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White water treatment using organically tailored heulandite minerals

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ABSTRACT

Heulandite aggregates were tailored with hexadecyltrimethylammonium (HDTMA) cations for treatment of TMP closed-cycle white waters. Over a range of mineral concentrations of 2.5–350 kg/m³ and a pH range of 5–7, the HDTMA layer on the mineral surface preferentially removed low-molecular-weight substances as a result of the size selectivity exerted by HDTMA-tailored minerals. These substances included fatty acids and resin acids. Because only the external surfaces of the mineral particles were accessed, large mineral doses were required to remove most of the resin and fatty acids from closed-cycle white water. Work is continuing on finding ways to reduce the mineral dose required.

Application:

Organically tailored heulandite minerals could be used to remove dissolved and colloidal substances from TMP white water as mills are progressively closed.

THE PULP AND PAPER INDUSTRY has embarked on a program to reduce water use through water conservation, reclamation, and recycling. One process stream that has been targeted for treatment is white water, which is the water that drains from the pulp mat as it forms. White water contains dissolved and colloidal substances that are released from wood pulping and bleaching operations, from chemical additives, and from the mill water supply. These contaminants can cause problems in paper machine runnability. Consequently, some of the white water must be purged and replaced with fresh water, which accounts for a large fraction of the total amount of fresh water used.

Closing white water circuits increases the levels of dissolved and colloidal substances. Among the low-molecular-weight substances found are lipophilic extractives, such as resin and fatty acids, sterols, terpenes, and glycerides, and semi-lipophilic phenolic extractives, such as lignans (*1*). These extractives are found in concentrations as high as 100 mg/L in white waters experimentally prepared to resemble those of closed systems (*2*). Detrimental to machine runnability, the buildup of extractives leads to pH drops, corrosion, microbial growth, deposits on papermaking equipment, and sheet breaks. The accumulation of extractives is detrimental to product quality as well, possibly causing specks, holes, odor, and losses in strength.

The high-molecular-weight fraction is composed of lignin-like material, neutral polysaccharides (cellulose and hemicellulose), and hydrophilic and highly negatively charged polysaccharides (*3*). These anionic polysaccharides are the primary offenders responsible for changes in the balance of chemical charges, and their presence increases the consumption of cationic retention aids (*4*).

Clarifiers, flotation cells, and filters can remove only a fraction of the dissolved and colloidal substances. Separation technologies need to be developed for maintaining acceptable concentrations of these substances as mills are progressively closed. Therefore, to evaluate their potential for use in processing mill white waters, we examined natural zeolites, or ion-exchange agents, treated with organophilic quaternary ammonium cations. Large, world-wide reserves of these minerals make them suitable and inexpensive adsorbents ($30–300/ton), while quaternary ammonium cations are commercially available in large quantities at reasonable costs ($0.50–1.00 per pound) (*5*).

BACKGROUND

Tailored minerals can be manufactured by a wet or dry process. In either approach, the quaternary ammonium cations first exchange with naturally present inorganic cations, such as Na^+ and Ca^{2+}. Once all of the cation exchange sites are replaced, excess quaternary ammonium cations can bind to the already-in-place quaternary ammonium cations through hydrophobic tail-to-tail electrostatic interactions (*6*).

Although tailored zeolites have been used in the removal of aromatics (*7–9*), phenols (*10*), and chlorinated organics (*11*, *12*), research has not focused on their use in the pulp and paper process and wastewater treatment. In our preliminary trials, heulandite aggregates treated with a dose of hexadecyltrimethylammonium (HDTMA) cations removed 45% to 77% of the dehydroabietic acid (DHA) from a synthetic process water containing 33 mg/L of DHA (*13*). Based on these promising results, this study was conducted to evaluate the potential use of the same tailored minerals in removing

White water	Fatty acids, mg/L	Resin acids, mg/L
1	173 ± 13	307 ± 25
2	14 ± 2	91 ± 7
3	12 ± 1	65 ± 2
4	12 ± 1	65 ± 2

I. Resin and fatty acid content of the four white waters

White water no.	Initial conc., mg/L	Na^+-SATURATED Uptake capacity, mg/kg	R^2	HDTMA-TAILORED Uptake capacity, mg/kg	R^2
		Fatty acids			
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
		Resin acids			
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

II. Characteristics of the uptake of fatty and resin acids by Na^+-saturated and HDTMA-tailored heulandite

dissolved and colloidal substances from TMP white waters like those of closed-cycle mills.

The overall objective included three specific goals. The first goal was to determine if the efficient removal of DHA from synthetic process water could be attained with simulated closed-cycle white water. The second goal was to determine the effect of mineral concentration and white water pH on the removal of fatty acids and resin acids. The third goal was to determine the effects of constituent size and shape. To make this determination, we compared the removal of low-molecular-weight organics—specifically fatty acids and resin acids*—with the removal of high-molecular-weight substances. These removal efficiencies were measured as chemical oxygen demand (COD), soluble COD, total organic carbon (TOC), dissolved organic carbon (DOC), total dissolved solids (TDS), and total dissolved volatile solids (TDVS).

RESULTS AND DISCUSSION

Removal of resin and fatty acids

Sample white waters were prepared to resemble the white waters in closed-cycle mills. The samples were prepared by mixing and heating pulp with water or white water to increase the concentrations of the dissolved and colloidal substances. **Table I** gives the contents of resin and fatty acids for each of the four white waters.

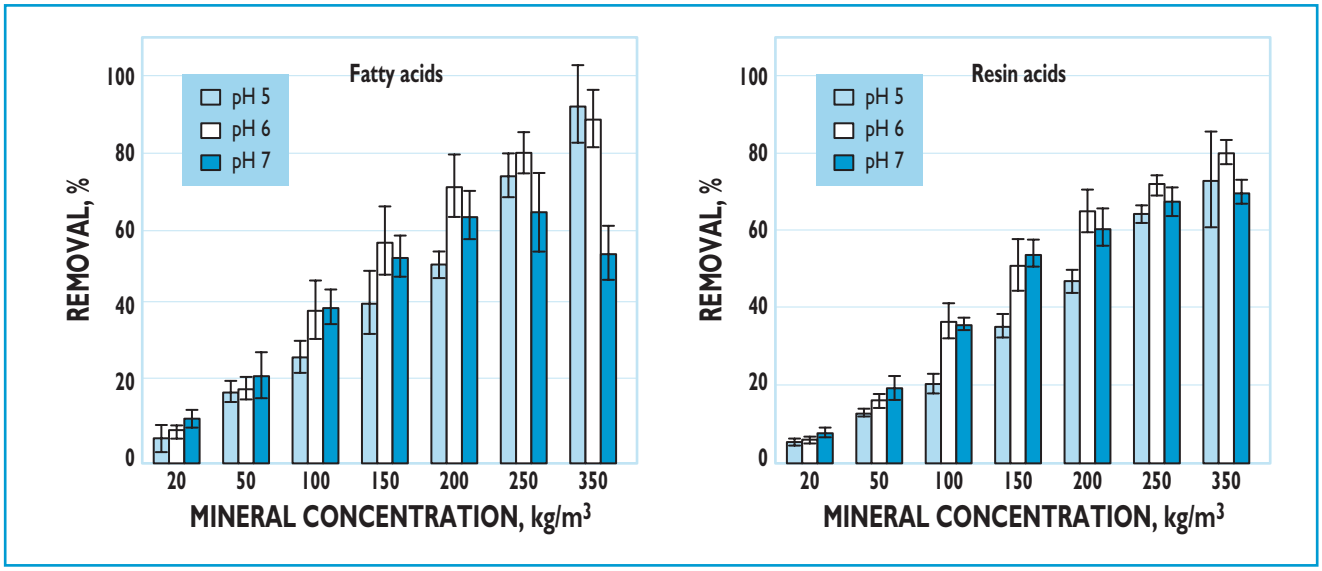
White waters No. 1, 2, and 4, adjusted to pH 5, were each treated with a dose of HDTMA-tailored aggregates ranging from 2.5 kg/m^3 to 350 kg/m^3. Similar treatments using Na^+-saturated aggregates served as controls. The uptake of fatty and resin acids from each white water could be modeled by a linear regression. Results are presented in **Table II**. For all three white waters, the uptake capacity of tailored heulandite for resin and fatty acids was approximately 2–5 times larger than the uptake capacity of Na^+-saturated heulandite aggregates. Apparently, the sorption of HDTMA increased the mineral hydrophobicity, which increased the uptake of extractives.

The uptake capacity (the slope of the linear regression) was directly proportional to the initial and equilibrium concentrations of the resin and fatty acids, as the table shows. This outcome is in keeping with Brunauer's five types of adsorption isotherms (*14*). Based on the uptake capacity values, the removals of fatty acids and resin acids ranged from 10–90% and 5–70%, respectively, over a range of mineral doses of 20–350 kg/m^3.

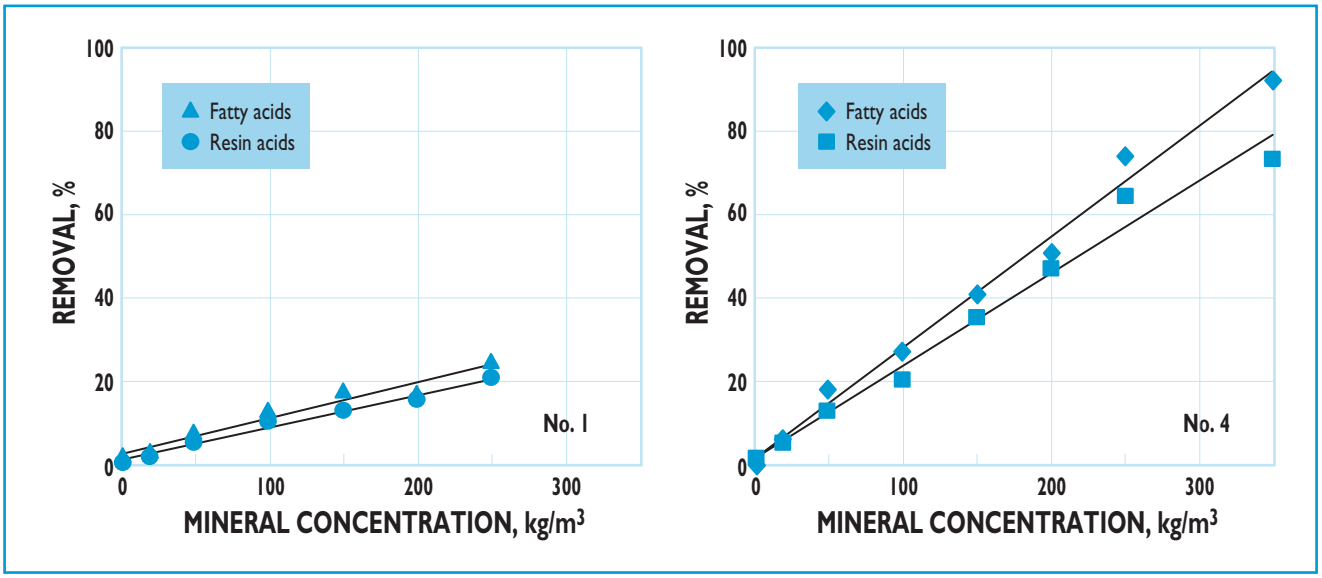
To compare how the white water and the synthetic process water responded to treatment, we first had to evaluate the effect of white water pH. This work was carried out at pH 5, as opposed to pH 7.25 in the previous study (*13*). Samples of white water No. 4 were adjusted to pH 5, 6, and 7 and were treated with doses of tailored aggregates ranging from 20 to 350 kg/m^3. The uptakes of fatty and resin acids were not affected by changes in pH within the range of pH 5–7, as illustrated in **Fig. 1**.

Previous work has shown that the surface charges of colloidal material released from mechanical pulp remain roughly constant over the pH range of pH 5–7 (*4*). Furthermore, Boyd *et al.* (*15*) demonstrated that hydrophobic interactions between HDTMA chains and pentachlorophenolate solute are more important than coulombic forces. Therefore, the fact that changes in pH did not affect the uptake over the range of pH 5–7 is explained by the hydrophobic character and the water insolubility of the resin and fatty acids (*16*). Thus, the results presented in Fig. 1 provide a basis for comparing tests conducted at different pH values in the range of pH 5–7.

The maximum total uptake capacity for resin and fatty acids was 387 mg/kg, as derived from the data in Table II for white water No. 1. This value is about three times lower than the value of 1032 mg/kg for dehydroabietic acid dissolved in synthetic process water (*13*). Expressed in another way, it took 200 kg/m^3 of mineral to remove 63% of the resin and fatty acids from white water No. 4, whereas the same percent removal of DHA from the synthetic process water could be achieved with a dose of 20 kg/m^3 of tailored aggregates.



1. Removal of fatty and resin acids after mineral treatment of white water No. 4 at pH 5, 6, and 7.

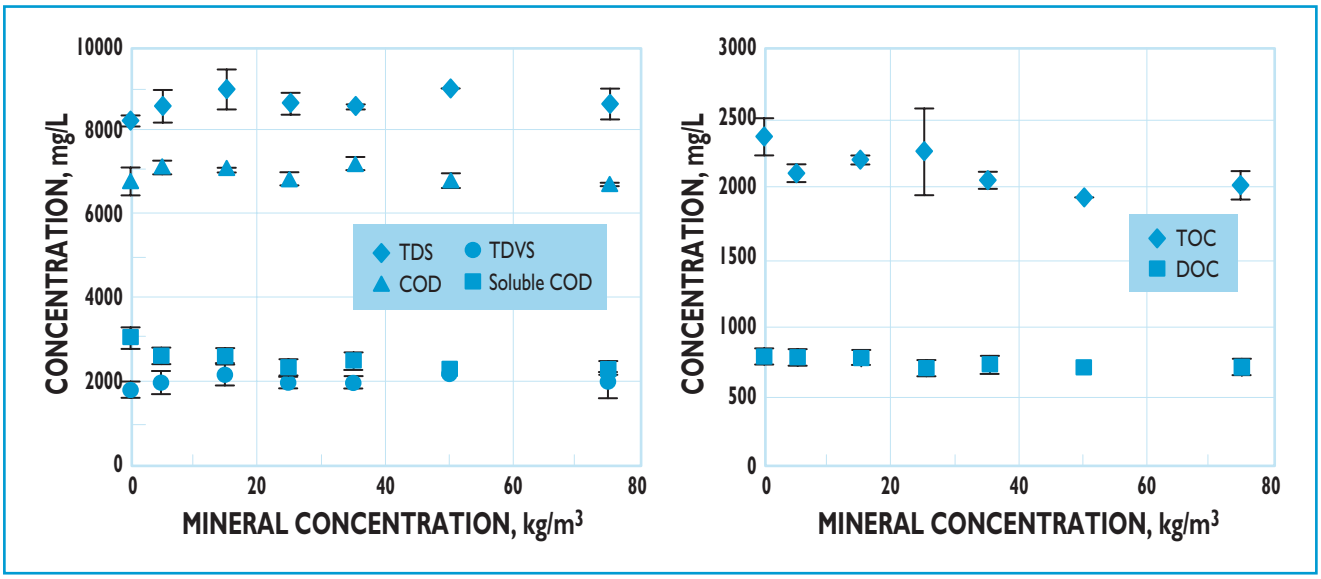


2. Effect of mineral concentration on the removal of resin acids and fatty acids from white water No. 1 and from white water No. 4.

Part of this difference may have been caused by variable removal efficiencies of different resin and fatty acids, but it is also likely that performance may have been influenced by the simultaneous dissolution of other low-molecular-weight white water constituents into the hydrophobic layer.

In this study, we measured the uptake of only resin and fatty acids, but a comparison of the removal efficiencies of fatty and resin acids supports the conclusion that equally troublesome low-molecular-weight compounds may have simultaneously dissolved into the hydrophobic layer. These low-molecular-weight organics are compounds such as sterols, terpenes, glycerides, and lignans. The initial concentrations of resin acids in the three white waters of Table II were about 1.75, 6.5, and 5.5 times larger, respectively, than the initial concentrations of fatty acids. Nevertheless, the profiles for the removal efficiencies for both were similar for white waters No. 1 and No. 4 (**Fig. 2**), as well as for white water No. 2 (profile not shown).

These results suggest that both resin acids and fatty acids partitioned into the HDTMA surface layer despite their different chemical structures. The HDTMA surface layer probably exhibited similar affinity for other organics of low molecular weight. The absence of competitive effects among dissolved organic substances is characteristic of partitioning processes (*17*, *18*). These results indicate that the HDTMA layer was



3. Effect of mineral concentration on COD, soluble COD, TDS, and TDVS removal and on TOC and DOC removal from white water No. 3.

not selective in regard to molecular shape. Other dissolved and colloidal substances of low molecular weight must have dissolved into the layer. This outcome partially explains why more efficient removal of dehydroabietic acid was achieved previously with the synthetic process water (*13*).

In addition, there are two other reasons for high mineral doses being required to obtain efficient removal of resin and fatty acids. First, the heulandite mineral tested had a relatively low total cation exchange capacity (44 meq/100 g of mineral) (*13*). Second, the small pores of this mineral limited the exchange of sodium ions and HDTMA to the external surface, which held less than 5% of the total number of exchange sites (*13*). To reduce the mineral dose required to practical levels, future research will focus on mineral properties such as porosity and the cation exchange capacity.

Removal of high-molecular-weight substances

White water from TMP operations contains a large proportion of dissolved and colloidal substances of high molecular weight in addition to the low-molecular-weight substances such as fatty acids, resin acids, and sterols. These high-molecular-weight substances include lignin-like material and polysaccharides, with molecular weights of 5 kDa and 20–30 kDa, respectively (*19*). As another study showed, half of the dissolved and colloidal substances released from mechanical pulping and bleaching operations have molecular weights of more than 10 kDa (*20*).

To evaluate the removal of other white water constituents, we chose white water No. 3 because it was from a TMP mill. Its initial concentrations were acceptable for this determination:

- Fatty acids: 12 mg/L
- Resin acids: 65 mg/L
- COD: 6785 mg/L
- Soluble COD: 3046 mg/L
- TOC: 2388 mg/L
- DOC: 803 mg/L
- TDS: 8217 mg/L
- TDVS: 1823 mg/L

These concentrations are similar to levels proposed for closed white water systems (*2*, *20*).

Treatment of white water No. 3 with mineral doses ranging from 5 g/L to 75 g/L resulted in no statistically significant removal of COD, TDS, and TDVS, as shown in the plot on the left in **Fig. 3**. In the graph on the right, the concentrations measured for TOC and DOC are plotted. The initial TOC and DOC concentrations were reduced by 15±7% and 11±4%, respectively. In contrast, up to 36% of the fatty acids and 28% of the resin acids were removed in the same tests. The low removal of high-molecular-weight substances suggests that their size probably precluded them from being sorbed by the HDTMA layer. These high-molecular-weight substances are 10–75 times larger than the HDTMA cations (0.4 kDa). Similar size exclusion has previously been observed in the uptake of phenols by the HDTMA monolayer (*18*).

Two important observations can be made concerning these data. First, low-molecular-weight materials such as extractives have been identified as having the most detrimental effect on machine runnability (*1*, *2*). As our work has shown, tailored minerals remove exclusively the low-molecular-weight material while excluding the less detrimental high-molecular-weight material. This selectivity will result in maximal use of the mineral's sorptive capacity.

Second, through judicious selection of the length of the tailoring cation, it is possible to exert some control over the molecular weight fraction to be removed. The relative

size and magnitude of van der Waals interactions between the HDTMA cations and the materials sorbed should dictate the size of the tailoring cations. The use of tailoring cations larger than HDTMA could possibly ensure the removal of substances of higher molecular weight from closed-cycle white water. Depending on the size, availability, and cost of larger tailoring cations, alternatives such as acid and heat treatments, coupled to HDTMA cations, could be used to increase the hydrophobicity of the zeolites (*21*, *22*).

CONCLUSIONS

Dehydroabietic acid, resin and fatty acids, and other low-molecular-weight organic compounds partitioned from concentrated white waters into the HDTMA layer of tailored heulandite aggregates. White water treatment using HDTMA-tailored heulandite is a size-selective process that favors the removal of low-molecular-weight substances, including resin acids and fatty acids. The size and relative hydrophobic–hydrophilic character of high-molecular-weight substances prevent them from being partitioned into the HDTMA layer.

In this initial study, large doses of HDTMA-tailored heulandite were required for effective removal of resin and fatty acids from concentrated white waters. However, the heulandite mineral tested in the study had both a low cation exchange capacity and a small pore size, which meant that only about 5% of its cation exchange capacity could be organically tailored. A mesoporous material that would allow tailoring cations access to its internal structure has the potential to dramatically decrease the mineral dose required.

METHODS AND MATERIALS

Preparation of HDTMA-tailored heulandite

Heulandite aggregates were ground, sieved to a size of 0.5–1.0 mm, and pretreated to produce dried Na^+-saturated aggregates (*13*). Precisely weighed samples of pretreated minerals were tailored with an aliquot of 50 m*M* HDTMA–bromide (Sigma–Aldrich) to yield a cation dosage equivalent to 150% of the heulandite external cation exchange capacity (1.5 meq/100 g) (*13*).The suspension was mixed at 25°C for 24 h in an end-over-end rotator at 18 rpm. After 10 min of settling, the supernatant was decanted, and the aggregates were subjected to five successive 5 min washes with deionized water.

After overnight drying at 60°C, tailored aggregates were analyzed for TOC with a Shimadzu TOC-5050 analyzer equipped with a solid sampling module (SSM-5000). Because of its detection limit of 0.15 g carbon/100 g mineral, the apparatus could not quantitatively determine the HDTMA loading by TOC analysis.

The HDTMA-tailored aggregates were stored in polyethylene containers prior to use.

Preparation of the white waters

The preparation of white water No. 1 consisted of diluting 1.5 kg of 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 was mixed and heated for 1 h at 60°C in a jacketed stainless steel tank.The suspension was manually dewatered and allowed to stand overnight to let coarse suspended solids settle out. Afterwards, the suspension was filtered through a screen with a 1.3 mm mesh.

After the pH was adjusted to 12, the filtrate was mixed at 90°C for 1 h and filtered through a Whatman No. 41 filter paper (pore size of 25 μm). The filtrate was collected in a clean, fired, amber glass bottle containing a preweighed mixture of Na_2HPO_4 and NaH_2PO_4 to yield a 50 m*M* phosphate buffer at pH 5. The buffered filtrate was 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 No. 2, with the exception that 0.4 kg of unbleached TMP pulp from the secondary refiner was mixed with 3.3 L of clarified white water. This pulp consisted of 55% lodgepole pine, 35% white spruce, and 10% alpine fir, and it had a consistency of 19.9%. Both the pulp and the clarified white water were obtained from the Quesnel River Pulp Company BCTMP/TMP mill in Quesnel, BC.

White water No. 3 was obtained from PAPRICAN in Vancouver, BC. The preparation consisted of diluting 3.6 kg of TMP pulp at 47% consistency to 2% consistency with 180 L of fresh tap water. The pulp was obtained from Howe Sound Pulp and Paper Ltd. in Port Mellon, BC, and was made from a spruce, pine, fir, and hemlock furnish.The suspension was mixed for 30 min at 60°C and was dewatered to approximately 40% consistency with a screw press (*2*).A fraction of the filtrate was transferred to a clean plastic pail that contained preweighed amounts of Na_2HPO_4 and NaH_2PO_4 to yield a 50-m*M* phosphate buffer at pH 7. The buffered filtrate was stored at 4°C.

The remaining filtrate was used to prepare white water No. 4. After being subjected to the same steps as white water No. 1 (pH adjustment, heating, mixing, and filtration), the pH of white water No. 4 was adjusted to pH 5, 6, or 7. All of the No. 4 white waters were prepared from the same stock solution of white water No. 3. Thus, all No. 4 white waters had the same concentrations of fatty acids and resin acids (11.6 mg/L and 64.5 mg/L, respectively).As mentioned, the resin and fatty acids contents of the white waters are given in Table I.

Batch tests and analytical methods

All glassware was washed and fired at 450°C to remove any trace organics prior to use. Batch tests for removing resin and fatty acids were conducted in 10 mL glass vials that contained a preweighed amount of HDTMA-tailored aggregates. To these vials was added 5 mL of white water (25°C). The vials were capped with Teflon® lids and were placed in an end-over-end rotator for 24 h of mixing at 18 rpm at 25°C. Although treatment was essentially complete after 1 h (*13*), we chose a contact period of 24 h for convenience.

Aggregates were allowed to settle out for 30 s. The supernatant was discarded, and a 25 µL aliquot of 1*N* NaOH was added to the minerals. Samples were stored at –10°C before the resin and fatty acids were analyzed. Fatty acids and resin acids sorbed to minerals were mixed with an aliquot of 50-m*M* CH_3COONa buffer (pH 5). Two extractions were performed with a mixture composed of 70% v/v methyl-ter-butyl-ether, 25% dichloromethane, and 5% methanol.

The extraction was centrifuged, and the solvent phase was transferred to a glass vial, which was dried under vacuum. The dried vials were spiked with heneicosanoic acid methyl ester and tricosonoic acid prior to methylation with diazomethane gas. The methylated samples were analyzed with a Hewlett-Packard 6890 gas chromatograph. This chromatograph was equipped with a flame ionization detector and a 30 m DB-1 fused silica column (internal diameter of 0.25 mm, film thickness of 0.25 µm) (J&W Scientific, Folsom, CA). The oven temperature program entailed a temperature rise of 4 C° per minute from 150° to 265°C.

Tests for removing other water-quality parameters were performed in a similar fashion, with the exception that a larger volume of white water was transferred to a 100 mL amber glass bottle. After 24 h of mixing and after the minerals were allowed to settle, the treated white water was divided into three portions.

One portion was filtered on prewashed Whatman 934AH glass filters for the analyses of TDS and TDVS according to Standard Method Procedures 2540C and 2540E, respectively (*23*). Another portion was acidified with 50% w/v H_2SO_4 to pH 2 for subsequent analysis of COD and TOC according to Standard Method Procedures 5220D and 5310B, respectively (*23*). Finally, the remaining portion was filtered on 0.45 µm filter paper and was acidified for analyses of soluble COD and dissolved organic carbon, according to the same procedures as those used in COD and TOC analyses. **TJ**

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