in order to calculate the zeolite treatment efficiency.

Removing the suspended solids by centrifugation, however, affected the concentrations of the RFA present in the WW samples. The RFA removal caused by the centrifugation process ranged from 10% to 100% in the Millar WW sample. On the other hand, the RFA concentrations in the Quesnel WW sample decreased by about 3-22% as the result of the centrifugation process. All of these results are shown in Appendix A.

4.4 Batch Treatment Tests of SPW and WW

All the needed glassware was washed and fired in a muffle furnace at 520°C to eliminate any traces of organics prior to use. The synthetic process water (SPW) and white water (WW) samples were mixed on stirring plates for 8-10 minutes until they reached room temperature. The batch treatment tests of the SPW and WW samples were also carried out at room temperature, since reaction temperature had been shown to have no effect on the removal of DHA by HDTMA-tailored heulandite (Bouffard and Duff,
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2000). With the exception of runs where contact time was a variable, all other treatment tests were completed after 24 hours of mineral contact. Bouffard (1998) has shown that a 24-hour contact time was sufficient to achieve equilibrium between the liquid and the solid phase for the partitioning of the DHA molecules. All of the centrifugation processes were performed using an IEC-CU 5000 instrument.

4.4.1 Uptake of Dehydroabietic Acid (DHA) from SPW

As mentioned in Section 4.3, the synthetic process water (SPW) contained only DHA. Batch experiments conducted with the SPW were to compare the effectiveness of five untailored synthetic zeolites for the uptake of the DHA to that of the same five synthetic zeolites, which had been organically tailored. This determination was carried out using the SPW so that comparison between the performances of the two zeolite conditions could be attained in the absence of confounding variables that would otherwise be present if white water was used.

The treatment tests using SPW were also to study the effects of different mineral loadings, treatment times, pH, and buffers on the removal efficiencies of the DHA from the SPW by organically-tailored zeolites. Table 4.3 outlines the conditions used for these studies.
### Table 4.3. Conditions for batch tests with synthetic process water

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Effects</th>
<th>Mineral Types</th>
<th>Organic Cations</th>
<th>Mineral Loading (g/L)</th>
<th>Time</th>
<th>pH</th>
<th>Buffer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral Types</td>
<td>A, B, C, D, E</td>
<td>C17</td>
<td>20</td>
<td>24 (h)</td>
<td>7.25</td>
<td>Phosphate</td>
<td></td>
</tr>
<tr>
<td>Organic Cations</td>
<td>A, B, C, D</td>
<td>C15, C17, C20, C28, C32, C40</td>
<td>20</td>
<td>24 (h)</td>
<td>7.25</td>
<td>Phosphate</td>
<td></td>
</tr>
<tr>
<td>Mineral Loading (g/L)</td>
<td>D</td>
<td>C17</td>
<td>1, 2, 5, 10, 15</td>
<td>24 (h)</td>
<td>7.25</td>
<td>Phosphate</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>D</td>
<td>C17</td>
<td>1, 5</td>
<td>1, 2, 3, 4, 5 (min)</td>
<td>7.25</td>
<td>Phosphate</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>D</td>
<td>C17</td>
<td>1</td>
<td>24 (h)</td>
<td>5, 6, 7.25, 9, 10</td>
<td>Phosphate, Acetate</td>
<td></td>
</tr>
<tr>
<td>Buffer</td>
<td>D</td>
<td>C17</td>
<td>1</td>
<td>24 (h)</td>
<td>5, 6, 7.25, 9, 10</td>
<td>Phosphate, Acetate</td>
<td></td>
</tr>
</tbody>
</table>

To interpret Table 4.3: for example, in the batch experiment that determined the effect of different mineral loadings on the removal of the DHA, zeolite D that had already been tailored with organic cation C17 was used to treat the SPW at pH 7.25 in a phosphate buffer environment for 24 hours. The mineral concentrations studied were 1, 2, 5, 10, and 15 g/L.

All of the batch treatment tests conducted with the SPW were carried out on duplicate samples using 10-mL glass vials with Teflon caps. Knowing both the desired mineral loading and the volume of the SPW to be used, the amount of zeolites needed could be calculated and dispensed into a vial. A precise volume of the SPW was then pipetted into the vial that contained a precisely (± 0.0001 g) preweighed amount of tailored zeolites. The zeolite suspension was then mixed using an end-over-end rotator that revolved at 8 rpm. After 24 hours of treatment, the suspension was centrifuged (2250 x g, 10 minutes). Three mL of the supernatant was carefully pipetted, transferred into another vial, and immediately preserved with 300 μL of 1N NaOH. All samples were then stored at -10°C prior to DHA analysis.
There was, however, one exception to the standard method outlined above. In the case where the treatment time was the variable, the use of the end-over-end rotator for mixing the suspension was impractical because of the short contact time of the tailored zeolite with the SPW (from 1 to 5 minutes). Consequently, to overcome this problem, the zeolite suspension was shaken vigorously by hand immediately after the SPW was added to the tailored zeolite. Centrifugation was then performed on the zeolite suspension for 1-5 minutes, depending on the treatment time.

The short centrifugation of the suspension, however, only produced partial segregation of the zeolite samples. There were some zeolite particles that remained on the liquid surface. To overcome this difficulty, a filter-syringe was used immediately after the centrifugation process to separate the tailored zeolite from the SPW. However, this raised a question of whether or not the use of a filter-syringe would affect the overall adsorption efficiency of the tailored zeolite in removing the DHA. Preliminary experiments showed that the concentration of DHA slightly decreased from (29 ± 1) mg/L to approximately (28 ± 0.2) mg/L when a filter-syringe was used. The small reduction in the DHA concentration permitted the use of the filter-syringe in this case.

4.4.2 Zeolite Batch Treatment of WW

Batch treatment tests were also carried out with the white water (WW) samples to determine the possibility of using organically-tailored zeolites to remove resin and fatty acids (RFA), sterols, soluble biochemical oxygen demand (SBOD), soluble chemical oxygen demand (SCOD), and acute toxicity.

As previously mentioned, the WW samples were first centrifuged to remove the suspended solids before being contacted with the tailored zeolites to avoid any potential overestimation of the mineral treatment efficiency. The solids content of each WW sample was determined according to the Standard Methods 2540 B – 2540 E (American Public Health Association, 1992).

All batch treatment tests performed with the WW samples were conducted using 10-mL glass vials with Teflon caps in quadruplicate to ensure that enough samples could
be collected for analyses. Zeolite D that had already been tailored with TDTMA (C17 cation) was used in these experiments at loadings of 1 and 20 g/L.

First, the pH of each centrifuged WW sample was readjusted to 7.25 in a non-buffered environment. A precise volume of each centrifuged WW sample was then pipetted into a vial that contained precisely (± 0.0001 g) preweighed amount of tailored zeolites. The zeolite suspensions were mixed for 24 hours using an end-over-end rotator, which revolved at 8 rpm. To separate the two phases, the zeolite suspensions were centrifuged (2250 x g, 10 minutes). After 5 mL of the supernatant in each vial had been carefully pipetted and transferred into another vial, 500 µL of 1 N NaOH was immediately added to the latter vial to preserve the sample. All samples were then stored at -10°C prior to analyses.

4.5 Analytical Methods

4.5.1.1 Extraction and Silylation of Resin and Fatty Acids (RFA)

The procedure to determine the RFA concentrations of the samples was adapted from the methods of Voss and Rapsomatiotis (1985) and Orsa and Holmbom (1994). The method required that the RFA first be extracted from the aqueous phase of the sample to an organic phase solvent that could fully solublize the RFA. Methyl tert-butyl ether (MTBE) has been shown to be an effective solvent for the extraction of RFA in pulp mill effluents (Voss and Rapsomatiotis, 1985). The RFA was then derivatized by silylation to increase its volatility prior to GC analysis.

In this study, 1 mL of each sample was extracted and analyzed for RFA. The pH of the sample was adjusted to 5 with 10 µL of glacial acetic acid (CH$_3$COOH) to reduce the aqueous solubility of the RFA prior to its extraction. The sample was first spiked with 0.5 mL of a 135-µg/mL solution of O-methylpodocarpic acid (O-MPCA) (Helix Biotech, Richmond, BC) in MTBE. The O-MPCA served as the sample extraction surrogate or recovery standard (RS).
The aqueous phase was then subjected to two successive 1-minute extractions with 1 mL of MTBE by hand-shaking the sample tube vigorously. Patoine et al. (1997) found that increasing the number of extractions from two to four did not improve the recovery of resin acids. Centrifugation was selected as a means to separate the aqueous phase from the organic phase. After the first centrifugation (2250 x g, 10 minutes), the clear organic MTBE solvent was carefully pipetted off and transferred to a 2-mL Teflon-lined glass gas chromatography (GC) vial. The volume of the MTBE in the GC vial was then reduced to about 0.4 mL by evaporating with nitrogen gas to make room for the supernatant from the second successive extraction. The volume of the combined MTBE phases was again reduced to approximately 0.3 mL before adding 0.5 mL of a 125-μg/mL solution of heneicosanoic acid (Helix Biotech, Richmond, BC) in MTBE. The heneicosanoic acid was used as the internal standard (IS).

Next, the mixture in the GC vial was completely dried in a stream of nitrogen gas. Silylation of the RFA was carried out by adding 0.5 mL bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) (Sigma-Aldrich) using a syringe. The solution was heated at 70°C for 30 minutes and was thereafter ready for analysis by GC.

4.5.1.2 Gas Chromatography (GC) Analysis of RFA

The silylated samples were analyzed by injecting 1 μL of the samples into a Hewlett-Packard (HP) 5890 Series II gas chromatograph (GC), which was equipped with a HP 7673 GC/SFC automatic injector and sample tray, a HP 3396 Series II integrator, and a flame ionization detector (FID). The GC analysis also used a HP-5 non-polar column made up of (5%)-Diphenyl-(95%)-dimethylpolysiloxane copolymer, which was 30 m long with an inner diameter of 0.25 mm and a film thickness of 0.25 μm. The column head pressure was fixed at 15 psi, the septum purge flow was set to approximately 3 mL/min, and the split/splitless flow was adjusted to about 50 mL/min. Helium was used as the carrier gas. Air, hydrogen, and helium gases at flow rates of 400, 30, and 20 mL/min, respectively, comprised the flame ionization detector make-up gases. The injection and the detector temperatures were held at 275°C and 300°C, respectively. The oven temperature was initially set at 150°C was held for 1 minute before being
linearly ramped at 4°C/min to the final temperature of 250°C. The total analysis time, including cooling of the column oven, followed by temperature stabilization, was about 30 minutes. The integrator was set up at a chart speed of 1.0, a peak width of 0.04, and an area reject of 200.

The quantification of DHA was accomplished by using the normalized response of 99% pure DHA standards, which were prepared from a 100-mg/L stock solution in MTBE. Each set of samples was analyzed with two blanks and seven DHA standards. The DHA concentration was reported in mg/L units. The DHA removal efficiency was calculated by the difference between the amount initially present and remaining in the liquid sample. Other RFA were not quantified, but their removal efficiencies were calculated by comparing their peak areas before and after treatments. Bouffard (1998) found that the detection limit of the entire extraction and GC analysis procedure for each individual RFA was 0.1 mg/L.

One of the initial experiments conducted with the white water (WW) samples was to identify the types of RFA present in the samples. The identification process was performed by comparing each WW RFA peak retention time to that of a single RFA compound, analyzed by the GC one at a time. However, there were only 12 types of RFA compounds that were available in this study for the identification process. Consequently, there were some RFA in the WW samples that could not be identified. Table 4.4 shows the list of RFA analyzed in this study and the retention times of the RFA as determined by the GC, respectively.
Table 4.4. The retention times of the RFA as determined by using a GC equipped with a 30-m HP-5 capillary column

<table>
<thead>
<tr>
<th>Compound</th>
<th>Type</th>
<th>Retention Times (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic</td>
<td>FA</td>
<td>14.43</td>
</tr>
<tr>
<td>Linoleic</td>
<td>FA</td>
<td>18.26</td>
</tr>
<tr>
<td>Oleic</td>
<td>FA</td>
<td>18.32</td>
</tr>
<tr>
<td>Linolenic</td>
<td>FA</td>
<td>18.40</td>
</tr>
<tr>
<td>Pimmaric</td>
<td>RA</td>
<td>19.99</td>
</tr>
<tr>
<td>Sandaracopimaric</td>
<td>RA</td>
<td>20.32</td>
</tr>
<tr>
<td>Isopimaric</td>
<td>RA</td>
<td>20.61</td>
</tr>
<tr>
<td>Palustric</td>
<td>RA</td>
<td>21.09</td>
</tr>
<tr>
<td>Levopimmaric</td>
<td>RA</td>
<td>21.48</td>
</tr>
<tr>
<td>Dehydroabietic</td>
<td>RA</td>
<td>21.77</td>
</tr>
<tr>
<td>Abietic</td>
<td>RA</td>
<td>22.29</td>
</tr>
<tr>
<td>Neoabietic</td>
<td>RA</td>
<td>24.17</td>
</tr>
</tbody>
</table>

4.5.2 Sterols Analysis

In addition to the RFA analysis, each white water (WW) sample was also analyzed for its sterol content. The types of sterols analyzed in this research were campesterol, β-sitosterol, and β-sitostanol.

The analytical procedure proposed by the National Council of the Paper Industry for Air and Stream Improvement Inc. (NCASI, 1997) was used in this study to determine the sterols concentrations of the WW samples. This procedure adopted the method of Orsa and Holmbom (1994), which was originally used for RFA extractions. Consequently, the procedure for this sterol analysis was similar to that of the RFA analysis. It involved extraction of the sterols from the aqueous phase of the sample to an organic phase solvent, such as MTBE, that could fully solubilize the sterols.

In most cases, 10-mL samples were used for the sterol analysis. In some tests in which the sample volume was limited, 5-mL samples were used, and the reagent volumes
were adjusted accordingly. All centrifugation processes were done using an IEC-CU 5000 instrument (2250 x g, 10 minutes).

First, the WW sample was spiked with 0.5 mL of a 10-µg/mL solution of cholesterol in methanol. The cholesterol served as the sample extraction surrogate or recovery standard (RS). The aqueous phase was then subjected to two successive 1-minute extractions with 10 mL of MTBE, followed by centrifugation. The organic solvent was carefully transferred to a glass Erlenmeyer flask, and 1 g of magnesium sulphate (MgSO₄) was added to absorb any water present. The suspension was then filtered to remove the MgSO₄ solids. The filtered solvent was reduced to about 0.5-mL volume by evaporating with nitrogen gas before transferring to a 2-mL Teflon-lined glass GC vial.

Using a syringe, 0.5 mL of bis-(trimethylsilyl)-trifluoro-acetamide (BSTFA) was added to the GC vial, and the capped vial was heated to 70°C for 3 hours. The heated solution was then completely dried in a stream of nitrogen gas before adding 1 mL of a 10-µg/mL solution of dotricontane in hexane. The dotricontane was used as the internal standard (IS). The solution was thereafter ready for analysis by GC, which was equipped with mass spectrometry detector (GC-MS). The GC conditions used for the sterols analysis are presented in Appendix B.

4.5.3 Determination of Biochemical Oxygen Demand (BOD)

Both BOD and soluble BOD (SBOD) of the white water (WW) samples were measured according to the Standard Method 5210 B, 5-day BOD Test (American Public Health Association, 1992). Prior to analysis, the pH of each sample was adjusted to 7 using 1 N NaOH or H₂SO₄. The analysis was done at a minimum of two dilutions per sample in triplicate. The biomass used to seed the tests was obtained from Western Pulp Limited Partnership, Squamish, BC.
4.5.4 Determination of Chemical Oxygen Demand (COD)

Both COD and soluble COD (SCOD) of the white water (WW) samples were measured in triplicate each according to the Standard Method 5220 D, Closed Reflux, Colorimetric Method (American Public Health Association, 1992). The pH of each sample was not adjusted prior to analysis. As shown in Figure 4.2, the analysis is independent of the sample pH since concentrated $\text{H}_2\text{SO}_4$ was added when digesting the sample.

![Figure 4.2. COD of DHA measured at pH 7.25 and pH 10](image)

As stated in the Standard Method, all samples, blanks, and standards were incubated for 2 hours at 150°C in a COD reactor with a heating block. A new calibration curve was prepared whenever new COD chemicals were made up, using standards of known COD concentrations that ranged from 50 to 900 mg $\text{O}_2$/L. After each sample had been cooled, its absorbance was measured using a HACH DR-2000 spectrophotometer, which was set at 600 nm, and compared to the absorbances of the standards.
4.5.5 Acute Toxicity Analysis by Microtox

The acute toxicity of each white water (WW) sample was determined using the full-range Microtox assay, according to the standard procedure (Microbics, 1992). The analysis utilized a Microtox 500 analyzer and photoluminescent marine bacterium (*Vibrio fischeri*) as the indicator organism. When a test sample was added, the greater the decrease in the level of light emitted by the bacteria, the greater the toxicity of the sample.

Prior to analysis, the pH of each sample was adjusted to about 7 using 0.05 M NaOH or H₂SO₄. The toxicity data were analyzed using the Microtox computer software (Microbics Corporation).

In this study, the toxicity results were reported as EC50 (%v/v) instead of toxicity units (TU). It is important to note that converting the results from EC50 values to TU can cause a distortion that produce misleading results. Such conversion causes higher weighting of the smaller EC50 values, since for the same EC50 removal efficiency, different TU reductions can be obtained. For example, an EC50 value change from 1% to 2% means 50-point TU reduction. However, the same 50% change (EC50: 4 to 8%) only means 12.5-point TU reduction.

4.5.6 Determination of Solids Content of WW

Each uncentrifuged white water (WW) sample was analyzed for its initial solids content according to the Standard Methods 2540 B – 2540 E (American Public Health Association, 1992). The WW samples were analyzed for: (1) total solids (TS), (2) total suspended (TSS) and dissolved solids (TDS), (3) total volatile suspended (TVSS) and dissolved solids (TVDS), (4) total volatile (TVS) and fixed solids (TFS), and (5) total fixed suspended (TFSS) and dissolved solids (TDFS).
4.6 Data Analysis

4.6.1 Average Data and Error Analyses

Microsoft Excel program (version 97) was used to calculate the average and its estimated error value from replicate data for each sample. The sample error was approximated as the 95% confidence interval (CI) of the average value by using the built-in confidence function in the software package, which assumes a symmetric Gaussian distribution and uses a student-t test.

Error analyses were performed on every test, with the exception of those where the built-in function could not return a value due to the nature of the collected data, such as the average of two zeros.

4.6.2 Determination of Equation of Line

Linear regression was also performed using Microsoft Excel program (version 97). The square of the Pearson product ($R^2$ value) reflects the closeness of the best-fit line to the data points.

4.6.3 Reported Results

The results presented in this thesis are reported as the (average ± 95% CI) values. In addition, results in graphical forms (with some exceptions) are plots of average values, with the error bars representing the 95% CI.
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5.1 Characteristics of Synthetic Zeolites

The synthetic zeolite samples supplied were odourless, white, opaque, and had chalk-like appearances. Initial experiments with the zeolite samples showed that the solubilities of the zeolite samples in water, methanol, and ethanol were negligible.

The grinding of the zeolite samples prior to their use raised a question of whether or not the zeolite structures would be destroyed or broken down. It was found, however, that the dimensions of the zeolite crystals in most minerals do not exceed 10 to 15 microns (Tsitsishvili et al., 1992). Therefore, the grinding of the zeolite samples with a mortar and a pestle in the current research did not likely affect the crystal structures of the zeolite samples.

5.1.1 Particle Size Distributions of Synthetic Zeolites

The particle size distribution of each zeolite sample was automatically determined by assuming the zeolite particles to be spherical. Therefore, this determination is an approximation to the actual particle size, since the shapes of the particles were not characterized. Microscopic observations (section 5.1.3) indicated that zeolite particles deviated significantly from sphericity. Figure 5.1 shows the particle size distribution curves of the zeolite samples.
The curves, however, are not symmetrical about their centers and maxima, and hence the particle size was not normally distributed. Consequently, the interpretations of the properties of each curve are limited. The size of the zeolite particles ranged from 0.3 to 90 \( \mu \text{m} \). Ming and Dixon (1986) found that the size of individual crystals of clinoptilolite was between 2 and 20 \( \mu \text{m} \). Also, Breck (1974) reported that the largest particle size measured for single crystals of synthetic zeolites appeared to be approximately 100 \( \mu \text{m} \). In this analysis, zeolite D seemed to dominate the lower particle size range, while zeolite A dominated the upper class. The mean value of each zeolite sample size distribution is presented in Table 5.1. Breck (1974) reported that the average particle size of synthetic zeolite crystals ranged from 1 to 10 microns.

In addition to being able to determine the particle size distributions, the instrument was also able to determine the uniformity of the zeolite samples. Since the model assumed was a sphere, the more spherical a zeolite particle was, the closer the uniformity value would approach unity. Based on this analysis, the spherical model could be reasonably applied to zeolites B, C, and D.
Table 5.1. Mean particle size and uniformity of zeolite samples

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Particle Size (μm)</th>
<th>Uniformity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10.6</td>
<td>0.6</td>
</tr>
<tr>
<td>A</td>
<td>10.6</td>
<td>0.6</td>
</tr>
<tr>
<td>A</td>
<td>10.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Average</td>
<td>10.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Particle Size (μm)</th>
<th>Uniformity</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>7.1</td>
<td>1.2</td>
</tr>
<tr>
<td>B</td>
<td>7.0</td>
<td>1.2</td>
</tr>
<tr>
<td>B</td>
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<td>1.2</td>
</tr>
<tr>
<td>Average</td>
<td>7.0</td>
<td>1.2</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Particle Size (μm)</th>
<th>Uniformity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.3</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>7.3</td>
<td>1.1</td>
</tr>
<tr>
<td>C</td>
<td>7.3</td>
<td>1.1</td>
</tr>
<tr>
<td>Average</td>
<td>7.3</td>
<td>1.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Particle Size (μm)</th>
<th>Uniformity</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>4.4</td>
<td>1.1</td>
</tr>
<tr>
<td>D</td>
<td>4.4</td>
<td>1.1</td>
</tr>
<tr>
<td>D</td>
<td>4.4</td>
<td>1.1</td>
</tr>
<tr>
<td>Average</td>
<td>4.4</td>
<td>1.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Particle Size (μm)</th>
<th>Uniformity</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>4.2</td>
<td>0.5</td>
</tr>
<tr>
<td>E</td>
<td>4.2</td>
<td>0.5</td>
</tr>
<tr>
<td>E</td>
<td>4.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Average</td>
<td>4.2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

5.1.2 Pore Size Distributions of Synthetic Zeolites

The underlying theory of the mercury porosimetry analysis is based on a cylindrical pore model (Webb and Orr, 1997). Therefore, the results from the analyses are approximations to the actual volumes of pores available in the zeolite samples.
Figure 5.2 shows the pore size distribution curves of the zeolite samples in terms of cumulative mercury intrusions. Other graphical results obtained from the pore size analysis are shown in Appendix C.

![Figure 5.2. Cumulative mercury intrusion (mL/g) versus log pore diameter (μm)](image)

The results from the pore size analyses of the zeolite samples are also summarized in Table 5.2. Median pore diameter (by volume) is defined as the diameter that corresponds to 50% of the total intrusion volume on the cumulative mercury intrusion volume versus log pore diameter plot.

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>Total Intrusion Volume (mL/g)</th>
<th>Total Pore Area (m^2/g)</th>
<th>Median Pore Diameter (by Volume) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.52</td>
<td>158.9</td>
<td>0.8</td>
</tr>
<tr>
<td>B</td>
<td>2.00</td>
<td>10.5</td>
<td>1.1</td>
</tr>
<tr>
<td>C</td>
<td>1.93</td>
<td>41.5</td>
<td>0.7</td>
</tr>
<tr>
<td>D</td>
<td>1.63</td>
<td>19.9</td>
<td>1.2</td>
</tr>
<tr>
<td>E</td>
<td>1.78</td>
<td>37.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

All of the pore size distribution curves of the zeolite samples have a similar trend. Approximately 25% of the pores present in all of the zeolite samples were 10 μm or greater. Most of the pores, however, concentrated in the size range between 0.2 and 5
Zeolite A was found to be the most porous sample mainly because of the presence of some very small pores (< 0.03 μm) in the sample.

Interestingly, the pore size diameters of chabazite, heulandite, mordenite, clinoptilolite, ferrierite and faujasite were found to be approximately 4.3 Å, 4.4-7.2 Å, 6.7-7.0 Å, 4.4-7.2 Å, 4.2-5.5 Å, and 7.4 Å, respectively (Breck, 1974; Gates, 1991; Wagner and Davis, 2000). The results from the pore size analyses showed that the synthetic zeolite samples contained pores that were much larger than the pores present in those natural zeolites.

Unfortunately, the sizes of the tailoring cations, except for C15 and C17, used in the study were not available for comparison with the pore sizes of the zeolite samples. A single DDTMA (C_{15}H_{34}NBr) molecule has an average head group diameter of approximately 0.7 nm, a chain diameter of about 0.4 nm, and a chain length of approximately 3.1 nm (Israelachvili, 1991; Walz, 2001). A single TDTMA (C_{17}H_{38}NBr) molecule has an average head group diameter of approximately 0.7 nm, a chain diameter of about 0.4 nm, and a chain length of approximately 3.3 nm (Israelachvili, 1991; Walz, 2001). In addition, an elementary monoclinic primitive cell lattice of four dehydroabietic acid (DHA) molecules was determined to have a dimension of (a = 11.67 Å, b = 11.87 Å, c = 13.52 Å) (Lazarev, 1971).

5.1.3 Scanning Electron Microscopy (SEM) Analysis of Zeolites

The two-dimensional SEM photographs of the zeolite samples are shown in Figures 5.3-5.15. All of the zeolite samples were made up of particles that did not have definite shapes and fixed sizes. Haggerty and Bowman (1994) also found that their mineral samples, which were clinoptilolite-dominated natural zeolites, consisted of aggregates with no defined crystalline structure.

The SEM photograph of zeolite A is shown in Figure 5.3 at 800X-magnification level. By zooming in further to 2000X-magnification level on one of the particles (Figure 5.4), the rough surface of the particle can be observed. The SEM instrument was auto-calibrated at this magnification level to determine the specific size of this particle,
which was found to have a dimension of approximately 32 μm by 32 μm. As can be seen from the photograph, this particular particle had a spherical shape.

Figure 5.3. SEM photograph of zeolite A particles captured at 800X-magnification level

Figure 5.4. A zeolite A particle viewed by SEM at 2000X-magnification level
Figure 5.5. SEM photograph showing the surface porosity of a zeolite A particle taken at 15000X-magnification level

Figure 5.6. SEM photograph of a zeolite B particle depicting its surface and porosity captured at 4000X-magnification level
Figure 5.7. A specific surface pore of a zeolite B particle viewed at 20000X-magnification level

Figure 5.8. SEM photograph of a zeolite C particle captured at 1500X-magnification level
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Figure 5.9. A zeolite C particle as seen by SEM at 15000X-magnification level

Figure 5.10. Surface pores of a zeolite C particle viewed at 40000X-magnification level
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Figure 5.11. SEM photograph of a zeolite D particle captured at 4000X-magnification level

Figure 5.12. A zeolite D particle viewed by SEM at 10000X-magnification level
Figure 5.13. A specific surface pore of a zeolite D particle captured at 40000X-magnification level

Figure 5.14. SEM photograph of a zeolite E particle captured at 8000X-magnification level
5.1.4 Energy Dispersive X-Ray (EDX) Diffusion of Zeolites

The elemental compositions of the zeolite samples were determined using EDX analyses. The zeolite structures were predominantly composed of oxygen atoms, followed by silicon and aluminum atoms (Table 5.3). This was as expected since zeolites are made up of lattice crystals that are comprised of silica-alumina frameworks, which incorporate oxygen as the sole "bridging" atoms for the aluminosilicate building blocks (Breck, 1974; Gates, 1991; Marcus and Cormier, 1999). The appearance of potassium and calcium in the structure of zeolite B were most likely caused by the presence of impurities during the analysis, as indicated in Table 5.3.

Table 5.3. Elemental compositions of zeolite samples

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>53</td>
<td>3</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>49</td>
<td>11</td>
<td>32</td>
<td>8</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>C</td>
<td>53</td>
<td>0.5</td>
<td>46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>51</td>
<td>5</td>
<td>40</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>53</td>
<td>2</td>
<td>45</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The silica (Si) to alumina (Al) mole ratio of each zeolite is presented in Table 5.4, where zeolites B and C were found to have the smallest and largest Si/Al ratio, respectively. The Si/Al ratio of a zeolite framework has been found to be a critical factor that regulates the zeolite ion-exchange sites and therefore its cation exchange capacity (Martinez et al., 1998; Godelitsas, 1998). Martinez et al. (1998) also stated that a zeolite with a lower Si/Al ratio would have higher loading capacity.

These findings were in good agreement with those characteristics supplied by Zeolyst International (Table 4.1). However, the concentrations of ammonium and hydrogen in zeolites A and E, and C, respectively, were not determined because of the sensitivity limits of the instrument's detector.

**Table 5.4. Si to Al ratios of zeolite samples from EDX analysis**

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al Mole Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>14.2</td>
</tr>
<tr>
<td>B</td>
<td>2.9</td>
</tr>
<tr>
<td>C</td>
<td>85.6</td>
</tr>
<tr>
<td>D</td>
<td>7.6</td>
</tr>
<tr>
<td>E</td>
<td>21.0</td>
</tr>
</tbody>
</table>

**5.1.5.1 CEC, ECEC, and ICEC of Synthetic Zeolites**

For reasons described in section 5.2, the CEC, ECEC, and ICEC determinations were not carried out with zeolite E. The CEC values of the zeolite samples ranged from approximately 80 to 240 meq/100g (Table 5.5). The results from the analyses also show that the zeolite samples had ECEC and ICEC values that ranged from 20 to 160 meq/100g and 11 to 33 meq/100g, respectively.

**Table 5.5. CEC, ECEC, and ICEC values of zeolite samples**

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>CEC (meq/100g)</th>
<th>ECEC (meq/100g)</th>
<th>ICEC (meq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>126 ± 10</td>
<td>72.3 ± 0.9</td>
<td>33.2 ± 2.6</td>
</tr>
<tr>
<td>B</td>
<td>241 ± 12</td>
<td>158.8 ± 0.6</td>
<td>11.6 ± 0.6</td>
</tr>
<tr>
<td>C</td>
<td>81 ± 8</td>
<td>20.2 ± 6.8</td>
<td>21.0 ± 3.8</td>
</tr>
<tr>
<td>D</td>
<td>156 ± 5</td>
<td>138.1 ± 20.2</td>
<td>11.9 ± 0.6</td>
</tr>
</tbody>
</table>
The results show that there was indeed an inverse relationship between the CEC values of the zeolite samples and their corresponding Si/Al ratios. Zeolite B, which had the lowest Si/Al ratio, had the highest CEC value. These results lend support to the contention that a zeolite with a lower Si/Al ratio would have higher loading capacity (Martinez et al., 1998).

The natural minerals (bentonite, clinoptilolite, heulandite, and chabazite) that Bouffard (1998) used in her work had CEC values that ranged from 9 to 268 meq/100g. The CEC and ECEC values of the clinoptilolite-dominated natural zeolite that Haggerty and Bowman (1994) employed were 50 and 15 meq/100g, respectively. Ming and Dixon (1987), on the other hand, found that clinoptilolite zeolite had CEC and ECEC values of 175 and 10 meq/100g, respectively. Other typical CEC (meq/100g) values are 1, 5, 10, and 100 for mica, illite, kaolinite, and montmorillonite (Caine et al., 1998).

The direct determinations of ECEC and ICEC values of the zeolite samples provided estimates of the numbers of exterior and interior exchange sites potentially available to organic surfactants for the tailoring process. The ECEC and ICEC values ranged from approximately 25% to 90% and 5% to 26%, respectively, of the total CEC values (Table 5.6). In her work, Bouffard (1998) showed that the ECEC values of heulandite and chabazite were 2% and 5%, respectively, of the total CEC of each mineral.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>ECEC (% CEC)</th>
<th>ICEC (% CEC)</th>
<th>Total (%CEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>57.3%</td>
<td>26.3%</td>
<td>83.6%</td>
</tr>
<tr>
<td>B</td>
<td>66.0%</td>
<td>4.8%</td>
<td>70.8%</td>
</tr>
<tr>
<td>C</td>
<td>24.8%</td>
<td>25.9%</td>
<td>50.7%</td>
</tr>
<tr>
<td>D</td>
<td>88.7%</td>
<td>7.6%</td>
<td>96.3%</td>
</tr>
</tbody>
</table>

Theoretically, the sum of the ECEC and ICEC values must equal the CEC value of the zeolite. In this study, the sum of the ECEC and ICEC fractions of each zeolite sample did not equal the CEC (Tables 5.5 and 5.6). Similar deviation has been previously observed by Ming and Dixon (1987), who showed that the experimental CEC value (175
meq/100g) of their clinoptilolite zeolite was lower than its theoretical CEC value (200-220 meq/100g) (Ming and Mumpton, 1987).

The difference between the experimental and theoretical CEC values can be attributed to a number of possible errors during the CEC determination process. Bouffard (1998) mentioned some factors, such as the pH and ionic strength of the extracting solution, and the reaction time, that could possibly affect the process of extracting cations from minerals. Rhoades (1982) further added that there was a possibility that the replacing power of the saturating cation was insufficient to replace the more strongly adsorbed cations, thus resulting in an underestimate of the CEC value. Moreover, there was a potential that the adsorbed cation was removed by hydrolysis and replaced by the H⁺ ion in the washing step. Rhoades (1982) also stated that cation exchangers, especially fine particles, could be lost during decantation because of their tendency to disperse as the excess electrolyte was removed during washing, hence causing the CEC value to be underestimated as well. Furthermore, Bower (1950) found that an underestimate of CEC could occur if the saturating cation was entrapped between the contracting interlayers and thus its replacement during extraction was being prevented.

5.1.5.2 Determination of Tailoring Cation Penetration into Pores of Synthetic Zeolites

To determine whether or not the tailoring cations penetrate into the pores of the zeolite samples, an experiment was conducted on the basis of comparing the ECEC and ICEC values of one of the zeolite samples using C4 and C32 cations. Zeolite A was selected for the experiment, since it was the most porous sample. Similar ECEC values, but different ICEC values, were obtained from the experiment (Table 5.7).

Table 5.7. ECEC and ICEC values of zeolite A

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>ECEC (meq/100g)</th>
<th>ICEC (meq/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A C4</td>
<td>74.2 ± 5.1</td>
<td>15.1 ± 1.1</td>
</tr>
<tr>
<td>A C32</td>
<td>70.4 ± 2.3</td>
<td>6.8 ± 0.3</td>
</tr>
<tr>
<td>A C17</td>
<td>72.3 ± 0.9</td>
<td>33.2 ± 2.6</td>
</tr>
</tbody>
</table>
The results, however, did not provide any concrete evidence that the tailoring cation penetrated into the pores of the zeolite sample. The results were inconclusive because of the limitations in the methodology used to determine the ECEC and ICEC values of the zeolite sample. The procedure assumes that the organic cation used in the determination does not have access to the zeolite internal pores and/or channels. The method also assumes that the internal pores of the zeolite are still accessible to Na\(^+\) ions after the external exchange sites of the zeolite have been completely occupied by the organic cations.

5.2 Uptake of DHA Using Untailored and Organically-Tailored Synthetic Zeolites

DHA removal efficiency from the synthetic process water (SPW) using untailored synthetic zeolite samples ranged from 19 to 45% (Figure 5.16). The maximum and minimum DHA removals were achieved when zeolites A and D were used, respectively. Using commercially available natural zeolite minerals (clinoptilolite, heulandite, and chabazite) under similar test conditions, Bouffard (1998) was able to achieve maximum DHA removals of 25%, 8%, and 15%, respectively. These results lend support to the contention that synthetic zeolites have larger and more uniform pores or channels than naturally occurring minerals (Breck, 1974; Knaebel, 1995; Marcus and Cormier, 1999), thereby providing more adsorption sites.
The low affinity of natural zeolites for DHA may have been attributed to a number of potential factors. First, at the pH tested, DHA was predominantly in its deprotonated, negatively-charged form (McLeay et al., 1979; Nyren and Back 1958). The low attraction of negatively charged natural zeolites for negatively charged solutes has been previously reported (Jaynes and Boyd, 1991a).

Second, the hydrophilic nature of the synthetic zeolite samples could have resulted in the presence of presorbed water molecules (Boyd and Sheng, 1998). The water molecules could have then hindered the access of the DHA molecules to the internal pores of the zeolites. Peterson (1980) reported that sorption of nonpolar substances was strongly influenced by the presence of sorbed water. Moreover, Gao et al. (1991) found that the adsorption of organic compounds in micropores was affected by the hydration of the nominal exchangeable cations that were naturally present in the zeolites. Limited adsorption of solute due to hydrations of free mineral surfaces has been previously observed (Lee et al., 1989; Kukkadapu and Boyd, 1995).
Next, the same five synthetic zeolite samples were tailored with C17 cationic surfactant, which was in the form of tetradecyltrimethylammonium (TDTMA) bromide (C_{17}H_{38}NBr), prior to contact with the SPW. With the exception of zeolite E, an improvement in DHA removal efficiency was observed with tailored zeolites as compared to using untailored zeolites (Figure 5.17).

![Bar chart showing DHA removal efficiencies using TDTMA-tailored synthetic zeolites at 20 g/L mineral dose.](image)

**Figure 5.17.** DHA removal efficiencies using TDTMA-tailored synthetic zeolites at 20 g/L mineral dose

The comparatively low DHA removal observed with zeolite E may have been due to decomposition of the mineral during pretreatment. During pretreatment, mineral E turned black and emitted noxious fumes. Similar decomposition upon exchange with barium ions (Ba^{2+}) has been previously observed (Kim *et al.* 1980).

Nonetheless, the other tailored zeolites showed promise for the removal of DHA. The increase in the DHA uptake capacities of the zeolites can be attributed to the formation of an organic hydrophobic layer on the zeolite surface (Boyd *et al.* 1988a; Boyd and Sheng, 1998). At the pH tested, resin acids were found to be hydrophobic, as measured by the octanol-water partition coefficient (Werker and Hall, 1997). When the tailored zeolites were introduced into the SPW, the surfactant amine chains (C17 organic tails) would become activated, that is, extend into the water due to their hydrophobic
nature (Alther, 2000). Vertical orientation of hexadecyl chains relative to the aluminosilicate surface due to solvation, and high charge density and CEC has been reported (Boyd and Sheng, 1998). The two cyclohexanes and one benzene ring of the DHA molecules may interact through hydrophobic bonding with the hydrocarbon chains of the TDTMA layer (Bouffard, 1998). Furthermore, the ion-dipole interaction to water molecules could have bound the deprotonated carboxylic group that was most likely be oriented outwards. These two types of interactions have been shown to promote the adsorption of an amphipathic compound on organoclays (Brixie and Boyd, 1994). In addition, the access of water molecules to the free aluminosilicate framework could have been obstructed by the presence of the hydrophobic organic film, making additional adsorption sites in the zeolite internal pore structures available for the uptake of the DHA molecules.

From this point on, all subsequent experimental work was carried out with organically-tailored zeolites because of their superior performance in removing DHA.

5.3 Batch Treatment Test of Synthetic Process Water (SPW)

5.3.1 Effects of Using Different Tailoring Cations on DHA Removal Efficiency

![Figure 5.18. Effects of using different tailoring cations on DHA uptake efficiencies](image-url)
Complete DHA removals were achieved with all of the zeolite samples that had been tailored with the C15 and C17 organic cations (Figure 5.18). The lower DHA uptake capacities of the zeolites tailored with longer chain organic cations can be attributed to several factors that may have affected the tailoring process of the zeolite samples.

First, alcohol molecules, specifically methanol and ethanol, which were used to dissolve the organic surfactants (C20, C28, C32, and C40) in the tailoring process, may have occupied the exchange sites of the zeolites during contact. Hydrophilicity of zeolites has been reported to increase in the presence of alcohol molecules (Wagner and Davis, 2000). As a result, the zeolite samples may not have been completely tailored.

Second, the shape and dimension of the tailoring cations may have affected the tailoring process (Barrer, 1978; Colella, 1998). Some of the organic surfactants used for tailoring the zeolite samples were found to have branched-chains (Figure 5.19) (Walz, 2001; Sigma-Aldrich, 2001). The dependency of the adsorption of tailoring cations onto zeolites on the structure of the tailoring surfactants has been previously reported (Barrer et al., 1967).

Third, the adsorbed tailoring cations may have hindered additional organic cations from accessing the pores of the zeolite samples during the tailoring process (Gao et al., 1991).

Fourth, although the tailoring process was performed for 24 hours and even if the organic cations were able to penetrate into the zeolite pores, the diffusion of the tailoring surfactants may have occurred at very slow rates (Sullivan et al., 1998a; Sayari, 1998).
In addition, the difference in the adsorption of DHA molecules may have also been caused by the difference in thickness of the hydrophobic organic layers formed on the surface of the tailored zeolites. The branch tailoring cations have shorter (5-10 carbons) chains than those of C15 and C17 cations (12 and 14 carbons, respectively).

Based on these results, and to reduce the number of experimental run in batch trials, zeolite D tailored with TDTMA (C17 cation) was used in subsequent work. Zeolite D was a prime candidate because of its size, shape, porosity, low Si/Al ratio, and high CEC.
and ECEC values. Meanwhile, TDTMA was selected because of its water solubility, straight hydrocarbon chain, and superior performance in the screening trial.

5.3.2 Determination of Minimum Mineral Dose for Uptake of DHA

Bouffard (1998) and Bouffard and Duff (2000) found that mineral concentration strongly affected (41% variability) the partitioning of the DHA molecules into the hydrophobic HDTMA layer.

To determine the minimum practical mineral dose, trials were carried out over a range from 1 to 15 g/L (Figure 5.20). Mineral doses as low as 5 g/L removed 90% of the DHA, and complete DHA removal was observed at doses of 10 g/L and higher.

Figure 5.20. Effects of various mineral loadings on DHA removal efficiencies

The result shows promise for the use of tailored minerals as a polishing technology to treat white water. Such a low mineral concentration would enable the zeolite to be recycled as filler along with fibers in the white water recycle system (Tsitsishvili, 1985; Tsitsishvili et al., 1992).

5.3.3 Effects of Treatment Time on DHA Adsorption

For contact time evaluations, a mineral loading of 1 g/L was employed to treat the synthetic process water. The treatment efficiency reached its maximum after being
contacted for 3 minutes, at which the removal efficiency started to level off at about 30% (Figure 5.21). Based on the results, the treatment can be performed using a small size reactor, since the uptake of DHA molecules occurred within minutes of contact. Not only would the reactor be cheaper, a smaller reactor also requires less space.

![Graph showing DHA removal efficiencies as a function of treatment time at 1 g/L mineral dose.](image)

**Figure 5.21. DHA removal efficiencies as a function of treatment time at 1 g/L mineral dose**

In comparison to the mineral loading study, further increases in the DHA removal effectiveness were not observed when the contact time was extended to 24 hours (Figures 5.20 and 5.21).

In their work, Bouffard (1998) and Bouffard and Duff (2000) found that the time of treatment did not strongly affect the DHA removal efficiency. It is worth pointing out, nevertheless, that they only examined contact times of 1, 10, and 24 hours.
5.3.4 Effects of pH and Buffers on DHA Uptake Capacity

The uptake of DHA at high pH (10 and 12) is independent of pH (Figure 5.22). This could be attributed to the high solubility and low hydrophobicity of DHA at high pH (Werker and Hall, 1999). Hydrophobic interaction between the tailored zeolites and the DHA molecules at high pH would be insignificant. Boyd et al. (1988b) showed that hydrophobic interactions for the sorption of pentachlorophenol by organoclays were more important than coulombic interactions. Consequently, complete dissolution or partitioning of the DHA molecules in the hydrophobic film of TDTMA organic chains could not be achieved.

On the other hand, at low pH, higher DHA removals were observed due to reasons opposite of the high pH trial. The DHA molecules would likely have free access to the hydrophobic TDTMA organic layer on the mineral surface and be partitioned through hydrophobic interaction.
At pH 6, however, the uptake of DHA was surprisingly low. The cause of such low removal in the current study was not known. However, at pH values below 7.25, the confounding influence of initial DHA concentration likely exerted a strong effect. The TDTMA formation of hydrophobic organic layer on the zeolite surface could not have been affected by the pH, since it has been shown by Zhang et al. (1993) and Haggerty and Bowman (1994) that the stability of large quaternary ammonium cations (QUAT) sorbed through ion exchange was not affected by extreme pH, ionic strength, and solvent conditions.

In summary, it was found that the lower the pH, the higher the treatment efficiencies. Also, DHA removal was not affected by the nature of the buffering system used.

5.4 Batch Treatment Test of White Water (WW)

The results discussed thus far were obtained from work carried out with synthetic process water (SPW) that contained only DHA and no other dissolved and colloidal substances (DCS). Although these results have shown promise for the uptake of DHA, the experiments were performed in the absence of confounding variables that would otherwise be present in a white water (WW) system. Consequently, there was still a need to determine the effectiveness of using organically-tailored minerals to treat WW, if this proposed polishing treatment technology were to be implemented in a mill as a solution to the problems encountered in closure. Two samples of pulp mill WW, Millar and Quesnel, were tested for the determination.

5.4.1 Characteristics of White Water (WW) Samples

The characteristics of the white water (WW) samples are shown in Tables 5.8 and 5.9. The high quantity of solids in each WW sample was not surprising. Wearing et al. (1985a) and Francis et al. (1998) have reported that closing the white water systems could increase the concentrations of the solids to as high as 8 g/L.
Table 5.8. Characteristics of white water (WW) samples

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Millar</th>
<th>Quesnel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Cloudy/Milky</td>
<td>Brownish and Clear</td>
</tr>
<tr>
<td>Initial pH</td>
<td>5.4</td>
<td>8.5</td>
</tr>
<tr>
<td>TS (g/L)</td>
<td>10.4 ± 0.1</td>
<td>4.8 ± 0.1</td>
</tr>
<tr>
<td>TVS (g/L)</td>
<td>7.0 ± 0.1</td>
<td>2.3 ± 0.02</td>
</tr>
<tr>
<td>TFS (g/L)</td>
<td>3.4 ± 0.03</td>
<td>2.5 ± 0.02</td>
</tr>
<tr>
<td>TSS (g/L)</td>
<td>2.5 ± 0.2</td>
<td>0.1 ± 0.01</td>
</tr>
<tr>
<td>TVSS (g/L)</td>
<td>2.4 ± 0.1</td>
<td>0.1 ± 0.002</td>
</tr>
<tr>
<td>TFSS (g/L)</td>
<td>0.1 ± 0.02</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>TDS (g/L)</td>
<td>7.9 ± 0.3</td>
<td>4.2 ± 1.0</td>
</tr>
<tr>
<td>TVDS (g/L)</td>
<td>4.7 ± 0.2</td>
<td>1.6 ± 1.2</td>
</tr>
<tr>
<td>TDFS (g/L)</td>
<td>3.2 ± 0.04</td>
<td>2.7 ± 0.3</td>
</tr>
</tbody>
</table>

TS = Total Solids  
TVS = Total Volatile Solids  
TFS = Total Fixed Solids  
TSS = Total Suspended Solids  
TVSS = Total Volatile Suspended Solids  
TFSS = Total Fixed Suspended Solids  
TDS = Total Dissolved Solids  
TVDS = Total Volatile Dissolved Solids  
TDFS = Total Dissolved Fixed Solids

Table 5.9. BOD, COD, BOD to COD ratios, and DHA concentrations of white water (WW) samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BOD (mg/L)</th>
<th>COD (mg O₂/L)</th>
<th>BOD/COD Ratio</th>
<th>[DHA] (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quesnel Uncentrifuged</td>
<td>1845 ± 100</td>
<td>3840 ± 8</td>
<td>48%</td>
<td>19.2</td>
</tr>
<tr>
<td>Millar Uncentrifuged</td>
<td>3245 ± 233</td>
<td>14135 ± 225</td>
<td>23%</td>
<td>56.0</td>
</tr>
<tr>
<td>Quesnel Centrifuged/Feed</td>
<td>1735 ± 28</td>
<td>3785 ± 17</td>
<td>46%</td>
<td>18.6</td>
</tr>
<tr>
<td>Millar Centrifuged/Feed</td>
<td>2705 ± 219</td>
<td>9745 ± 500</td>
<td>28%</td>
<td>45.6</td>
</tr>
</tbody>
</table>
The removals of BOD and COD by the centrifugation process were more pronounced in the Millar WW than in the Quesnel WW because of the larger amount of solids being removed from the former sample than from the latter. The BOD to COD ratios show that the Millar WW sample contained more non-biodegradable components than the Quesnel WW sample (Table 5.9).

5.4.2 Uptake of RFA from White Water (WW) Samples

At the mineral loadings used, not only did the organically-tailored zeolites remove DHA from the white water (WW) samples, they were also able to adsorb other resin and fatty acids (RFA) (Figures 5.23 and 5.24). The different RFA removal efficiencies were not likely dependent on the different molecular structures of the RFA. Hence, the differences in the DHA uptake capacities of the tailored zeolites may have been caused by competition from other RFA and DCS that were present in the WW samples for access to the TDTMA hydrophobic organic layer on the zeolite surfaces (Figure 5.25).

Nevertheless, complete RFA removals were achievable using organically-tailored zeolites at 20 g/L mineral dose. In previous work, Bouffard (1998) and Bouffard and Duff (1999) were only able to remove 35% and 28% of FA and RA, respectively, from a WW sample that had initial FA and RA concentrations of 25 and 84 mg/L, respectively, using higher (75 g/L) mineral doses.
Figure 5.23. Percent removal of RFA from Millar WW sample at 1 and 20 g/L mineral loadings (U = unidentified RFA)

Figure 5.24. Percent removal of RFA from Quesnel WW sample at 1 and 20 g/L mineral loadings (U = unidentified RFA)
Figure 5.25. Comparison of DHA removals from WW samples and SPW at 1 and 20 g/L mineral concentrations

The results show promise for the use of tailored minerals as a polishing technology to treat white water. The removal of dissolved and colloidal substances (DCS) from WW would have a positive implication for mill operations, since build up of DCS in the white water system can be minimized. Also, the physical and optical properties of pulp and/or paper would be much improved (Francis and Ouchi, 2001; Tay, 2001).

5.4.3 Removals of SBOD, SCOD, and Acute Toxicity

Removals of 9-36% of SBOD and 6-38% of SCOD from the WW samples were achieved (Table 5.10). The positive implications from these results are the possible reduction of several problems, such as microbial activity, odour, corrosion, foaming, and scaling in the white water recycle system (Blanco et al., 1997; Habets et al., 1996; Panchapakesan, 1992; Geller and Gottsching, 1982; Wenzl, 1981).

Using higher mineral dose of 75 g/L, Bouffard (1998) and Bouffard and Duff (1999) were only able to achieve 24% reduction of SCOD from a WW sample that had an initial SCOD concentration of 3046 mg O₂/L. This SCOD removal corresponded to a mass uptake of 10 mg O₂/g mineral.
In the current study, at 1 g/L mineral dose, the mass uptake of SCOD from the WW samples ranged from approximately 252 to 971 mg O₂/g mineral. The results simply implied that synthetic zeolites have higher mass uptake of SCOD than natural minerals.

Table 5.10. Removals of SBOD and SCOD from white water (WW) samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>SBOD (mg/L)</th>
<th>SBOD Removal Efficiency</th>
<th>SCOD (mg O₂/L)</th>
<th>SCOD Removal Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated Quesnel (1 g/L)</td>
<td>1570 ± 101</td>
<td>9.7% ± 5.8%</td>
<td>3530 ± 225</td>
<td>6.7% ± 6.0%</td>
</tr>
<tr>
<td>Treated Millar (1 g/L)</td>
<td>2460 ± 138</td>
<td>9.1% ± 5.1%</td>
<td>8775 ± 206</td>
<td>10.0% ± 2.1%</td>
</tr>
<tr>
<td>Treated Quesnel (20 g/L)</td>
<td>1170 ± 46</td>
<td>32.6% ± 2.7%</td>
<td>2775 ± 76</td>
<td>26.6% ± 2.0%</td>
</tr>
<tr>
<td>Treated Millar (20 g/L)</td>
<td>1730 ± 11</td>
<td>36.0% ± 0.4%</td>
<td>6020 ± 95</td>
<td>38.2% ± 1.0%</td>
</tr>
</tbody>
</table>

The organically-tailored zeolite was also able to remove some of the acute toxicity from the WW samples (Tables 5.11 and 5.12). The uptake of RFA and other toxic contaminants, which were not determined in the study, by the tailored zeolite reduced the acute toxicity of the WW samples.

Table 5.11. EC50 (%v/v) acute toxicity values of the untreated and treated (at 1 and 20 g/L mineral loadings) WW samples

<table>
<thead>
<tr>
<th>Condition</th>
<th>Time (Min.)</th>
<th>Millar</th>
<th>95% CI</th>
<th>Quesnel</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>5</td>
<td>0.37</td>
<td>0.29</td>
<td>0.47</td>
<td>1.38</td>
</tr>
<tr>
<td>Untreated</td>
<td>15</td>
<td>0.54</td>
<td>0.44</td>
<td>0.70</td>
<td>1.86</td>
</tr>
<tr>
<td>Untreated</td>
<td>30</td>
<td>0.62</td>
<td>0.52</td>
<td>0.74</td>
<td>1.85</td>
</tr>
<tr>
<td>Treated - 1g/L</td>
<td>5</td>
<td>2.49</td>
<td>2.22</td>
<td>2.81</td>
<td>8.62</td>
</tr>
<tr>
<td>Treated - 1g/L</td>
<td>15</td>
<td>1.62</td>
<td>1.43</td>
<td>1.72</td>
<td>4.89</td>
</tr>
<tr>
<td>Treated - 1g/L</td>
<td>30</td>
<td>1.03</td>
<td>0.95</td>
<td>1.12</td>
<td>3.17</td>
</tr>
<tr>
<td>Treated - 20g/L</td>
<td>5</td>
<td>4.06</td>
<td>3.55</td>
<td>4.67</td>
<td>13.44</td>
</tr>
<tr>
<td>Treated - 20g/L</td>
<td>15</td>
<td>1.50</td>
<td>1.31</td>
<td>1.79</td>
<td>4.56</td>
</tr>
<tr>
<td>Treated - 20g/L</td>
<td>30</td>
<td>1.08</td>
<td>0.99</td>
<td>1.22</td>
<td>3.32</td>
</tr>
</tbody>
</table>
Much of the observed acute toxicity was likely due to RFA. Chung et al. (1979) showed that the acute lethal concentration of resin acids fall in the range of 0.4-1.1 mg/L. The Millar WW was more toxic than the Quesnel WW because the former sample contained more RFA, whose concentration has been shown to correlate with the acute lethal toxicity of pulping effluents (Chung et al., 1979; Kovacs and Voss, 1992). The acute toxicity removal efficiencies decreased with increasing exposure time (Table 5.12) due to the increasing trend in the EC50 values with longer exposure time (Table 5.11). The increase in the EC50 values may have been attributed to interactions between the toxic compounds contained in the WW samples that would likely have interfered with the analysis (Eickhoff, 2001).

### 5.4.4 Uptake of Sterols

Organically-tailored zeolite was also able to remove sterols from the WW samples (Table 5.13). The analysis revealed that the Quesnel WW sample did not contain campesterol, β-sitosterol, and β-sitostanol. Complete sterols uptake from the Millar WW sample was achievable with mineral dose of 20 g/L (Table 5.13). The differences in the sterol removal efficiencies of the tailored zeolites may be attributed to the different molecular structures of the sterols (Figure 5.26).

The ability of tailored zeolite to remove sterols may reduce the endocrine disrupting potential of the mill effluent. Endocrine disrupting chemicals (EDC) from pulp and paper mill effluent have been shown to affect the sexual maturity of rainbow trout, from pulp and paper mill effluent (Tremblay and Van der Kraak, 1999).
Table 5.13. Removals of sterols from Millar WW sample

<table>
<thead>
<tr>
<th>Compound</th>
<th>RT (Min.)</th>
<th>1 g/L</th>
<th>20 g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Campesterol</td>
<td>19.61</td>
<td>20% ± 7%</td>
<td>100%</td>
</tr>
<tr>
<td>β-Sitosterol</td>
<td>20.95</td>
<td>12% ± 4%</td>
<td>87% ± 9%</td>
</tr>
<tr>
<td>β-Sitostanol</td>
<td>21.17</td>
<td>24% ± 5%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Figure 5.26. Molecular structures of campesterol, β-sitosterol, and β-sitostanol
CHAPTER 6:
CONCLUSIONS

This study examined the technical feasibility of using organically-tailored synthetic zeolites for the treatment of white water in mechanical pulp and paper mills. Synthetic zeolites were found to have large pores and high cation exchange capacities (CEC) and external CEC (ECEC) values. The effectiveness of untailored synthetic zeolites was compared to that of organically-modified zeolites for uptake of dehydroabietic acid (DHA). Different tailoring cations were used to modify the synthetic zeolites at 100% of the mineral CEC.

6.1 Uptake of DHA

Several conclusions can be made from the batch treatment tests of synthetic process water (SPW) for the uptake of DHA. They are:

1. Synthetic zeolites have shown larger DHA uptake capacities (19-45% DHA removals) than natural minerals (8-25% DHA removals) (Bouffard, 1998), under similar test conditions.

2. Complete DHA removal was achieved using organically-tailored synthetic zeolites, while untailored synthetic zeolites were only able to remove 19-45% of the DHA from SPW.

3. Removal of DHA was affected by the types of organic cations used for tailoring the synthetic zeolites. Complete DHA removals were achieved when water-soluble organic cations (C15 and C17) were used to tailor the zeolites. However, lower DHA uptake capacities (9-71% removal efficiencies) were observed when alcohol-(methanol and ethanol) soluble organic surfactants (C20-C40) were used for tailoring the zeolite. The shape and dimension of the tailoring cations may have played a significant role in the tailoring process of the zeolites, which in turn affected the removal of DHA.
4. Mineral doses of TDTMA-tailored synthetic zeolite as low as 5 g/L removed 90% of the DHA from SPW, and complete DHA removal was observed at doses of 10 g/L and higher.

5. Uptake of DHA from SPW by TDTMA-tailored synthetic zeolite occurred within minutes of contact. Maximum removal efficiency was achieved after 3 minutes of contact.

6. Higher DHA removal efficiencies were observed at pH equal to the pKa value of DHA (7.25). Also, DHA removal was not affected by the nature of the buffering system used (unbuffered, acetate, and phosphate).

6.2 Technical Feasibility of White Water Treatment

The conclusions that can be made from the batch treatment tests of white water samples are:

1. At 1 g/L mineral dose, removals of RFA using organically-tailored synthetic zeolites ranged from 0.5% to 51% and from 1% to 28% for Millar and Quesnel white water samples, respectively. In addition, at higher (20 g/L) mineral dose, removals of RFA ranged from 40% to 100% and from 35% to 100% for Millar and Quesnel white water samples, respectively.

2. Removals of soluble BOD (SBOD) were 9-10% and 32-36% at 1 and 20 g/L mineral concentrations, respectively.

3. Removal of 6-10% and 26-38% of soluble COD (SCOD) were achieved at 1 and 20 g/L mineral concentrations, respectively.

4. At 1 g/L mineral loading, acute toxicity removals ranged from 39% to 85% and from 42% to 84% for Millar and Quesnel white water samples, respectively. Removals of acute toxicity also ranged from 43% to 91% and from 44% to 90% for Millar and Quesnel white water samples, respectively, at higher (20 g/L) mineral loading.
5. Not only were organically-tailored zeolites able to remove RFA, BOD, and COD and reduce the acute toxicity, they were also able to uptake sterols from the white water samples. Complete sterols uptake was achievable at a mineral dose of 20 g/L. At lower mineral loading of 1 g/L, sterol uptake ranged from 12% to 24%.
CHAPTER 7:
FUTURE WORK

The following recommendations are suggested for future work:

1. A determination of whether or not organic cations are able to penetrate the internal pores of the zeolites is needed. Therefore, a study on the adsorption of the organic tailoring cations onto synthetic zeolites needs to be considered. The adsorption isotherms may be able to provide useful information on whether or not the organic cations are accessing the pores of the zeolites.

2. A study is needed to determine the effects of the presence of alcohol molecules on the tailoring process. Once the determination has been established, the use of higher molecular weight tailoring cations may be possible for tailoring of the synthetic zeolites.

3. Other methods of modifying and/or tailoring the zeolites need to be considered, since chemical and thermal treatments on zeolites have been shown to increase the hydrophobicity of the zeolites.

4. The technical possibility of applying organically-tailored zeolites as fillers in the wet end of the paper machine need to be studied. A pilot-scale experiment could be performed to determine the effect of such compounds on paper quality.

5. If minerals are found to have a negative impact on paper quality, removal and regeneration could be practiced. Many authors have discussed the possibility of regenerating the zeolites for reuse. Different techniques of regeneration therefore need to be studied in order to determine the potential of reusing the zeolites.

6. In the current study, batch tests were used for treatments of synthetic process water and white water samples. A continuous treatment trial needs to be considered, especially if regeneration of zeolites is possible.
7. The possibility of using organically-tailored zeolites in pulp and paper mills for treatment of other process water and/or wastewater needs to be determined.

8. Finally, several authors have used high-performance liquid chromatography (HPLC) to analyze resin and fatty acids. Analysis by HPLC has been shown to be much easier than by gas chromatography (GC), even though the HPLC analysis may be longer. Nevertheless, the procedure for preparing the samples for HPLC analysis is much simpler and does not require extractions of resin and fatty acids (RFA).
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The graphs presented in this appendix are the results of the centrifugation process (2250 x g, 20 minutes) of the white water (WW) samples (Millar and Quesnel).

**Figure A.1.** Percent reductions in RFA concentrations of Millar WW sample due to centrifugation (2250 x g, 20 minutes)

**Figure A.2.** Percent reductions in RFA concentrations of Quesnel WW sample due to centrifugation (2250 x g, 20 minutes)
APPENDIX B

The gas chromatography (GC) conditions presented in this appendix are those used for the sterols analysis of the white water (WW) samples (Millar and Quesnel) in the current study.

Model: Hewlett-Packard (HP) 6890 Series Gas Chromatograph/Mass Spectrometer (GC/MS), equipped with HP 5973 mass spectrometer detector.

Column:
- Type: J&W DB-5MS.
- Length: 29 m.
- Film thickness: 0.25 μm.
- Internal diameter: 0.25 mm.

Injection temperature: 290°C.

Oven temperature:
- 130°C – held for 1 minute,
- 130°C to 285°C – ramped at 15°C/min,
- 285°C – held for 3 minutes,
- 285°C to 310°C – ramped at 2°C/min,
- 310°C – held for 1 minute,
- 315°C – post run temperature, held for 3 minutes.

Detector temperature: 280°C.

Carrier gas: Helium at 11.2 psi and 53.6 mL/min.
APPENDIX C

The graphs presented in this appendix are supplementary graphical results obtained from the pore analysis of the synthetic zeolite samples.

Figure C.1. Incremental intrusion (mL/g) versus log pore diameter (µm)

Figure C.2. Log differential intrusion (mL/g) versus log pore diameter (µm)