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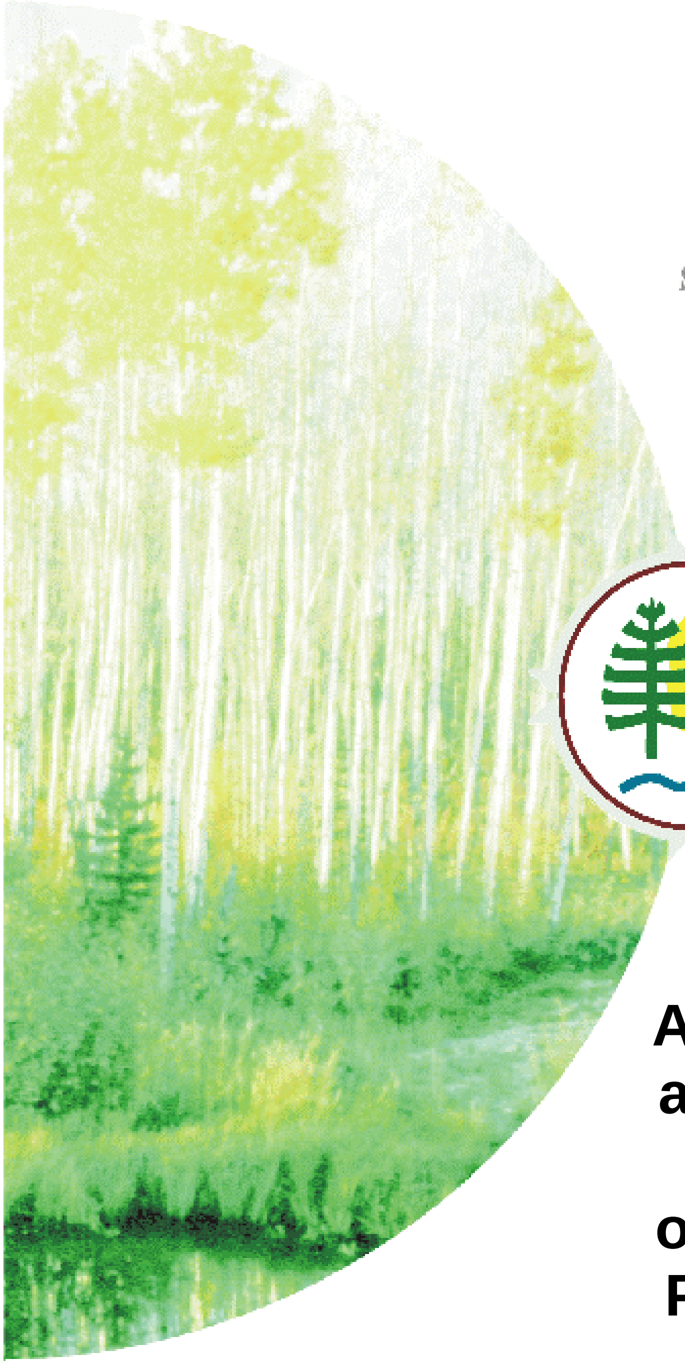

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Sustainable Forest Management Network
G208 Biological Sciences Building
University of Alberta
Edmonton, Alberta, T6G 2E9
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Application of Natural and Tailored Minerals to the Treatment of Thermomechanical Pulp Mill White Water

by

Sheldon J.B. Duff

Sylvie Bouffard

Chris Kurniawan

Department of Chemical and Biological Engineering
University of British Columbia, Vancouver, BC

June 2000

ABSTRACT

Buildup of dissolved and colloidal substances in closed white water systems is detrimental to machine runnability and product quality. This research investigated the technical feasibility of using natural and tailored minerals for treatment of synthetic process water (approximately 40 mg/L of dehydroabietic acid (DHA)) and three simulated thermomechanical paper mill white waters. Treatment of synthetic process water with 20 g/L of natural minerals, ground to less than 0.180 mm aggregate size, resulted in maximum DHA removal of 55%.

Tailored minerals were prepared by mixing zeolites with short-chain and long-chain organic cations. When applied in doses less than the external cation exchange capacity (CEC) of zeolites, cations were firmly bound through coulombic interactions on the external surfaces only. Only long-chain hexadecyltrimethylammonium (HDTMA) cations improved the uptake capacity of zeolites for DHA. Partitioning of DHA into the HDTMA layer was strongly dependent on the mineral concentration and CEC value. HDTMA-tailored minerals with CEC values above 90 meq/100 g ensured complete removal of DHA from synthetic process water.

Application of 75 g/L of HDTMA-tailored heulandite to the treatment of white water (pH 7) resulted in removal of FA and RA ranging from 10-90% and 5-70%, respectively over a range of mineral doses from 20-350 kg/m^3. Other constituents, measured as chemical oxygen demand, total dissolved solids and total dissolved volatile solids, were not removed because of the low surface area of heulandite covered with HDTMA cations. The HDTMA layer most likely selectively rejected high molecular weight substances.

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LIST OF ABBREVIATIONS AND ACRONYMS

AB	Alberta
ANAMET	Anaerobic-aerobic methane
ANOVA	Analysis of variance
AR	Arizona
BC	British Columbia
BCTMP	Bleached chemi-thermomechanical pulp
BET	Brunauer Emmett Teller
BOD	Biological oxygen demand
BUT	n-butylamine
C	Contrast
CA	California
CEC	Cation exchange capacity
CL	Control limit
COD	Chemical oxygen demand
COFI	Council of Forest Industries of British Columbia
CMC	Critical micelle concentration
CTMP	chemi-thermomechanical pulp
DCS	Dissolved and colloidal substances
DF	Degree of freedom
DHA	Dehydroabietic acid
DICOCO	Dicocodimethylammonium
DOC	Dissolved organic carbon
ECEC	External cation exchange capacity
FA	Fatty acids
GA	Georgia
GC	Gas chromatography
HDTMA	Hexadecyltrimethylammonium
HMW	High molecular weight
HPLC	High performance liquid chromatography
ICEC	Internal cation exchange capacity
IL	Illinois
LC	Lethal concentration
LCL	Lower control limit
LMW	Low molecular weight
LOI	Loss on ignition
MA	Massachusetts
MBR	Membrane biological reactor
MS	Mean squares
MTBE	Methyl-tert-butyl-ether
MVR	Mechanical vapour recompression

MW	Molecular weight
nd	None detected
NF	Nanofiltration
NSERC	Natural Sciences and Engineering Research Council of Canada
O-MPCA	O-methylpodocarpic acid
ON	Ontario
OR	Oregon
PAPRICAN	Pulp and Paper Research Institute of Canada
QUAT	Quaternary ammonium cations
R	Variability
RA	Resin acids
RFA	Resin and fatty acids
SBR	Sequencing batch reactor
SCOD	Soluble chemical oxygen demand
SK	Saskatchewan
SS	Suspended solids
SSQ	Sum of squares
TAPPI	Technical Association of the Pulp and Paper Industry, Inc.
TBA	Tetrabutylammonium
TDS	Total dissolved solids
TDVS	Total dissolved volatile solids
TEA	Tetraethylammonium
TMA	Tetramethylammonium
TMP	Thermomechanical pulp
TOC	Total organic carbon
TPA	Tetrapropylammonium
UASB	Upflow anaerobic sludge blanket
UBC	University of British Columbia
UCL	Upper control limit
UF	Ultrafiltration
USA	United States of America
UV	Ultraviolet
XRD	X-ray diffraction
Y	Removal efficiency of DHA

LIST OF UNITS

Å	Angstrom
adt, (t)	Air dried tonne, (tonne)
cm^3, (m^3)	Cubic centimeter, (cubic meter)
Da, (kDa)	Dalton, (kilodalton)
d	Day
eq, (meq)	Equivalent, (milliequivalent)
g, (μg), (mg), (kg)	Grams, (microgram), (milligram), (kilogram)
h	Hour
K	Kelvin
kV	Kilovolts
L, (μL), (mL)	Litre, (microlitre), (millilitre)
lb	Pound
m^2	Square meter
mM, (M)	Millimolar, (molar)
mA	Milliampere
min	Minute
mm, (nm), (μm)	Millimeter, (nanometer), (micrometer)
N	Normal
°C	Degrees Celcius
ppm	Parts per million
rpm	Revolution per minute
s	Second
v/v	Volume by volume
w/v	Weight by volume

INTRODUCTION

Progressive closure of water cycles in pulp and paper mills will lead to increasing levels of dissolved and colloidal extractives (fatty acids, resin acids, sterols, lignans) in process water streams such as white water. Extractives, among the most detrimental substances affecting machine runnability, paper quality and effluent toxicity (Welkener *et al.*, 1993), may be present in concentrations of the order of 100 mg/L in the more closed whitewater circuits (Francis and Ouchi, 1997). In the face of such extractive concentrations, existing white water treatment operations ("save-all" clarifiers and filters) may be unable to maintain acceptable levels of extractives, providing an impetus for the development of a dedicated treatment operation.

Natural minerals such as clays, bentonites and zeolites have found many applications as adsorbants. The capacity of such minerals for the removal of hydrophobic contaminants can be greatly improved by mineral tailoring; exchanging organic cations such as quaternary ammonium ions with naturally-occurring cations in the mineral lattice (Boyd *et al.*, 1991). Application of tailored zeolites in adsorption offers several advantages, including: abundant zeolite deposits, low cost of natural zeolites and organophilic cations, and versatility in the preparation of selective tailored zeolites for target contaminants (Boyd *et al.*, 1991; Knudson, 1993).

Tailored zeolites have shown promise for removal of aromatics (Gao *et al.*, 1991; Kruglitskaya *et al.*, 1985; Neel, 1992), phenols (Garcia *et al.*, 1993) and chlorinated organics (Rustamov *et al.*, 1992; Huddleston, 1990) from contaminated soils, hazardous waste landfills and waste waters. This NCE research project examined the potential for application of organically-tailored zeolites to the removal of dissolved extractives from pulp and paper process streams. To simplify the initial study, a solution of dehydroxyabietic acid (DHA) was used as a model process stream. DHA, one of the most common resin acids in softwood species, is comprised of one carboxylic function, two cyclohexane groups and one benzene ring which give the overall structure an amphiphathic character. The ionizable (pK_a 7.2) carboxyl group and the amphipathic character of DHA strongly influence aqueous solubility and can result in complex phase behaviors such as micelle formation (Spevack and Deslandes, 1996).

The study was divided into four parts. First, commercially available zeolites, bentonites and organo-clays were screened to determine their potential for DHA uptake. Second, the mechanism of adsorption of tetramethylammonium (TMA) and HDTMA cations onto two zeolites was examined. Third, the work examined the effect of a number of experimental parameters on the application of tailored zeolites to the removal of dissolved DHA. Finally, the performance of the minerals in a simulated, high strength whitewater was assessed.

RESEARCH OBJECTIVES

The overall objective of this study was to evaluate the suitability of tailored minerals for the removal of dissolved and colloidal substances from pulp and paper mill whitewater. Included in this general objective were a number of specific objectives:

1. Determine the effectiveness of a wide variety of natural (bentonites and zeolites) and tailored minerals for DHA removal from synthetic process water.
2. Investigate the adsorption mechanisms and the stability of tailoring cations sorbed to zeolites.
3. Determine the influence of several factors (Table 1) on the uptake capacity of tailored minerals by performing single-factor and factorial experiments.

Table 1: Factors investigated in single-factor and factorial experiments

Mineral	Tailoring cations	White water
Aggregate size	Chain length	Temperature
Cation exchange capacity	Dosage	pH
Concentration		Initial solute concentration
		Time of contact

4. Investigate the technical feasibility of using tailored minerals to treated concentrated, highly-recycled white water. Variables measured included RFA, COD, SCOD, TOC, DOC, TDS and total dissolved volatile solids (TDVS) from white water under pH conditions varying from 5 to 7.

MATERIALS AND EXPERIMENTAL METHODS

In this section, an abbreviated version of the materials and experimental methods used in this research is presented. For a more complete description of these methods, the reader is referred to the M.A.Sc. thesis of Sylvie Bouffard (Bouffard, 1998).

Model Process Water

In order to minimise the confounding influences of other constituents present in process waters, batch tests were carried out with a model process water (pH 7.25) containing only dissolved DHA (300.44 g/mole molecular weight). DHA (Helix Biotech, Richmond, BC) was dissolved in deionized water to yield a 1000 mg/L stock solution, adjusted to pH 12. The model process water was prepared by diluting an aliquot of stock solution in a volumetric flask containing preweighed mixtures of Na_2HPO_4 and NaH_2PO_4 to yield a 50 mM phosphate buffer at pH 7.25. The model process water was stored at 4°C and allowed to warm up to 25°C prior to the batch tests. If necessary, the pH was readjusted to 7.25 with 1 N NaOH or 50% w/v H_2SO_4.

Minerals

Mineral samples were provided by: (1) Teague Minerals Products (Adrian, OR), (2) GSA Resources Inc. (Cortaro, AR), (3) Polar Powders & Technologies Inc. (Calgary, AB), (4) Canmark International Resources Inc. (Vancouver, BC), (5) Western Industrial Clay Minerals Ltd. (Kamloops, BC) and (6) UBC Civil Engineering Department (Vancouver, BC). In total, twenty-one different mineral samples were used in this study. They consisted of six bentonites/diatomites (B-1 to B-6), eight clinoptilolites (Cl-1 to Cl-8), one heulandite (H-1), two chabazites (Ch-1, Ch-2) and four organo-clays (O-1 to O-4). The organo-clays were prepared by mineral suppliers by substituting quaternary ammonium cations for naturally-present cations in clays. Prior to batch tests, each mineral was ground with a mortar and pestle to less than 0.180 mm aggregate size, and stored in polyethylene containers.

Preparation of Tailored Minerals

Following tests conducted with natural minerals and commercially-available organoclays, a subset of the minerals was tailored to examine in detail the effects of mineral and tailoring cation properties on DHA removal. The zeolite minerals best satisfied most criteria, in that they were characterized by: (1) a wide diversity of clinoptilolite, heulandite and chabazite minerals, (2) a large range of CEC values, and (3) a high degree of structural integrity. From the minerals available, heulandite H-1 (CEC 44 meq/100 g), clinoptilolite Cl-6 (CEC 92 meq/100 g), clinoptilolite Cl-9 (CEC 9 meq/100 g), and chabazite Ch-1 (CEC 268 meq/100 g) were chosen for tailoring.

Prior to the introduction of organic cations, Na^+-saturated zeolites were prepared. Natural zeolites were ground and sieved to the desired aggregate size**.** Ten grams of each mineral were dispensed into a polyethylene bottle, and mixed on a magnetic stirring plate for 15 min at 80°C with 200 mL of 0.3 M tribasic sodium citrate, 1.0 M sodium bicarbonate and 0.2 g sodium hydrosulfite per g mineral to eliminate free-iron oxides (Jackson, 1958). After 10 min of settling, the supernatant was decanted and minerals were washed three times with 200 mL of 1 N NaCl for 4 h in an end-over-end rotator (18 rpm), followed by three 200 mL deionized water rinses (15 min). Na^+-saturated minerals were dried at 60°C overnight and stored in polyethylene containers.

Precisely-weighed samples of Na^+-saturated zeolites were tailored with aliquots of 50 mM HDTMA-bromide or 50 mM TMA-chloride to yield cation dosages in the range from 0 to 150% of zeolite total or external cation exchange capacity (CEC and ECEC, respectively). The CEC value of aggregates smaller than 0.180 mm was measured using the procedure of the Environmental Protection Agency (USEPA, 1986), while the ECEC value of same size aggregates was determined according to the method of Ming and Dixon (1987), later adapted by Haggerty and Bowman (1994). The suspensions of zeolites and tailoring cations were mixed for

24 h in an end-over-end rotator (18 rpm) at 25°C, and then centrifuged (2960 × g, 15 min). The supernatant was decanted and analysed for total organic carbon (TOC) using a Shimadzu TOC-500 analyser. The minerals were subjected to five successive 5 min washes with deionized water and centrifuged (2960 × g, 15 min). All supernatants were collected in a flask, diluted to a specific volume and analysed for TOC. Tailored minerals were dried at 60°C overnight and analysed for TOC using a Shimadzu TOC-5050 analyser equipped with a solid sampling module (SSM-5000). Assuming complete conversion of organic cations to CO_2 during solid TOC analysis, the TOC content of mineral samples was converted to (meq cation/100 g mineral) or (g cation/100 g mineral). Tailored minerals were stored in polyethylene containers.

Simulated White Water

White water system closure was simulated by successive washings of pulp with recycle filtrates. This approach was used previously because it mimics industrial DCS behaviour on a laboratory-scale (Wearing et al. 1985b; Ekman et al. 1990; Francis and Ouchi, 1997). In this research, four simulated white waters from three different sources (Millar, Quesnel and Paprican) were prepared by mixing and heating pulp and white water in order to increase the concentration of DCS in the whitewater.

Four simulated white waters (#1, #2, #3, #4) were prepared by mixing and heating pulp with water or white water to increase the concentration of dissolved and colloidal substances. The white waters used were not tested prior to mixing. The preparation of white water #1 consisted of diluting 1.5 kg alkaline peroxide bleached BCTMP pulp (19.5% consistency) to 2% consistency with 12 L of white water (both obtained from Millar Western Pulp Ltd. BCTMP mill, Whitecourt, AB). The pulp suspension was mixed and heated for 1 h at 60°C in a jacketed stainless steel tank then manually dewatered, and, after standing overnight to remove coarse suspended solids, filtered through a 1.3 mm mesh screen. After pH adjustment to 12, the filtrate was mixed at 90°C for 1 h, and immediately filtered through Whatman #41 grade filter paper (25 μm pore size). The filtrate was collected in a clean, fired, amber glass bottle containing preweighed mixture of Na_2HPO_4 and NaH_2PO_4 to yield a 50 mM phosphate buffer at pH 5, and then stored at 4°C. Prior to the batch tests, the pH was readjusted to the same value with 1 N NaOH or 50% w/v H_2SO_4. The same procedures were applied in the preparation of white water #2, with the exception that 0.4 kg of (55% lodgepole/35% white spruce/10% alpine fir) unbleached TMP pulp (19.9% consistency) from the secondary refiner was mixed with 3.3 L of clarified white water (both obtained from Quesnel River Pulp Company BCTMP/TMP mill, Quesnel, BC).

White water #3 was obtained from the Pulp and Paper Research Institute of Canada (Vancouver, BC). The preparation consisted of diluting 3.6 kg of 55% (spruce/pine/fir)/45% (hemlock/balsam fir) TMP pulp (47% consistency) obtained from Howe Sound Pulp and Paper Ltd. (Port Mellon, BC) to 2% with 180 L of fresh tap water. The pulp suspension was mixed for 30 min at 60°C then dewatered to approximately 40% consistency with a screw press (Francis and Ouchi 1997). A fraction of the filtrate was transferred to a clean plastic pail containing preweighed amounts of

Na_2HPO_4 and NaH_2PO_4 to yield a 50 mM phosphate buffer at pH 7, and then stored at 4°C. The remaining filtrate was used to prepare white water #4. After being subjected to the same steps (pH adjustment, heating, mixing, filtration) as white water #1, the pH of white water #4 was adjusted to 5, 6 or 7. All white waters #4 were prepared from the same stock solution of white water #3, and thus had the same concentration of FA (11.6 mg/L) and RA (64.5 mg/L). The RFA content of each simulated closed-cycle white water is shown in Table 2.

Table 2. RFA content of white waters.

White water	FA (mg/L)	RA (mg/L)	RFA (mg/L)
1	173 ± 13	307 ± 25	480 ± 35
2	14 ± 2	91 ± 7	104 ± 8
3,4	12 ± 1	65 ± 2	77 ± 3

Treatment of White Water with Minerals (Batch Tests)

Batch tests were performed in duplicate or triplicate according to the following procedure: 5 mL of model process water were pipetted into a glass vial containing preweighed amount (0.1 ± 0.001 g) of tailored zeolites, ground to less than 0.180 mm aggregate size. Vials were capped with Teflon lids, and mixed in an end-over-end rotator (18 rpm) at 25°C for 24 h. Tailored minerals were then collected by centrifugation (2960 × g, 10 min), the liquid phase was decanted, and a 25 µl aliquot of 1 N NaOH was immediately added to the minerals. Samples were preserved at -20°C before analysis.

Heulandite H-1 and HDTMA cations were selected for a 2^{6-1} fractional factorial design examining the main and interactive effects of six factors on DHA uptake (Table 3). Test procedures were identical to those described above. An analysis of variance was performed based on the mean of the duplicate values of each thirty-two experimental tests and centre point. A main or interactive effect was statistically significant if, according to the Fisher test, the hypothesis $F > (F_{95\%,1,32} = 4.152)$ was true at a confidence level of 95% (Hines and Montgomery, 1990).

Analytical Methods

After incubation (15 min) in a water bath (20°C), each zeolite sample was mixed with 1.5 mL of 50 mM CH_3COONa buffer (pH 5) and spiked with o-methylpodocarpic acid (O-MPCA) which served as extraction surrogate. The aqueous phase was subjected to two successive 2 min extractions with 1.5 mL of a solution containing 70% v/v methyl-tert-butyl-ether (MTBE), 25% dichloromethane and 5% methanol (Voss and Rapsomatiotis, 1985; Morales *et al.*, 1992). For each extraction, the solvent phase was transferred directly to a 2 mL Teflon-lined glass vial and dried under vacuum. Dried vials were then spiked with heneicosanoic acid methyl ester and tricosanoic acid which served as internal standards. Methylation of DHA was accomplished by dispensing and vortexing, in the vials, 500 µL of chilled (4°C) (90% v/v MTBE/10% HPLC grade methanol) into which diazomethane gas was previously dissolved. Methylated samples were analysed using a Hewlett-Packard 6890 gas chromatograph, equipped with a flame ionization detector and a 30 m DB-5 fused silica column with an internal diameter of 0.25 mm and a film thickness of 0.25 µm (J&W Scientific, Folsom, CA). DHA was quantified using the normalized response of 99% pure DHA standards prepared from a 1000 µg/mL stock solution in MTBE. DHA removal was calculated by difference between the amount initially present in liquid phase and the amount sorbed to minerals.

Table 3. Experimental conditions selected for fractional factorial design

Factor	Symbol	Level		
		-1	0	+1
Aggregate size (mm)	a	< 0.180	1.0-1.4	2.0-2.4
Initial DHA concentration (mg/L)	b	6 ± 1	23 ± 2	37± 5
Mineral concentration (g/L)	c	1	10	20
HDTMA dosage (% ECEC)	d	20.0 ± 0.3	60 ± 1	100 ± 2
Time of treatment (h)	e	1	10	24
Temperature (°C)	f	20	40	60

RESULTS AND DISCUSSION

This section presents a shortened discussion of all results and data collected in batch tests. It includes five main headings: (1) performance of natural minerals and organo-clays, (2) mineral characterization, (3) interactions between organic cations and mineral surfaces, (4) influence of several factors on the uptake capacity of tailored minerals, and (5) application of tailored minerals to the treatment of Paprican, Millar and Quesnel white waters.

Screening of Natural Minerals and Organo-Clays

The screening of mineral samples indicated that zeolite minerals (clinoptilolite, heulandite, chabazite) removed a maximum of 25%, 8% and 15% of DHA, respectively (Figure 1). The low affinity of natural minerals for DHA can be explained by three factors. First, since the pH of the synthetic process water was similar to the pKa value (7.3) of DHA (McLeay *et al.*, 1979), a large proportion of DHA would be in a deprotonated, anionic form. The limited uptake of DHA can be partially attributed to the inherent negative charge and strong hydrophilic character (Tsitsishvili *et al.*, 1992; Jaynes and Boyd, 1991a). Second, it is possible that water molecules helped to limit access of DHA to microporous structure of the minerals, since it has been previously shown that the hydration of naturally-exchangeable cations in zeolites could sterically hinder adsorption of organic compounds in micropores (Gao *et al*., 1991). Third, the large size of the DHA molecule may have lead to an ion sieve effect, which has been observed to result in progressively lower sorption of large organic cations (Barrer *et al*., 1967).

Of the minerals screened, organo-clays showed the highest affinity for DHA (71-100% DHA removal) (Figure 1). The high DHA removal (120%) of sample O-1 resulted from loss of organo-clay during solid/liquid separation. The increased affinity of organo-clays for DHA can be attributed to the presences of a hydrophobic organic layer on the mineral surfaces (Boyd *et al*, 1988a,b). Because of their superior performance, further work was conducted with tailored minerals.

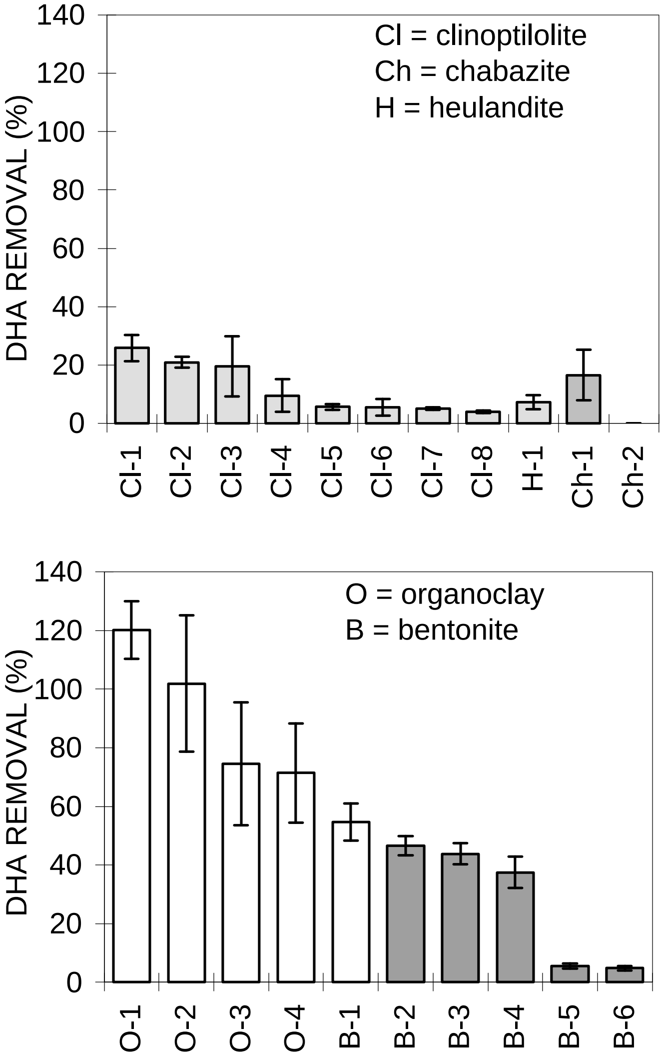

Figure 1: DHA removal efficiency of natural minerals and organo-clays.

Adsorption of Tailoring Cations on Zeolites

Chabazite aggregates were treated with doses of each tailoring cation ranging from 1 to 100% of the zeolite CEC (268 meq/100 g). Over the range examined, adsorption of TMA and HDTMA could be modeled using the Langmuir isotherm (Figure 2):

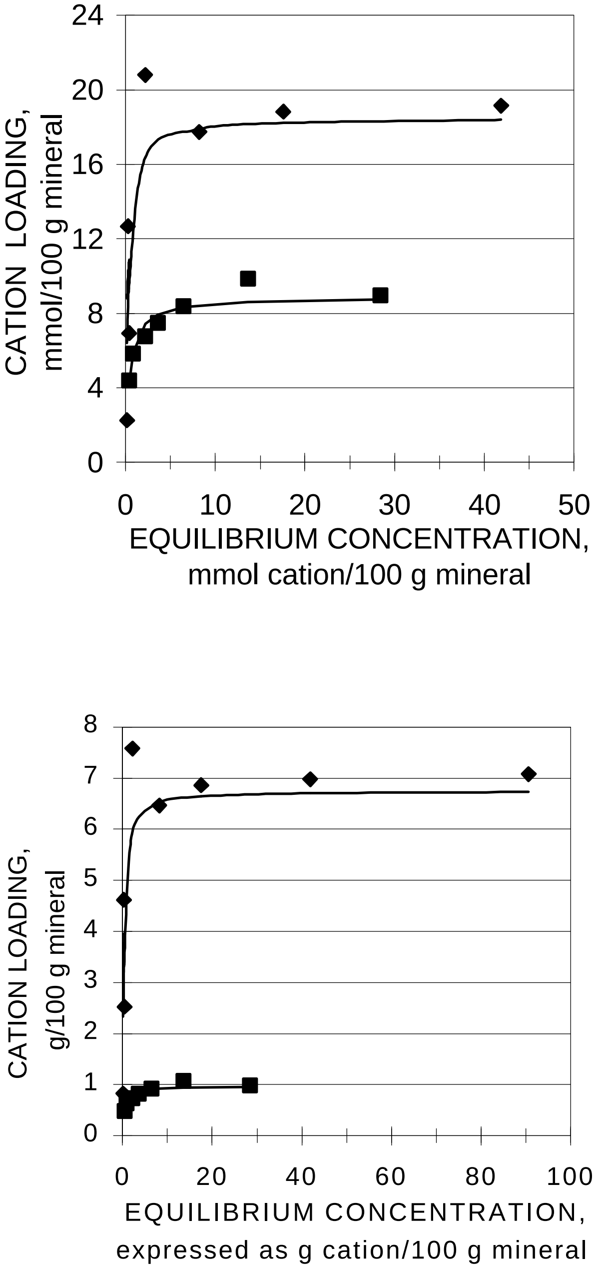

Figure 2. Experimental and modeled adsorption isotherms of (■) TMA and (◆) HDTMA cations on chabazite aggregates, ground to less than 0.180 mm.

$$\frac{n}{n_\infty} = \frac{Kc}{1 + Kc} \quad \text{where:}$$

n = Mass of cations sorbed per unit mass of solid (g cation/100 g mineral)
n_∞ = Mass of cations sorbed per unit mass of solid for monolayer coverage (expressed as g cation/100 g mineral)
c = Equilibrium concentration of unbound cations (calculated by difference between the equivalents initially added and the amount sorbed) (expressed as g cation/100 g mineral)
K = Empirical equilibrium constant at 25°C (expressed as g/g)

Values of the constants n_∞ and K were 0.97 and 2.4, respectively for TMA and 6.75 and 3.49, respectively for HDTMA. The measured loading of each cation was directly proportional to the equilibrium concentration in a range below 10 g cation/100 g mineral (equivalent to zeolite ECEC of 13.4 meq/100 g). For applied doses above the zeolite ECEC, adsorption reached monolayer coverage (plateau) (Figure 2).

Heulandite aggregates, ground to 0.180 mm size, were tailored with a dose of HDTMA cations equivalent to 20, 100 and 2940% of the zeolite ECEC (1.5 meq/100 g), then subjected to water rinses. Approximately 80% of HDTMA cations applied in doses less than the heulandite ECEC remained firmly bound to the zeolite surfaces, indicating that they replaced cations (Na^+) present in the zeolite lattice to form electrostatic interactions (Chen *et al*., 1992) (Table 4). This is in agreement with the chabazite adsorption isotherms and with previous work which showed that hexadecyltrimethylammonium (HDTMA) cations applied in doses less than the external cation exchange capacity (ECEC) of the zeolite become electrostatically-bound by replacing inorganic cations (Na^+, K^+, Ca^{2+}) in the zeolite lattice (Haggerty and Bowman, 1994). Once all exchange sites accessible to tailoring cations are occupied, HDTMA cations applied in excess of the zeolite ECEC will bind through hydrophobic tail-to-tail interactions to tailoring cations already sorbed on the zeolite surfaces (Haggerty and Bowman, 1994). As observed with the chabazite, cations applied in excess of heulandite ECEC (Table 4) were either left in solution, or bound through hydrophobic tail-to-tail interactions and subsequently easily washed off by water (Haggerty and Bowman, 1994; Zhang *et al*., 1993; Xu and Boyd, 1995).

That the maximum amount of cations firmly bound through electrostatic interactions was equivalent to the zeolite ECEC, suggests that the tailoring cations exchanged only with sodium ions from the external cation exchange sites. The large size of tailoring cations (for instance, head group diameter and chain length of HDTMA cations ≈ 6.9 and 35 Å, respectively

(Israelachvili, 1991), compared to the size of zeolite micropores (4.1 × 3.7 Å) (GSA Resources, 1993), most likely precluded exchange of TMA and TMA cations with cations (Na^+) present in the zeolite micropores. This sieving effect has previously been shown to affect adsorption of TMA, TBA and HDTMA cations onto clinoptilolite (Barrer *et al*., 1967).

Table 4. HDTMA loading onto heulandite mineral after tailoring and water rinsing

Applied dose (% ECEC)	20	100
Mass added (mg)	6.7	33.7
Mass remaining bound to minerals after washing (mg)	5.24	29.00
Mass left in solution after treatment (mg)	0.40	0.56
Mass collected in wash waters (mg)	1.09	4.12
Mass balance difference (mg)	+0.03	-0.02

DHA Uptake Using Tailored Minerals

Batch tests were performed with heulandite and chabazite minerals to elucidate the influence of the type and dose of tailoring cations on DHA removal. Each mineral was treated with a dose of TMA or HDTMA cations in a range from 0 to 100% CEC, washed with water and dried as described above. The dried tailored minerals were then applied to the treatment of model process water (approximately 40 mg DHA/L).

Influence of Tailoring Cation Dosage.

Experiments were conducted to investigate the effect of tailoring cation dosage on DHA removal. Two zeolites, tailored with doses of HDTMA cations ranging from 1 to 100% CEC, were used to treat model process water (33.4 mg DHA/L). Mineral tailoring increased DHA removal from 5-12% (Na^+-saturated minerals) to 20-100% (Figure 3). Consistent with previous observation uptake of DHA was proportional to tailoring cation dose up to approximately 4-5% of the mineral CEC while further increases in the dose of tailoring cation produced no further improvement in the uptake of DHA. The fact that the optimal dose for DHA uptake, corresponded closely with the ECEC of the heulandite and chabazite minerals (approximately 3.4 and 5% CEC, respectively) lends additional credence to the hypothesis that HDTMA exchanged only with the external cation exchange sites

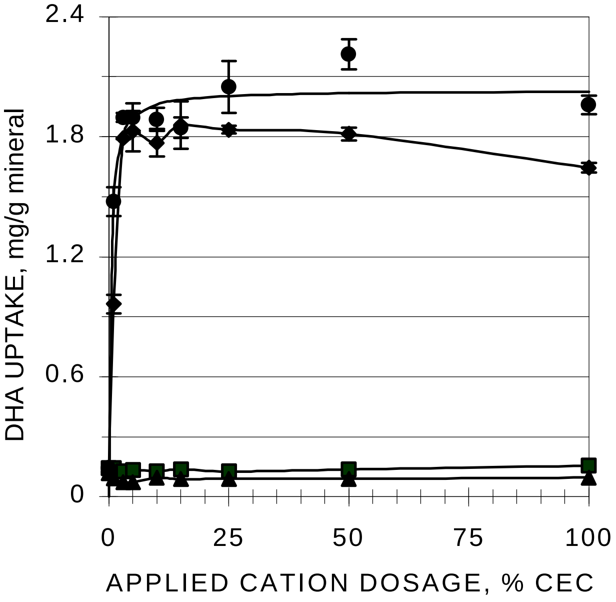

Figure 3. Influence of HDTMA cation dosage on DHA uptake using (●) H-1 (CEC 44 meq/100 g), (■) Cl-6 (CEC 92 meq/100 g), (▲) Cl-9 (CEC 9 meq/100 g), and (◆) Ch-1 (CEC 268 meq/100 g). Natural zeolites (HDTMA dosage = 0% CEC) served as control.

Higher CEC and ECEC minerals were better adsorbents for DHA molecules due to their larger HDTMA content, and thus higher uptake capacity (Figure 3). Previous work showed that, in addition to their increased hydrophobicity, high ECEC zeolites exhibited a closer packing of tailoring cations, forcing HDTMA chains to adopt an upright orientation and creating an effective partitioning phase (Jaynes and Boyd, 1991). On low ECEC zeolites, HDTMA cations were most likely loosely-packed as flat monomers or dimers, or might have formed amorphous monolayer and hemimicelles (Chen *et al.*, 1992). As was the case for DHA in the present study, higher CEC clays treated with a dose of HDTMA cations equal to 100% CEC had larger uptake capacity for a range of organics including ethylbenzene (Jaynes and Boyd, 1991), trichloroethylene (Sheng *et al.*, 1996), and chorinated phenolics (Brixie and Boyd, 1994).

Influence of Type of Tailoring Cations.

Over the range examined, the uptake capacity of TMA-tailored heulandite and chabazite (0.13-0.16 mg DHA/g mineral) was similar to the uptake capacity of the same Na^+-saturated zeolites (Figure 3). Previous work showed that solute uptake by clays treated with short-chain tailoring cations occurred by adsorption on hydrophobic mineral surfaces in between tailoring cation pillars (Jaynes and Boyd, 1991; Lagalay, 1994). In the present study, the inherent large size of DHA molecules, likely limited access of DHA molecules to the adsorption sites of TMA-tailored zeolites. The sorbate shape/size has been observed to result in progressively lower sorption of larger organic compounds on trimethylphenylammonium- and TMA-tailored clays (Jaynes and

Boyd, 1991; Lee *et al*., 1989; Nzengung *et al*., 1996). In addition to this steric effect, hydration of both short-chain organic cations and free aluminosilicate surfaces (Lee *et al*., 1989; Kukkadapu, 1995) could have occluded the adsorption sites.

In contrast to shorter-chain tailoring cations, HDTMA cations significantly increased the uptake capacity of heulandite and chabazite minerals to 1.8 and 2.0 mg DHA/g mineral, respectively (Figure 3), a twenty-fold increase in comparison to Na^+-saturated zeolites. Previous work showed that solute uptake by clays treated with long-chain tailoring cations occurred by partitioning in the hydrophobic surface layer of cation chains (Jaynes and Boyd, 1991). In the present study, HDTMA chains most likely promoted the dissolution (partitioning) of DHA molecules which, according to Brixie and Boyd (1994), could have been bound through van der Waals interactions to HDTMA chains.

Influence of Other Factors.

In order to determine the influence of a range of experimental parameters on DHA uptake, a factorial design was conducted. All seventeen main and interactive effects between the parameters examined (aggregate size, initial DHA concentration, mineral concentration, tailoring cation dosage, time of contact, temperature) were statistically significant (Table 5). However, based on the sum of squares of each main or interactive effect, the first eight accounted for 92% of the total variability. The mineral concentration itself accounted for 41% of the variability, while the cation dosage, initial DHA concentration and aggregate size each accounted for 9%. Of all significant interactive effects, the interactions of aggregate size, DHA concentration and cation dosage with mineral concentration were most important. Over the range tested, neither time of contact nor temperature influenced the uptake.

The uptake of DHA could be modelled using the equation:

$$\text{Removal (\%)} = 30.42 - 11.56a - 11.69b + 24.68c + 11.75d - 9.97bc + 9.54cd - 9.47ac$$

As indicated by their model coefficient (Table 5), larger cation dosages and mineral concentrations increased DHA removal as a result of larger HDTMA content and increased hydrophobic surfaces, respectively. That DHA removal was proportional to tailoring cation dosage less than zeolite ECEC was in agreement with the trend observed in Figure 3.

Table 5. Relative significance of main and interactive effects to DHA removal

Effect or interaction	Confounded effect or interaction	Statistic F	Model coefficient	Variability (%)
c	abdef	1347	24.7	40.8
d	abcef	306	11.8	9.3
b	acdef	302	-11.7	9.2
a	bcdef	295	-11.6	9.0
bc	adef	220	-10.0	6.7
cd	abef	201	9.5	6.1
ac	bdef	198	-9.5	6.0
ad	bcef	143	-8.0	4.3
acd	bef	83	-6.1	2.5
bd	acef	30	-3.7	0.9
f	abcde	26	-3.5	0.8
aef	bcd	25	-3.4	0.8
cf	abde	23	-3.2	0.7
ab	cdef	16	2.7	0.5
bf	acde	13	2.5	0.4
ef	abcd	12	-2.3	0.4
ade	bcf	6	1.7	0.2

White Water Treatment

RFA Removal from Simulated Closed-Cycle White waters

White waters #1, #2 and #4, adjusted to pH 5, were each treated with a dose of HDTMA-tailored aggregates ranging from 2.5 to 350 kg/m^3. Similar treatments using Na$^+$-saturated aggregates served as controls. As expected, uptake (mass sorbed) of FA and RA from each white water was directly proportional to the mass of minerals added (and thus the mineral concentration), and could be modeled by a linear regression (Tables II and III). For all three white waters, the uptake capacity of tailored heulandite for RFA was approximately 2 to 5 times larger than that of Na$^+$-saturated aggregates (Tables II and III), thereby suggesting sorption of HDTMA increased the mineral hydrophobicity of Na^+-saturated aggregates and allowed increased uptake of extractives. That the uptake capacity (slope of linear regression) was directly proportional to the initial and equilibrium RFA concentrations (Tables 6 and 7), was in good agreement with Brunauer's five types of adsorption isotherms (Perry's, 1984). Using the uptake capacity values, the removal of FA and RA ranged from 10-90% and 5-70%, respectively over a range of mineral doses from 20-350 kg/m^3.

Table 6. Characteristics of FA uptake using Na^+-saturated and HDTMA-tailored heulandite

White water	Initial [FA] (mg/L)	Na^+-saturated Uptake capacity (mg/kg)	R^2	HDTMA-tailored Uptake capacity (mg/kg)	R^2
1	173 ± 13	63.4 ± 3.1	0.991	148.0 ± 8.6	0.971
2	14 ± 2	5.2 ± 1.1	0.846	28.4 ± 0.3	0.999
4	12 ± 1	5.0 ± 0.2	0.987	25.5 ± 0.7	0.992

Table 7. Characteristics of RA uptake using Na^+-saturated and HDTMA-tailored heulandite

White water	Initial [RA] (mg/L)	Na^+-saturated Uptake capacity (mg/kg)	R^2	HDTMA-tailored Uptake capacity (mg/kg)	R^2
1	307 ± 25	107.5 ± 4.9	0.992	239 ± 6	0.994
2	91 ± 7	32.8 ± 4.4	0.931	163 ± 3	0.997
4	65 ± 2	30.8 ± 0.7	0.995	152 ± 6	0.985

In order to compare the treatment performance of white water and synthetic process water, it was first essential to evaluate the effect of white water pH since the present work was carried out at pH 5 versus pH 7.25 in the synthetic whitewater work. Samples of white water #4 were adjusted to pH 5, 6 and 7, and treated with a dose of tailored aggregates ranging from 20 to 350 kg/m^3. FA and RA uptake were not affected by changes of pH within a range from 5 to 7 (Figures 1 and 2). Previous work has shown that the surface charge of colloidal material released from mechanical pulp remained approximately constant over the pH range from 5 to 7 (Nylund *et al.*, 1993). Further, Boyd *et al.* (1988b) showed that hydrophobic interactions between HDTMA chains and pentachlorophenolate solute were more important than coulombic forces. Therefore, despite the presence of an ionizable carboxyl group on the RA, the hydrophobic character and water insolubility of the RFA (Markley, 1960) most likely explain the consistent removal observed over the pH range. These results thus provide a basis for comparison of tests conducted at different pH values in the range from 5 to 7.

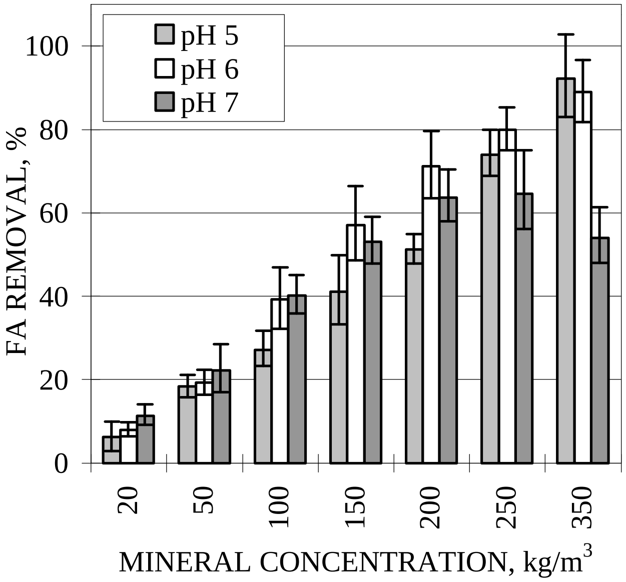

Figure 4. FA removal after mineral treatment of white water #4 at pH 5, 6 and 7

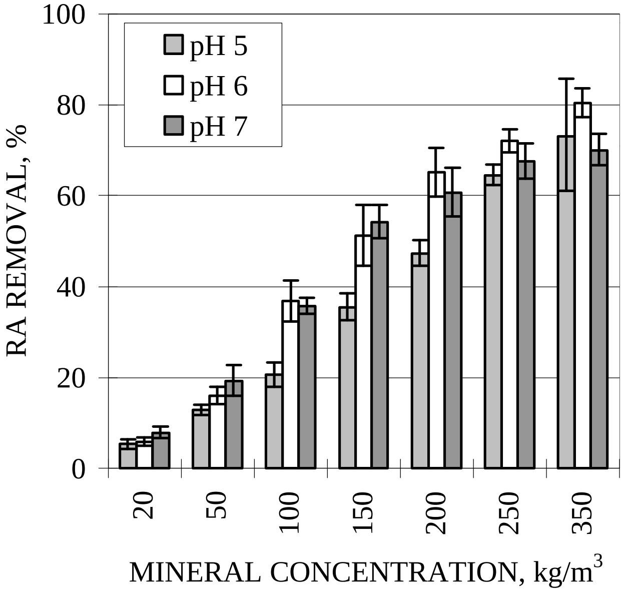

Figure 5. RA removal after mineral treatment of white water #4 at pH 5, 6 and 7.

The maximum total RFA uptake capacity (387 mg/kg) (Tables II and III) was approximately 3 fold lower than that observed for DHA dissolved in synthetic process water (1032 mg/kg). Expressed in another way, 200 kg/m^3 of mineral were required to achieve 63% removal of RFA from white water #4, while the same percent removal DHA from synthetic process water could be realized with a dose of 20 kg/m^3 of tailored aggregates. While part of this difference may have been due to variable removal efficiencies of different RFA (the previous study examined only DHA) it is also likely that the other constituents of white water affected the treatment performance. In particular, simultaneous dissolution of other LMW white water constituents into the hydrophobic layer, and/or RFA stabilisation through association with other white water DCS may have exerted an influence on performance.

Despite the fact this study only measured RFA uptake, a comparison of FA and RA removal efficiency from white waters #1, #2 and #4 provides evidence that equally troublesome LMW compounds such sterols, terpenes, glycerides, and lignans, may have simultaneously dissolved into the hydrophobic layer. Though the initial RA concentration of all three white waters was approximately 2 to 8 times larger than the initial FA concentration (Tables II and III), FA and RA removal efficiency profiles for white waters #1 and #4 (Figure 3), as well as for white water #2 (profile not shown), were very similar. These results suggested that, despite their different chemical structures, both RA and FA partitioned into the HDTMA surface layer, which most likely exhibited similar affinity for other LMW organics. Absence of competitive effects among dissolved organic substances is characteristic of partitioning processes (Boyd *et al.*, 1988a; Smith *et al.*, 1990). Based on these results, the HDTMA layer did not seem shape-selective. Other LMW DCS must have dissolved into the layer, and this partially explains why proportionally more efficient removal of RFA was observed in synthetic process water.

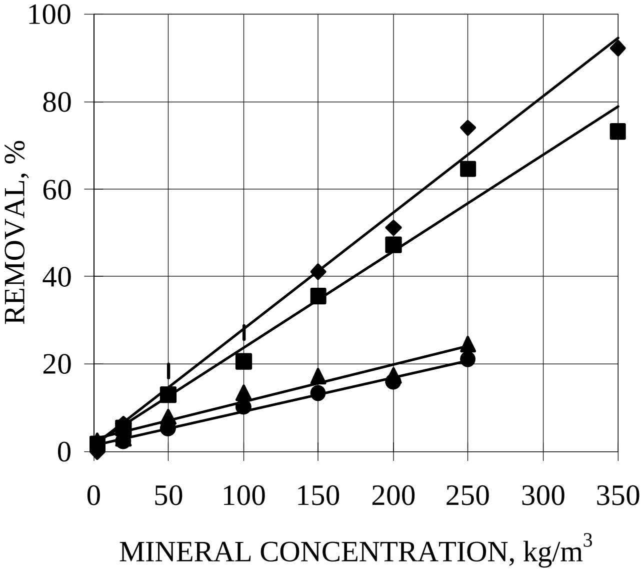

Figure 6. Effect of mineral concentration on removal of RA (●, ■) and FA (▲,◆) from white water #1 and #4, respectively.

In addition to the uptake of other LMW materials, there are two other reasons why high mineral doses were required to obtain efficient RFA removal. Firstly, the heulandite mineral tested had a relatively low total cation exchange capacity (44 meq/100 g mineral)\. Secondly, previous work has shown that the small pores of this mineral limited Na-HDTMA exchange to only the external surface, which represented less than 5% of the total number of exchange sites. In order to reduce the mineral dose required to practical levels, future research will focus on mineral properties, among which the porosity and cation exchange capacity are critical factors in the tailoring process.

Removal of High Molecular Weight Fraction of DCS

It has been previously shown that white water from TMP operations, in addition to the LMW substances (FA, RA, sterols), contains a large proportion of HMW substances, including lignin-like material and polysaccharides, of molecular weight 5 kDa and 20-30 kDa, respectively (Jour *et al.*, 1992). Another study previously showed that half of DCS released from mechanical pulping and bleaching operations was of high molecular weight (> 10 kDa) (Wearing *et al.*, 1985a). White water #3 was chosen to evaluate the removal of other white water constituents since it was from a TMP mill, and its initial concentrations of FA, RA, COD, SCOD, TOC, DOC, TDS and TDVS (25, 84, 6785, 3046, 2388, 803, 8217 and 1823 mg/L, respectively) were typical of levels expected in closed white water systems [Francis and Ouchi, 1997, Wearing *et al.,* 1985a).

Treatment of white water #3 with mineral doses ranging from 5 to 75 g/L resulted in no statistically-significant removal of COD, TDS and TDVS (Figure 4). The initial TOC and DOC concentrations were reduced by 15 ± 7% and 11 ± 4%, respectively (Figure 5). In contrast, up to 36 and 28% FA and RA, respectively were removed in the same tests. The low removal of HMW substances suggested that their relative size, which is 10-75 times larger than the molecular weight of HDTMA cations (0.4 kDa), most likely precluded their uptake by the HDTMA layer. Similar size exclusion has previously been observed in the uptake of phenols by HDTMA monolayer (Smith *et al.,* 1990).

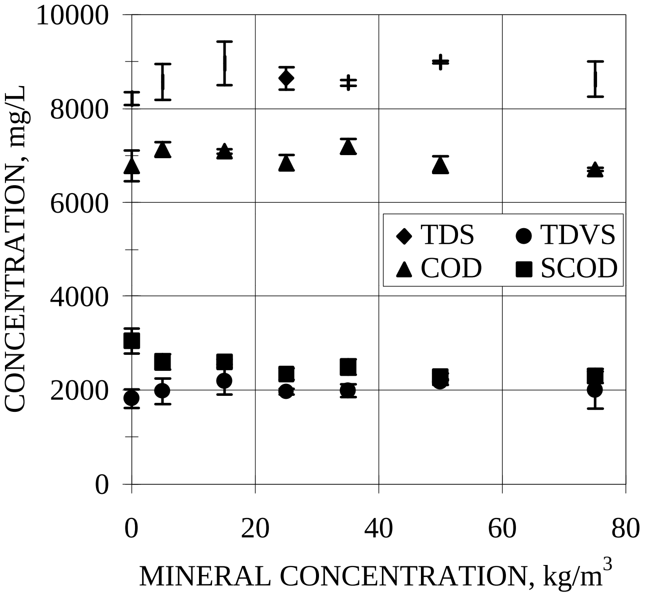

Figure 7. Effect of mineral concentration on COD, SCOD, TDS and TDVS removal from white water #3.

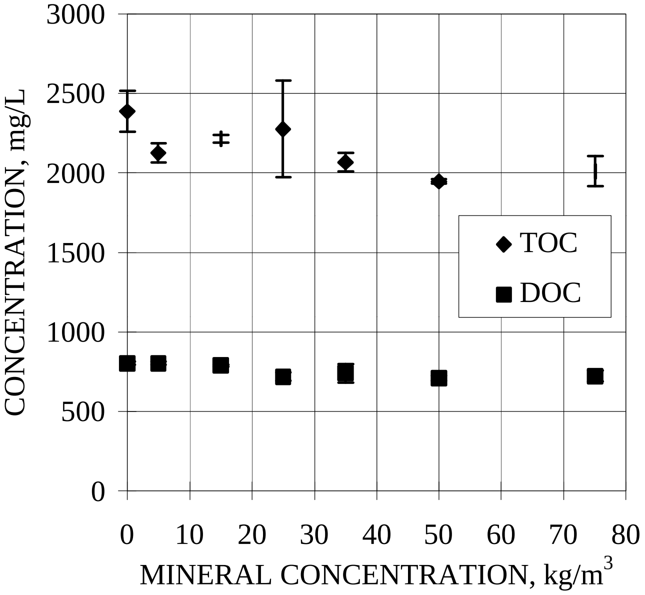

Figure 8. Effect of mineral concentration on TOC and DOC removal from white water #3.

There are two important observations which can be made concerning this data. Firstly, low molecular weight materials such as extractives have been identified as having the most detrimental effect on machine runnability (Ekman *et al.*, 1990; Francis and Ouchi, 1997). This work has shown that tailored minerals remove exclusively low molecular weight material while retaining the less detrimental high molecular weight fraction. This selectivity will result in maximal use of the mineral sorptive capacity.

Secondly, through judicial selection of the length (size) of the tailoring cation, there is the potential for exerting a degree of control over the molecular weight fraction removed. On the basis of the results, the relative size and magnitude of van der Waals interactions between sorbate (LMW or HMW substances) and sorbent (HDTMA cations) should dictate the size of the tailoring cations to be used in the tailoring process. If desired, the use of tailoring cations larger than HDTMA could possibly ensure removal of HMW substances from closed-cycle white water. Depending on the size, availability and cost of larger tailoring cations, other alternatives, including acid and heat treatments, coupled to HDTMA cations, could successfully increase the hydrophobicity of zeolites (Kim *et al.*, 1996; Pradas *et al.*, 1988).

CONCLUSIONS

This research investigated the performance of natural and tailored minerals for the treatment of synthetic process water and three simulated TMP white waters. After grinding and sieving, minerals were either applied in their natural form, or tailored with short-chain (TMA, BUT), branched (TBA) or long-chain (HDTMA) cations prior to the batch tests. Doses of the tailoring cations ranged from zero to 1.5 times the mineral CEC. Batch tests carried out with synthetic process water investigated DHA removal efficiency. Additional parameters (RFA, COD, SCOD, TOC, DOC, TDS, TDVS) were measured in tests conducted with white waters under pH conditions varying from 5 to 7.

Adsorption Capacity of Natural and Tailored Minerals

Twenty g/L of natural clinoptilolite, heulandite and chabazite minerals resulted in DHA removal of 25%, 8% and 15%, respectively. The negatively-charged DHA molecules and mineral surfaces, as well as the inaccessibility of the micropores already occupied by water molecules, explained the limited removal efficiency. Bentonite minerals were more efficient than zeolites, with a maximum removal of 55%. Organically-treated clays increased DHA adsorption up to 100%, and led to further investigation of the influence of mineral tailoring.

Interactions Between Organic Cations and Mineral Surfaces

1. The adsorption of TMA, TBA, BUT and HDTMA cations on chabazite Ch-1 was modeled using the Langmuir isotherm. The transition from the semi-linear zone to the plateau region occurred at the mineral ECEC value (approximately less than 5% of the mineral CEC). The ion sieve effect caused by the difference in size of the micropores and the tailoring cations, restricted the adsorption of tailoring cations to the external surfaces of chabazite Ch-1 and heulandite H-1.

2. Tailoring cations applied in doses less than the mineral ECEC were firmly bound to the mineral surfaces by coulombic interactions. Cations applied in excess of the mineral ECEC could have been bound through hydrophobic interactions to cations sorbed through coulombic interactions. The stability of hydrophobic bonds was strongly affected by water rinses.

Uptake Capacity of Tailored Minerals

1. Among the four organic cations tested, only the cation with the longest hydrocarbon chain (HDTMA) improved the uptake capacity of heulandite H-1 and chabazite Ch-1. Uptake capacity was improved to approximately 2 mg DHA/g after tailoring. Long-chain cations formed a dense monolayer where DHA molecules dissolved. HDTMA-tailored minerals with CEC values above 90 meq/100 g ensured complete removal of DHA from synthetic process water.
2. Removal of DHA was dependent on the measured cation loading, which was dictated by the mineral ECEC or CEC value. On low CEC minerals, the chains were loosely packed, while high CEC minerals displayed a closer packing of HDTMA cations, oriented vertically.
3. The effects of aggregate size, initial DHA concentration and cation dosage on DHA removal were relatively small in comparison to the mineral concentration, while the effects of temperature and time of treatment were negligible.

Technical Feasibility of White Water Treatment

1. Treatment of filtered Paprican white water with HDTMA-tailored H-1 was not affected by the pH of the white water in a range from 5 to 7.
2. RFA molecules bound to suspended solids most likely dissolved into the HDTMA layer.
3. The amount of RFA sorbed to HDTMA-tailored H-1 increased linearly with the mineral concentration in a range from 0 to 350 g/L for all three white waters, adjusted at pH 5.
4. The uptake capacity was strongly dependent on the initial RFA concentration, in accordance with Brunauer's five types of adsorption isotherms.
5. Excessive doses of HDTMA-tailored H-1 were required for good to excellent RFA removal. Seventy-five g/L of tailored H-1 resulted in reduction of 24% SCOD, 18% TOC, 10% DOC, while no removal of COD, TDS and TDVS occurred. The low surface area (15-30 m^2/g) and the low ECEC value (1.5 meq/100 g) of heulandite H-1 explained the performance.
6. The HDTMA layer of heulandite H-1 selectively rejected organic compounds on the basis of their molecular weight. LMW organics, including RA and FA, preferentially dissolved. The shape factor did not affect the mineral treatment since the removal efficiencies of RA and FA were similar.

RECOMMENDATIONS

Confirmation of the Technical Feasibility

The present study showed that large doses of HDTMA-tailored H-1 were required for satisfactory removal of RFA. In order to obtain the same performance but with much smaller mineral doses, it is mandatory to increase the surface area coated with organic cations. To do so, minerals should not only have a high surface area, but this surface should be accessible to large organic cations. This suggests the pore size is a criteria as important as the surface area. High CEC minerals are also desirable since they will form a thicker and more uniform organic layer. Synthetic zeolites are recommended since they can be custom-made to meet these requirements. The structural integrity should only be considered once the above criteria have been met. Indeed, even if the mineral selected has a low degree of structural integrity, previous work has shown that powdered bentonite could be successfully shaped into 3 mm height by 2 mm diameter pellets with an acrylic binder.

The HDTMA layer of heulandite H-1 was apparently selective with respect to the molecular weight of different constituents, as measured by RA, FA, COD, TOC and TDS. In order to confirm the selectivity of the HDTMA layer, several white water streams containing either LMW or HMW organics could be prepared by UF and NF membranes, and then subjected to mineral treatment. Secondly, a determination of the influence of the shape factor among LMW organics would require measurement of the concentration of other LMW organics, such as sterols and lignans, dissolved into the layer. Current analytical methods designed for liquid samples would need to be adapted for analysis of the solid phase. Most importantly, in order to enhance the removal of HMW compounds, long-chain tailoring cations should be considered and selected among the following list:

- C12: dodecyltrimethylammonium;
- C14: tetradecyltrimethylammonium, benzyldimethyltetradecylammonium;
- C16: hexadecylpyridinium, hexadecyltrimethylammonium;
- C17: dioctodecyldimethylammonium, and
- C18: octadecyltrimethylammonium.

Besides white water treatment, other process streams or wastewaters in the pulp and paper industry could potentially benefit from the application of tailored minerals in internal, external or "emergency" treatment.

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