

Mechanisms of removing resin and fatty acids in CTMP effluent during aerobic biological treatment

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IN CANADA, THE EFFLUENTS DISCHARGED from the pulp and paper mills are constrained to be nontoxic to fish. Regulations made this mandate effective in 1995 (1, 2). Consequently, Canadian pulp and paper mills are now required to remove effluent constituents that are toxic to fish.

Resin acids and fatty acids are released from wood chips during pulping. As constituents of pulping effluents, these chemical compounds are toxic (3–9). In fact, resin and fatty acids are the main sources of toxicity to fish in mechanical pulping effluents (4–10). Effluents high in resin and fatty acids content have been observed, especially for CTMP effluents (11–14). Therefore, removing the resin and fatty acids from a CTMP effluent before discharge is the key step in rendering the effluent nontoxic.

Aerobic biological treatment is an effective method for the elimination of resin and fatty acids from pulping effluents (13–20). Results from our study (18) on aerobic biodegradation of a CTMP effluent showed that about 92% of the resin and fatty acids in the effluent could be removed in an activated sludge treatment with an 8-h hydraulic retention time.

Biodegradation has been considered responsible for the removal of resin and fatty acids through aerobic biological treatment (11, 21). However, there may be other removal mechanisms at work, such as adsorption onto the biosolids and oxidation

by air. Our main objective in this study was to determine the removal mechanisms. We also evaluated the kinetics of resin and fatty acids removal in the batch treatment.

THEORETICAL CONSIDERATIONS

Properties of resin and fatty acids and possible mechanisms of their removal

Eight resin acids are usually released from wood chips during pulping: pimaric, isopimaric, sandaracopimaric, abietic, dehydroabietic, neoabietic, levopimaric, and palustric acids. These eight acids have been identified in pulping effluents (9), especially in CTMP wastewaters (10–14). In addition, there are three unsaturated fatty acids: oleic, linolenic, and linoleic acid. Among these acids, dehydroabietic acid occurs in the highest proportion.

As organic compounds in nature, resin and fatty acids could theoretically be used as food for microorganisms, meaning that the microorganisms would biodegrade the acids. Resin and fatty acids are nearly insoluble in water (22–23) and may adsorb onto the biosolids during biological treatment (24). In fact, resin and fatty acids, especially dehydroabietic acid, have been found in measurable quantities in sediments on the bottoms of rivers near pulp and paper mills (9, 25–27). These findings support the assumption that the constituents adsorb.

Because they have unsaturated double bonds in their molecules, these acids may also be oxidized by

ABSTRACT

Resin and fatty acids in CTMP effluent are removed by three mechanisms: biooxidation by microorganisms, adsorption onto the biosolids, and air oxidation during aerobic biological treatment. Among these three, biooxidation is the main mechanism. The second mechanism, adsorption, is important when the treatment time is very short. Oxidation by air plays only a marginal role. The adsorption of resin and fatty acids onto the biosolids follows both Langmuir and Freundlich models. The overall resin and fatty acids removal rate follows a zero-order reaction model.

atmospheric oxygen (28). Resin acids can be oxidized by photosensitized air oxidation (29–30) and by nonsensitized air oxidation (31–33) in organic solvents such as hexane and alcohol. Furthermore, aerobic treatment removes resin and fatty acids from pulping effluent more effectively than does anaerobic treatment, in which air is totally absent (34–36). Thus, during aerobic biological treatment, resin and fatty acids may be removed by three mechanisms: biooxidation by microorganisms, adsorption onto the biosolids, and air oxidation.

Proposed model for removal by aerobic biological treatment

We propose a model for resin and fatty acids removals by these three mechanisms during aerobic biological treatment. The model consists of instantaneous adsorption onto sludge, biooxidation by microorganisms, and air oxidation.

In this model, most of the resin and fatty acids in the feed adsorb quickly onto the sludge after contact with mixed liquor suspended solids (MLSS) in the bioreactor. The remaining resin and fatty acids are then removed gradually by both biooxidation and air oxidation. After biooxi-

dation and air oxidation, a part of the adsorbed resin and fatty acids is bio-oxidized by the microorganisms. The remaining adsorbed resin and fatty acids are removed with the excess sludge, which really represents the quantity removed by the adsorption mechanism. The longer the treatment time, the less important should be the removal of resin and fatty acids by adsorption, and the removal by biooxidation will increase accordingly.

KINETICS MODELS

Adsorption isotherm model

Adsorption behavior can be characterized by sorption isotherms, two of the most common being the Langmuir and Freundlich isotherms (37), as expressed by Eqs. 1 and 2, respectively. In this study, we employed both of these two isotherms to characterize the adsorption of resin and fatty acids onto sludge.

Langmuir model:

$$q = q_m bC / (1 + bC) \quad (1)$$

Freundlich model:

$$q = k C^{1/n} \quad (2)$$

where

q = amount of resin and fatty acids (RFA) adsorbed onto a unit mass of dry sludge, mg RFA/g MLSS, or μg RFA/g MLSS

q_m = asymptotic saturation value of q

b = energy-related constant, mg/g MLSS

C = resin and fatty acids concentration in the liquid phase or clarified liquid, mg/L or $\mu\text{g/L}$

k = a constant

n = a constant related to the inter-attraction between molecules in the Freundlich model.

In both models, q (the amount of adsorption per unit dry mass of sludge) in a batch bioreactor is deter-

THICKENED MIXED LIQUOR			
	Untreated CTMP effluent	Liquid phase	Sludge
RFA, mg/L	45	<0.5	1.38–1.78 mg/g
BOD ₅ , mg/L	3000	38	...
COD, mg/L	6200	1220	...
TSS, mg/L	110	...	...
pH	6.5	7.2	7.2

I. Characteristics of the CTMP effluent and the mixed liquor

mined by Eq. 3, using the equilibrium resin and fatty acids concentration C in the liquid.

$$q = [(V_o C_o^* + V_s C_{SL}) - VC] / XV \quad (3)$$

where

V_o = volume of raw CTMP effluent, L

C_o^* = RFA concentration in untreated CTMP effluent

V_s = volume of thickened mixed liquor, L

C_{SL} = RFA concentration in the liquid phase of the thickened mixed liquor, mg/L or $\mu\text{g/L}$

X = MLSS concentration, g/L

V = effective volume of beaker, L.

Overall removal rate of resin and fatty acids

The following zero-order reaction model is used to describe the overall removal rate of resin and fatty acids in the batch biotreatment of the CTMP effluent.

$$(C_o - C) / t = K_o X \quad (4)$$

where

C_o = initial value at C

t = treatment time, h

K_o = zero-order rate constant, mg/(g · h).

EXPERIMENTAL PROCEDURES

Materials

We used the effluent from the washing of CTMP in a mill as the source of resin and fatty acids. The mill produces CTMP for newsprint and coated papers, with a chip mixture composed of roughly 90% black spruce and 10% eastern hemlock. A sample of about 100 L of the effluent was grabbed in a sample tank.

The effluent sample was clarified by settling in the tank for one day. The clarified sample in the upper layer was poured out from the sample tank and filtered through a 500-mesh screen to further remove unsettled fibers and large particles. The filtered effluent (called "untreated effluent" or "CTMP effluent") was finally stored at 4°C. When it was used, the effluent had been stored for about one week.

The characteristics of the effluent sample are listed in Table I. The resin and fatty acids concentration was about 45 mg/L. All the resin and fatty acids standards were purchased from Helix Biotech Corp. (Vancouver, BC, Canada).

In all the experiments, the mixed liquor was taken from an activated sludge reactor used to treat the effluent from the mill. As a result, the microorganisms in the sludge were already acclimated to the effluent sample. The activated sludge reactor was operated at steady state to generate the mixed liquor uniformly for

Mechanism	pH	Temp., °C	MLSS conc., g/L	Aeration rate, L/(L min)*	Aeration time, h	Initial conc. of RFA, C ₀ , mg/L
Air oxidation	7	25	0	0.224	0–96	45.4
Static adsorption	7	25	3	0	0–7.5	10–33.9
Dynamic adsorption	7	25	3	0.224	0–12	32.5
Biooxidation	7	25	3	0.224	0–12	32.5

*Liter of air per liter of reactor effluent per min.

II. Experimental conditions used in the study

use in this study. A long hydraulic residence time of five days was used, with a mean sludge age of around 20 days. Before use, the mixed liquor collected was thickened. The resin and fatty acids concentration in the liquor phase of the mixed liquor was very low (on average less than 0.5 mg/L). The concentration of that adsorbed on the thickened sludge varied between 1.38 mg/g and 1.78 mg/g.

Static air oxidation of resin and fatty acids

Untreated effluent alone was aerated with air in the presence of light in a 3-L clean beaker containing no microorganisms and no nutrients. At the end of each aeration interval, a 100-mL aliquot of the aerated effluent was withdrawn from the beaker. We determined the resin and fatty acids concentrations in both untreated and aerated effluent samples, without centrifugation and filtration. These concentrations were determined in order that we might evaluate the removal of resin and fatty acids by the air oxidation mechanism.

Static adsorption of resin and fatty acids onto sludge

For the determination of static adsorption onto sludge, no biooxidation and air oxidation should take place. Before use, the pH of the untreated effluent was adjusted to 7, and the thickened mixed liquor was aerated for 1 h using nitrogen to

remove the air in the mixed liquor. The experiment was conducted in the same 3-L clean beaker.

According to calculated ratios, untreated effluent was well mixed with the thickened mixed liquor in the beaker. The mixing was done with a magnetic stirrer. To ensure that no air would enter the beaker, we continuously fed a small amount of nitrogen through a diffuser fixed at the bottom of the beaker and covered the top of the beaker with a plastic film. No nutrients were added to the effluent.

At each preselected time, a 100-mL sample of the mixed liquor was withdrawn from the beaker. To prevent aerobic biodegradation of the sample during the lengthy process of clarification through gravity, we separated the liquid and the sludge through filtration.

To avoid the loss of resin and fatty acids in the liquid phase by simple retention on the sludge layer formed during filtration, we first centrifuged the sample in a 150-mL centrifuge glass tube at 1500 rpm for 10 min to separate the liquid and the sludge. The concentration of resin and fatty acids in the liquid sample was then determined. We estimated the concentration of resin and fatty acids adsorbed on the sludge by subtracting the resin and fatty acids in the liquid phase from the total resin and fatty acids in the untreated effluent.

Dynamic adsorption of resin and fatty acids onto sludge

The term “dynamic adsorption” as used here refers to the adsorption of resin and fatty acids onto sludge during aerobic biological treatment. Dynamic adsorption is distinguished from the “static adsorption” of resin and fatty acids in which only adsorption takes place.

We directly determined the amount of dynamic adsorption of resin and fatty acids onto the sludge by analyzing the resin and fatty acids content in the sludge sample from the biotreatment. The experimental procedure we followed was the same as that for the biooxidation of resin and fatty acids, which is described in the next section. In the preparation of the liquid samples, we followed the same procedure used in analyzing the static adsorption.

After collecting the upper layer of clarified liquid, we completely transferred the sludge at the bottom of the tube to a glass fiber filter by washing the tube with 100 mL of distilled water. We filtered this to remove the residual liquid as well as the washing water. The sludge, together with the filtrate, was then ready for solvent extraction.

The total adsorbed resin and fatty acids in the sludge sample was finally determined. The amount of resin and fatty acids in the untreated effluent adsorbed onto the sludge by dynamic adsorption was the differ-

ence between the total resin and fatty acids adsorbed and the resin and fatty acids adsorbed initially on the sludge (static adsorption).

Biooxidation of resin and fatty acids

Untreated effluent, nutrients ($\text{BOD}_5/\text{N/P} = 100/5/1$), and the thickened mixed liquor were mixed in the same 3-L clean beaker. Compressed air was introduced into the beaker through a circular diffusor fixed at the bottom of the beaker at the rate of 0.224 L air/min per liter of effluent in the reactor. The action of air bubbling provided the dissolved oxygen for the growth of microorganisms and supplied good mixing for the contents of the beaker.

At each pre-selected time, a 100-mL sample of mixed liquor was taken. The clarified liquid and sludge samples were prepared as described in the section on static adsorption. The contents of resin and fatty acids in both the clarified liquid and the sludge were determined immediately.

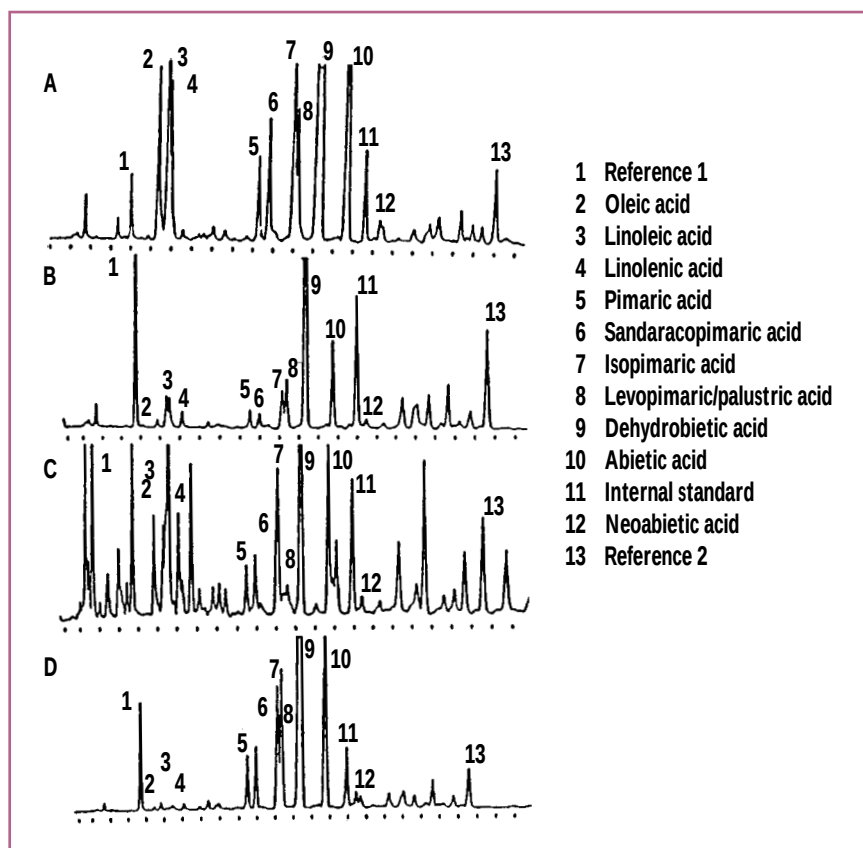
We used these quantities to evaluate both the overall resin and fatty acids removal by the treatment and the removal by the dynamic adsorption onto the sludge. We estimated the biooxidation of resin and fatty acids by subtracting the removals by both dynamic adsorption and static air oxidation from the overall removal.

Experimental conditions and design

Listed in Table II are the experimental conditions for evaluating the removal mechanisms and the overall removal kinetics. In all the experiments, the pH and temperature were automatically controlled at pH 7.0 and 25°C. All the experiments were run in batchwise mode.

Analysis

The concentrations of resin and fatty acids in the CTMP and treated effluents were determined and identified in comparison with standards



1. Chromatograms of resin and fatty acids. (A: untreated CTMP effluent. B: biotreated effluent. C: adsorption onto sludge. D: air-oxidized effluent.)

according to the GC-FID method (38), using a computer-controlled Varian 3600 gas chromatograph and a DB-5 (30 m by 0.53 m) glass Megabore column (Chromatographic Specialties Inc.).

In the step for extracting resin and fatty acids, we modified the solvent size to ensure a complete extraction. We used a larger ratio of solvent to sample of 1.5:1, instead of equal sizes as recommended in the method.

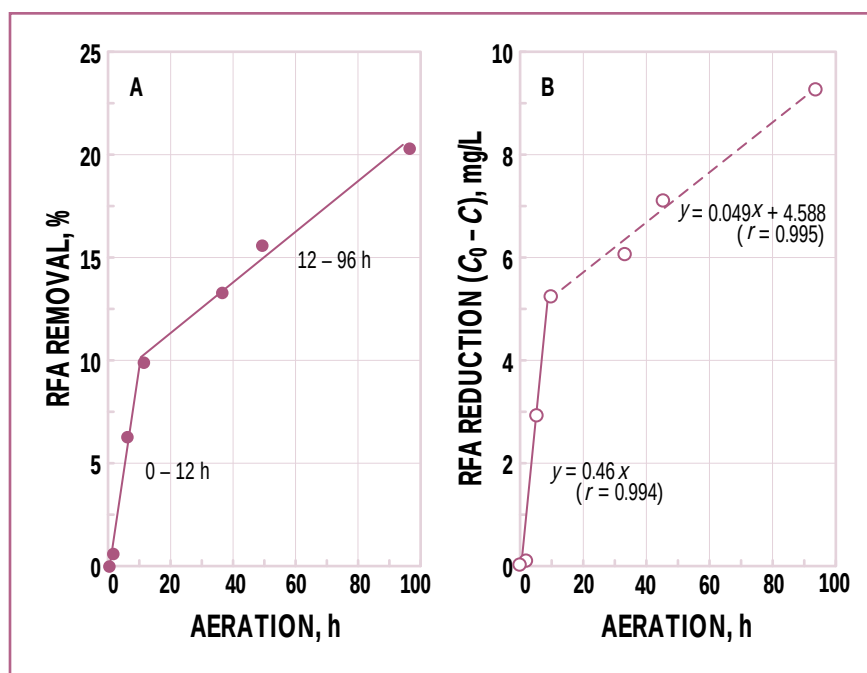
Adsorbed resin and fatty acids were first extracted from the sludge sample in a Soxhlet extraction tube for 24 h with a mixture of acetone and methanol in a ratio of 88:12 (volume:volume) in the presence of hydrochloric acid (39). The extract was then evaporated to dryness in a rotary evaporator.

The resin and fatty acids in the extract were finally analyzed. Concentrations of MLSS, TSS, BOD_5 , and COD in the samples were determined according to CPPA standard methods (H1, H1, H2, and H3.p). (MLSS = mixed liquor suspended solids. TSS = total suspended solids. BOD_5 = biological oxygen demand measured after 5 days, mg/L. COD = chemical oxygen demand, mg/L.)

RESULTS AND DISCUSSION

Mechanisms of removing resin and fatty acids

Figure 1 presents the chromatograms of resin and fatty acids. Chart A is for the untreated CTMP effluent. Chart B is for the treated effluent after 12 h of aerobic biological treatment. Chart C is for the resin and fatty acids adsorbed onto



2. Removal of resin and fatty acids by static air oxidation

the sludge over time (dynamic adsorption). Finally, Chart D is for the oxidation by air after 12 h of aeration.

After 12 h of biotreatment, most of the resin and fatty acids have been removed from the CTMP effluent. In the chromatogram of Chart B for the treated effluent, the peaks are much smaller than those in Chart A for the untreated CTMP effluent.

All the resin and fatty acids identified in the CTMP effluent were also found in large quantities in the sludge sample. The large peaks in the chromatogram of Chart C confirm the adsorption of resin and fatty acids onto the sludge.

After 12 h of static air aeration, the peaks of the fatty acids (Peaks 2, 3, and 4) disappeared, as the chromatograph in Chart D shows by comparison with Chart A. This result indicates that air oxidation of fatty acids would take place in static aeration with air.

As results from the static air oxidation experiments showed, resin

and fatty acids were reduced by about 10% after 12 h of aeration at 0.224 L of air/(min L). This removal could arise from air oxidation or biooxidation or both oxidations, as well as from adsorption on the wall of the beaker and onto the suspended solids in the unaerated effluent.

The adsorption onto the suspended solids should have reached an equilibrium long before the experiment was started, because the untreated effluent had been stored for about one week. The presence of suspended solids should not have a net effect on this removal. As mentioned, the samples of both unaerated and aerated effluents were prepared for analysis in exactly the same way (without filtration).

Since there were no microorganisms (seeds) in the beaker at the beginning of aeration and no nutrients available, the possibility that bacteria would grow in the beaker would be quite small. Thus, any biooxidation of the resin and fatty

acids would be negligible in the test. Furthermore, no significant changes in either COD and TSS concentrations were observed in the test, which also indicates the absence of significant bacterial growth; otherwise, the effluent COD would be measurably lower.

It is likely that resin and fatty acids adsorb on the wall of the beaker in the test. In principal, this adsorption should complete quickly, and there should be a limit for the adsorption. However, as the aeration proceeded, removal gradually and readily increased, without the influence of a limit, as Fig. 2A shows. Therefore, adsorption on the wall cannot characterize the removal rate, and another mechanism contributes to removal. The only possibility left is air oxidation.

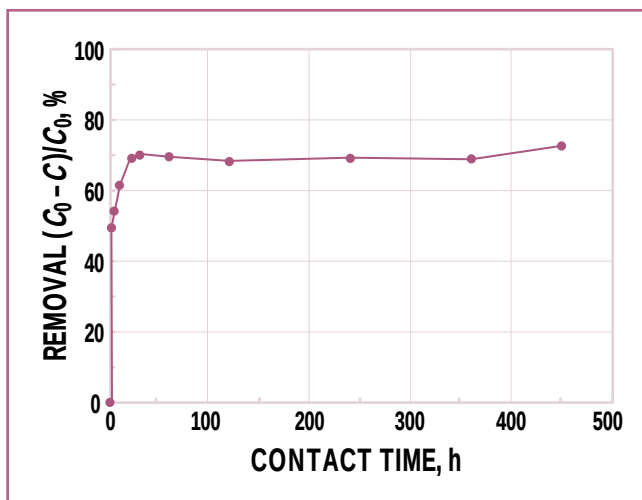
Resin acids can be readily air oxidized in an organic solvent such as hexane or ethanol (29–33). Therefore, this removal should be achieved mainly by air oxidation, confirming the occurrence of the air oxidation mechanism.

These results indicate that resin and fatty acids in the CTMP effluent were also removed by both adsorption onto sludge and air oxidation mechanisms, in addition to biooxidation.

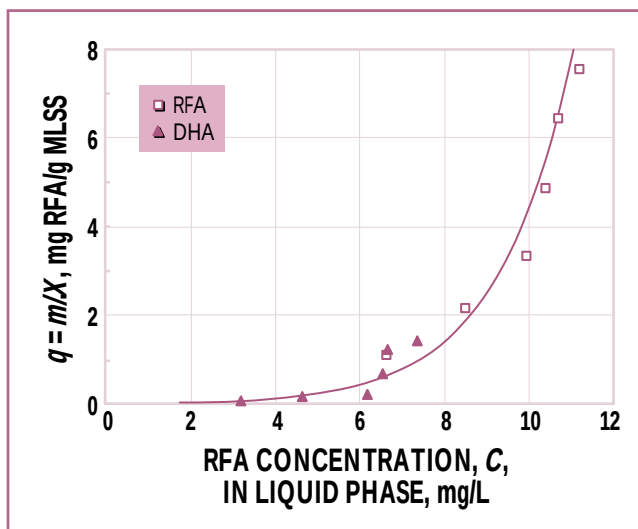
Static air oxidation of resin and fatty acids

Figure 2A presents the resin and fatty acids removals by air oxidation. In general, the air oxidation rate is low. Only about 10% of the resin and fatty acids was removed during a 12-h aeration period. Therefore, we do not consider air oxidation of resin and fatty acids in aerobic biological treatment to be a major mechanism by which resin and fatty acids are removed.

Air oxidation of resin acids initially forms intermediary products, such as transannular peroxides (29–33). These products could be



3. Removal of resin and fatty acids by static adsorption onto sludge (MLSS = 3 g/L, $C_0 = 33.9$, dissolved oxygen = 0 mg/L)



4. Isotherms for resin and fatty acids and for dehydroabietic acid at 25°C for static adsorption onto sludge (MLSS = 3 g/L, time = 2 h, dissolved oxygen = 0 mg/L)

more easily attacked by microorganisms. Thus, the oxygen in biological treatment should play an indirect role in microbiological oxidation, initially modifying the molecular structures of the resin and fatty acids. This effect is in addition to the direct tasks of oxidizing resin and fatty acids and supplying the oxygen for bacterial synthesis.

Under the conditions studied, the air oxidation of resin and fatty acids does not follow the kinetics of a first-order reaction. The air oxidation can be represented well by a zero-order reaction model, implying that the oxidation rate is independent of the resin and fatty acids concentration. However, the oxidation rates were quite different, depending on the aeration time.

As Fig. 2B shows, the oxidation rate within the first 12 h of aeration was about 10 times greater than that within the extended time of aeration. This difference in rates is attributable to the rapid removal of fatty acids in the first hours, as indicated in Fig. 1D.

This result further indicates that no bacterial growth takes place in

the test. Otherwise, the experimental results for the removal rates would be reversed. The bacteria would grow more rapidly the longer the aeration time, and the resin and fatty acids would be removed more and more rapidly as time elapsed.

Schuller (29) and Moore (30) also observed in their studies that the oxidation rate of resin acids was independent of the concentration during photosensitized air oxidation in organic solvents. Our results are in agreement with their findings.

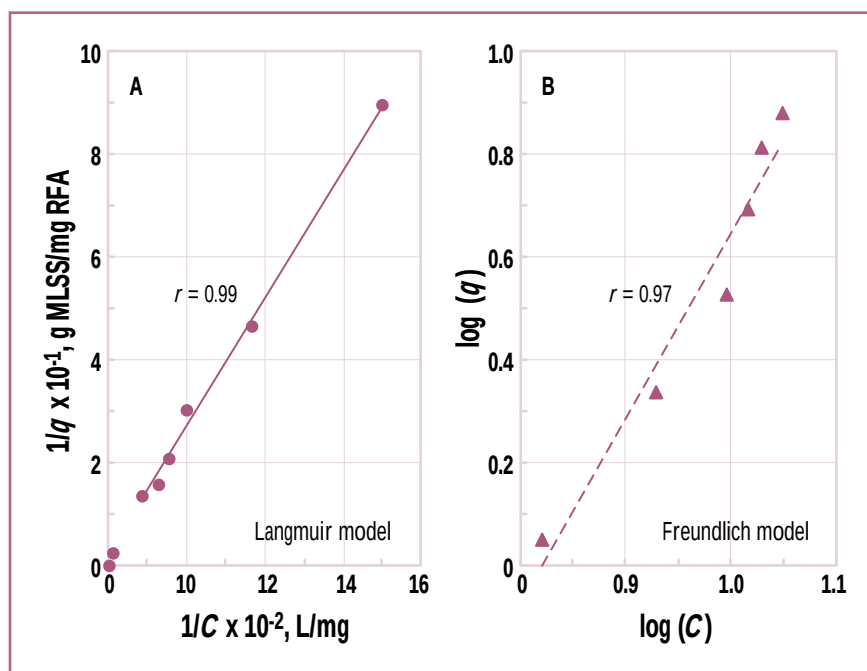
Static adsorption of resin and fatty acids onto sludge

Rate of static adsorption of resin and fatty acids. Hydrophobic organic compounds usually adsorb easily onto soils and sediments (40–44). Hydrophobic organic compounds have also been observed to adsorb onto pulp-derived solids (25). These compounds include chlorophenols and chloroguaiacol, which are generated in pulping and bleaching operations. Resin and fatty acids are hydrophobic and may also adsorb onto biosolids during biological treatment.

To evaluate the adsorption kinetics of resin and fatty acids onto biosolids, we tested the static adsorption of resin and fatty acids in the CTMP effluent using the thickened mixed liquor. The experimental results are presented in Fig. 3. We calculated the initial concentration C_0 of the resin and fatty acids in liquid phase in the beaker from the concentration C_0^* in the untreated effluent and the concentration C_{SL} in the liquid phase of the thickened mixed liquor, using Eq. 5:

$$C_0 = (C_0^* V_0 + C_{SL} V_S) / V \quad (5)$$

As shown in Fig. 3, the adsorption of resin and fatty acids onto the sludge is very rapid at the beginning and is completed within about 30 min of contact time. After 30 min, the adsorption reaches an equilibrium. This adsorption kinetic behavior of resin and fatty acids is quite similar to that of chlorinated organic compounds, or AOX, in bleached kraft mill effluents (45). As the figure shows, as much as 70% of the resin and fatty acids in the effluent has been removed, indicating that



5. Resin and fatty acids isotherm at 25°C, expressed by Langmuir and Freundlich models for static adsorption onto sludge (MLSS = 3 g/L, time = 2 h, dissolved oxygen = 0 mg/L)

	DEAD SLUDGE		ACTIVATED SLUDGE	
	Before	After	Before	After
Liquid	25,923	15,808	24,677	9,845
Sludge	33,952	44,500	40,223	57,390
Total	59,878	60,308	64,900	67,235

III. Balance in static adsorption for resin and fatty acid concentrations, m g/L

adsorption of resin and fatty acids onto sludge would take place.

Because nutrients and oxygen are not available, aerobic biodegradation should not take place. In such an unacclimated environment, the growth of anaerobic bacteria should not occur either; if any growth did take place, it would be negligible within a short period of time (30 min). An anaerobic treatment operated using a very high concentration of acclimated bacteria (10–40 g/L, or even higher) and a treatment time of at least one day usually produces low

removal of resin and fatty acids (34–36), of which a great part would be due to the adsorption onto biosolids. The growth of facultative organisms would most likely occur; however, it would also be quite marginal under the test conditions within such a short time of contact. In fact, no increase in resin and fatty acids removal after 30 min of contact indicates that no significant biodegradation of resin and fatty acids is taking place; otherwise, resin and fatty acids removal would increase continuously. Therefore, biodegradation in

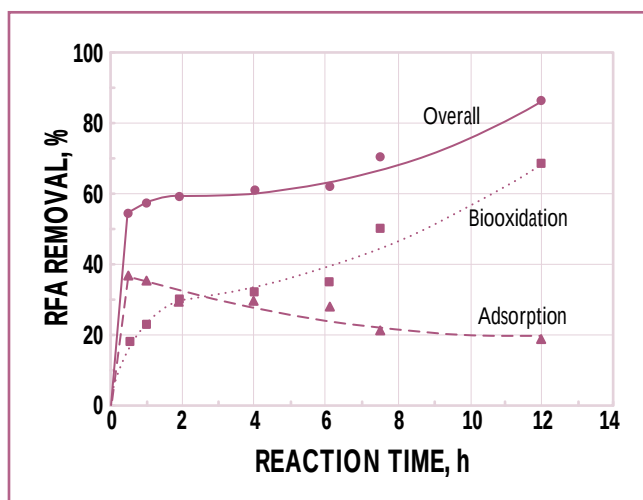
the test should not take place, or, if any did occur, it should be negligible under the testing conditions.

To confirm experimentally that no significant growth of bacteria is occurring, we ran experiments using both dead and live sludge for 2 h of adsorption. The experimental results are presented in Table III. In each of the two cases, we obtained an acceptable balance between the concentrations before and after static adsorption.

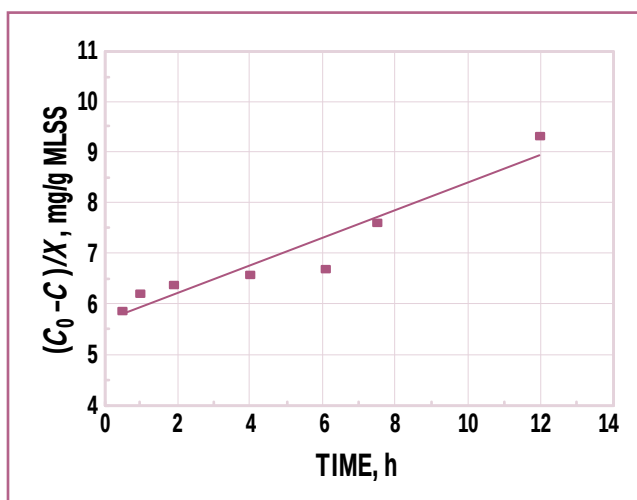
In both cases, however, the total resin and fatty acids in the tested sample after adsorption was a little higher than the total before adsorption. This discrepancy might be caused by experimental error, but it may arise from the amount of resin and fatty acids adsorbed onto the suspended solids in the untreated effluent. Such an amount was not determined before adsorption, because we knew the suspended solids content was low (0.12 g/L). Correspondingly, the amount lost in the liquid phase was also a little less than the amount adsorbed onto the sludge. Again, this similar discrepancy is attributed to the amount of resin and fatty acids adsorbed onto the suspended solids in the untreated effluent.

These results indicate that the removals observed in both cases are achieved by static adsorption alone, confirming the adsorption of resin and fatty acids onto biosolids. Therefore, adsorption onto sludge may be an important mechanism for the removal of resin and fatty acids by aerobic biological treatment of CTMP effluents.

Adsorption isotherm of resin and fatty acids. As an important feature of an adsorption process, the adsorption isotherm describes the equilibrium relationship between adsorbent and adsorbate. To establish the static adsorption isotherm of the resin and fatty acids onto the sludge, we experimented with different ini-



6. Removal of resin and fatty acids by biooxidation, removal by dynamic adsorption onto sludge, and removal by the overall treatment in a batch aerobic bioreactor (MLSS = 3 g/L, aeration = 0.224 L/(L min), $C_0 = 32.5$ mg/L)



7. Kinetics of overall resin and fatty acids removal in batch aerobic treatment (MLSS = 3 g/L, aeration = 0.224 L/(L min), $C_0 = 32.5$ mg/L)

KEYWORDS

Adsorption, aerobic process, bibliographies, biological treatment, chemithermomechanical pulping, effluent treatment, fatty acids, kinetics, mechanics, removal, resin acids, oxidation.

tial concentrations C_0 of resin and fatty acids at a constant temperature with the same amount of sludge. These different initial concentrations were achieved through mixing the untreated CTMP effluent, the thickened mixed liquor, and, if needed, fresh distilled water.

The plot of equilibrium resin and fatty acids concentration in the liquid phase versus q , the corresponding amount of adsorption onto a unit dry mass of sludge, presents the isotherm. Figure 4 presents the isotherms of the resin and fatty acids and dehydroabietic acid at 25°C. As the figure shows, adsorption isotherms for both resin and fatty acids and dehydroabietic acid were quite similar.

The isotherm for resin and fatty acids at 25°C can be represented well

by both the Langmuir and the Freundlich models with correlation coefficients greater than 0.97, as shown in Figs. 5A and 5B. The data for dehydroabietic acid gave similar fits. The value of $1/n$ in the Freundlich model (Eq. 2) was 3.59 for resin and fatty acids in the study; this value is greater than 1. The value of q_m in the Langmuir model for resin and fatty acids has no physical meaning since its value was negative (−1.02 mg/g). Therefore, the actual adsorption mechanisms of the resin and fatty acids onto the sludge may be very complicated.

Biooxidation and dynamic adsorption during aerobic biological treatment

Figure 6 presents the removal of the resin and fatty acids by biooxidation, the removal by dynamic adsorption onto sludge, and the overall removal. We subtracted the removal by adsorption onto sludge from the overall removal to get the removal by biooxidation. Actually, this removal by biooxidation is the sum of the removal by biooxidation and the removal by air oxidation. However, it is impossible to determine the

degree of removal by air oxidation in an aerobic biological treatment. Because the removal by air oxidation was very low, the removal by this mechanism was neglected in the calculation.

As the figure shows, about 20–35% of the resin and fatty acids had been removed by adsorption by the end of the treatment time. Therefore the adsorption mechanism would play a more important role in resin and fatty acids removal in high-rate aerobic treatment in which treatment time is usually very short (a matter of hours). The rest of the total removed was removed by biooxidation and by air oxidation. It is difficult to explain why the removal by dynamic adsorption was much less than that removed by static adsorption.

Both the overall removal and the adsorption of the resin and fatty acids increase rapidly in the first half hour, as Fig. 6 shows. The removal by biooxidation also increases rapidly, probably as a result of the oxidation of the fatty acids. During this 30-min period, the overall removal is mainly due to the adsorption.

From 30 min to 6 h, the removal by biooxidation increases slowly, and the removal by adsorption decreases gradually. There is almost no increase in the overall removal of the resin and fatty acids. The decrease in the removal by adsorption appears to be attributable to the biooxidation of the resin and fatty acids adsorbed on the sludge.

From about 6 to 12 h, the biooxidation increases readily, and the removal by adsorption still decreases. The overall removal increases, following a pattern similar to that of the biooxidation.

Kinetics of overall resin and fatty acids removal

Results obtained in the biooxidation experiment were used for evaluating the kinetics for the overall removal of resin and fatty acids. A number of kinetic models, including the Monod model and the first-order reaction models, were tested for fitting the overall removals observed under the conditions studied.

The best fit was obtained when the overall removal rate was modeled as a zero-order reaction (Eq. 4). Plotted in Fig. 7 is such a fit ($r = 0.96$). The value of K_0 obtained in the study was 0.273 mg/(g MLSS h).

In one of our studies (46), the overall rate of resin and fatty acids removal in a continuous aerobic biotreatment of a CTMP effluent was found to follow a first-order reaction model; the minimum treatment time used for the experiments was 12 h. Different kinetics of substrate removal obtained from batch and continuous cultures, except for the case of very low substrate concentration, were also observed in a study of straw paper wastewater treatment (47). The results from our study thus seem to be in agreement with their findings.

Theoretically, treatment time would produce a significant effect on substrate removal kinetics through substrate concentration (48), which

is time-dependent under a given set of conditions. Taking the Monod kinetic model as an example, we see that the substrate removal rate follows first-order reaction kinetics at a low substrate concentration. This pattern is probably the case in our earlier study (46), in which the concentration of resin and fatty acids in the treated effluent was very low. At a high substrate concentration, however, the removal rate follows a zero-order reaction model. This reaction rate pattern is probably the case with this study, in which the concentration of resin and fatty acids in the treated effluent was high.

Therefore, the differences that arise in the experimental mode (47), particularly as caused by differences in treatment time (48), probably result in different kinetics for the removal rates of resin and fatty acids in our studies.

CONCLUSIONS

The resin and fatty acids in CTMP effluents during aerobic biological treatment are removed by three mechanisms: biooxidation by microorganisms, adsorption onto sludge, and air oxidation.

Biooxidation is the main removal mechanism. Adsorption onto sludge is the primary mechanism, however, when the treatment time is very short. Air oxidation plays a minor role in the elimination of resin and fatty acids.

The adsorption isotherm of resin and fatty acids onto sludge can be represented by both the Langmuir and Freundlich models. The rate of overall removal of resin and fatty acids in batch aerobic biotreatment follows a zero-order reaction model under the conditions studied.

Further work will be carried out to investigate the effects of operating variables such as pH, temperature, treatment time, and microorganism concentration on the resin

and fatty acids removals by each mechanism. TJ

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