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**Estimating the Treatability of Mill Process Streams Using BOD Rate Constants**

Sara J. Cox  
*Western Michigan University*

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ESTIMATING THE TREATABILITY OF MILL PROCESS STREAMS
USING BOD RATE CONSTANTS

BY

Sara J. Cox

A thesis submitted
in partial fulfillment of
the course requirements for
The Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan
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ABSTRACT

This thesis estimates and compares the treatability of several internal mill process streams. This is important to the paper industry due to increasingly stringent regulations being placed on the effluent that is discharged from pulp and paper mills. The treatability of the process streams provides an indication of what processes are most effective on which process streams, identifies the major sources of COD, determines the treatability of the major sources, and will be very useful for emerging regulations regarding internal process streams. Samples from six different process streams within an integrated, bleach kraft mill employing their own wastewater treatment plant were analyzed using COD tests on both filtered and unfiltered samples and BOD tests on filtered samples. The process streams include (1) a blend of three main wastewater streams from the refiner mechanical pulp mill, (2) combined waste streams from the papermachine, coater, and color building, (3) kraft mill brownstock filtrate, (4) bleaching filtrate from kraft mill acid bleaching stages, (5) bleaching filtrate from kraft mill caustic bleaching stages, and (6) a combined influent to secondary treatment (following primary clarifiers). A combination of COD and BOD tests as well as the BOD rate constants were used to estimate the treatability of the different process streams in the mill.

The treatability was estimated by using the BOD test data obtained from the experiment to produce BOD rate constants, k-values, for each of the waste streams. The waste stream from the RMP mill exhibited the highest BOD and COD values, as well as the highest k-value. This indicated that while the RMP mill waste is high in BOD and COD loading, it is more-effectively treated by biological treatment when compared to the other waste streams. The results from this experiment also showed the unfiltered COD to be much higher than filtered COD in the paper machines/coater waste stream. Therefore, it can be deduced that the oxygen demanding materials are in a suspended form in solution and can be removed by filtration. These findings will help the mill to more effectively deal with the waste streams and meet the new environmental regulations.
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INTRODUCTION

In the age of the environmental revolution, strict environmental regulations have been placed on pulp and paper manufacturers. New regulations include the amount of post-consumer waste used in the product, and focus both on the internal and external wastes generated by the company. The effluent produced by the paper mills has historically been monitored to ensure that it is in accordance with regulations. Recently, the EPA has announced the framework for more stringent guidelines for mills to follow. This set of guidelines is known as the “Cluster Rule.” The “Cluster Rule” sets limitations on the nature of the effluent that a mill releases. There are a number of existing parameters that are modified by this new proposal including biochemical oxygen demand (5-day) and total suspended solids, as well as new parameters including chemical oxygen demand, adsorbable organic halides, and dioxins. These new regulations have forced companies to more-closely scrutinize the sources of waste loads and their fate in conventional treatment plants. This paper will focus on internal process stream waste loads and their relative treatability.

In the paper industry, the most convenient way to measure the waste load of the process streams is by measuring the amount of COD (chemical oxygen demand) and BOD (biochemical oxygen demand) present in the sample. The COD tests are used to measure the amount of oxygen required to oxidize the organic and inorganic fraction of a sample by a strong chemical oxidant in an acidic medium at a high temperature. This test is most often performed by mixing a small sample of the waste stream with the contents of a prepared COD vial, heating for two hours under reflux conditions, and titrating the mixture with a solution of FAS (ferrous ammonium sulfate). The contents of the prepared
mixture with a solution of FAS (ferrous ammonium sulfate). The contents of the prepared digestion vial include potassium dichromate to oxidize the organic matter and a silver sulfate catalyst to aid in the oxidation. The principal reaction (unbalanced) is:

\[
\text{Organic matter } C_{n}H_{b}O_{c} + (\text{Cr}_2\text{O}_7^{2-} + \text{H}^{+} \xrightarrow{\text{catalyst \& heat}} \text{Cr}^{3+} + \text{CO}_2 + \text{H}_2\text{O}
\]

Typically, COD values are higher than BOD values for a given waste because more compounds are subject to chemical than biological oxidation (1).

BOD tests are used to measure the amount of oxygen that organisms use to oxidize the dissolved or suspended organic matter in a sample. The quantity reported by this test is the mass of oxygen that the organisms use to metabolize/oxidize the organic matter in a known volume of waste in a specified incubation period (1). In this test, a certain volume of sample is added to a 300ml BOD bottle. Then the bottle is filled to the rim with oxygenated distilled water as well as micronutrients and seed bacteria which has been acclimated to the organic matter or other materials present in the waste. The initial dissolved oxygen is then measured and the bottle is capped. The bottle is then incubated and dissolved oxygen measurements are taken daily. The cumulative BOD values are then used to find the BOD rate constants for each waste stream.

*All materials and laboratory space necessary to execute this experiment were graciously donated by the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI).
BACKGROUND

The samples used in this experiment were obtained from an integrated, bleached kraft mill that employs their own wastewater treatment facility. This facility consists of two clarifiers, a thirty acre aerated stabilization pond, a six acre activated sludge basin, and a seventy acre lagoon. Each process stream is routed from its original process to primary clarification where readily settleable solids are removed by means of clarification (settling). After clarification, the combined wastes move to the aerated stabilization pond where the waste is treated by the use of natural processes involving algae and bacteria. These ponds typically consist of an earthen basin with surface aerators and pumps to provide the necessary oxygen requirements as well as adequate mixing. From the aerated stabilization pond, the waste then moves to the activated sludge basin. In the activated sludge basin, the waste is introduced to an aerobic bacterial culture in a reactor. Diffused or mechanical aeration keeps an aerobic environment within the reactor as well as keeping the contents of the reactor completely mixed. The bacterial culture present in the activated sludge acts on the organic waste material to convert it into new bacterial cells and other end products that can be removed more readily by means of settling. This settling of the mixture of new cells and old cells occurs in the lagoon. Once the solids have been removed, the treated wastewater can then be discharged.

The process streams that were investigated in this experiment include (1) a blend of three main wastewater streams from the refiner mechanical pulp (RMP) mill including filtrate from the disk decker and drum filter as well as chip thickener overflow, (2) combined waste streams from the papermachine, coater, and color building, (3) kraft mill (KM) brownstock filtrate, (4) bleaching filtrate from KM acid bleaching stages, (5)
bleaching filtrate from KM caustic bleaching stages, and (6) a combined influent to secondary treatment (following primary clarifiers). The information obtained about each waste stream will help to show major sources of COD, the treatability of those major sources, and will be useful for emerging regulations regarding internal process streams.
EXPERIMENTAL PROCEDURE

A two liter sample from each of the waste streams was sent in an air-tight plastic container and shipped overnight in coolers from the mill to the NCASI laboratory where the experiment was carried out. The samples of each waste stream were shaken vigorously and a portion of each was removed at this point and refrigerated for later use in the “unfiltered” COD experiment. The remainder of the samples were allowed to settle, refrigerated, for approximately 24 hours. Settling was done in order to simulate the action of the primary clarifiers in the wastewater treatment plant. Samples for the “filtered” COD and BOD tests were then taken by pipetteing the necessary amount of supernatant from each of the samples.

COD TESTS

Approximate COD values of each of the waste streams were available from previous work at the mill. From these values, it was determined that high-range digestion vials would be used. These vials called for a 1ml sample of each of the wastes. The following wastes were then tested:

<table>
<thead>
<tr>
<th>Filtered</th>
<th>Unfiltered</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMP mill</td>
<td>RMP mill</td>
</tr>
<tr>
<td>Kraft mill brownstock</td>
<td>Kraft mill brownstock</td>
</tr>
<tr>
<td>Alkaline stage</td>
<td>Alkaline stage</td>
</tr>
<tr>
<td>Acid stage</td>
<td>Acid stage</td>
</tr>
<tr>
<td>Paper mach./coaters</td>
<td>Paper mach./coaters</td>
</tr>
<tr>
<td>KHP standard</td>
<td>KHP standard</td>
</tr>
<tr>
<td>Blank (deionized water)</td>
<td>Blank (deionized water)</td>
</tr>
<tr>
<td>Combined waste</td>
<td></td>
</tr>
</tbody>
</table>

A sample of filtered combined waste was not used because the combined waste had already undergone clarification. After initial COD testing was performed, it was
determined that the samples from the RMP and alkaline waste streams had already reached their endpoint. Therefore, a smaller amount of sample was necessary. The waste streams were then each mixed with equal parts waste (0.5ml) and deionized water for additional testing.

COD testing was performed in the following manner:

1. The digestion block was preheated to 150°C.
2. 1ml (or 0.5ml) of each sample was pipetted into each of two pre-prepared digestion vials containing potassium dichromate, mercuric sulfate, and sulfuric acid/silver sulfate solution. Duplicates of each sample were performed and the results were averaged. The vials were then capped and mixed by inverting.
3. The vials were then placed in the preheated digestion block for two hours, maintaining a temperature of 150°C.
4. After two hours, the vials were removed from the digestion block, mixed, and allowed to cool to room temperature.
5. Each vial was then titrated in the following manner:
   a. Vial contents were poured into a 125ml Erlenmeyer flask.
   b. Each vial was rinsed twice with deionized water into the flask.
   c. Approximately 40-50ml of deionized water and 2-3 drops of ferroin indicator were added to the flask.
   d. The contents of the 125ml Erlenmeyer flask were then titrated with FAS, from a 10ml microburet, to the dark orange endpoint.
6. Contents of the flask were then discarded into a special COD waste container.
The FAS (ferrous ammonium sulfate) titrant was prepared by dissolving 39.2g Fe(NH₄)₂(SO₄)₂·6H₂O in deionized water, adding 20ml concentrated H₂SO₄, cooling the mixture, and diluting to 1000ml. The FAS was then standardized in order to find the exact molarity of the solution. This was done by titrating two pre-prepared vials with no other contents and averaging the volumes of FAS used in the titration. The molarity of the FAS was then found in the following manner:

\[
\text{Molarity of FAS} = \frac{(1.5 \text{ml } K_2Cr_2O_7 \times .2079)}{\text{ml FAS used in titration}}
\]

This value was then used for calculation of the COD values for each of the samples.

The KHP (potassium hydrogen phthalate) standard was prepared by dissolving 425mg dry KHP in deionized water and diluting the mixture to 1000ml. The theoretical COD of this mixture is 500mg/L. The analysis of this standard allowed for a critique of the COD procedure and performance.

(See Appendix B for calculations)

**BOD TESTS**

From the COD values of each of the waste streams as reported by the mill, BOD₅ values were approximated to be sixty percent of the COD values. This information was then inserted into the following equation using the BOD₅ value as \( y_1 \), 5 days as \( t \), and .2 as \( k \). This made it possible to solve for \( L \), the ultimate BOD. Once this was know, the estimated BOD exerted at day 1 could also be found by using the following equation:

\[
y_t = L(1-e^{-kt})
\]

where: \( y_t = \text{BOD exerted at time } t \)

\( L = \text{ultimate BOD (mg/L)} \)
k = BOD rate constant (assume .2 day⁻¹)

\[ t = \text{time (days)} \]

Once the BOD exerted at day 1 was known, it could be put into the following equation in order to achieve a dilution whose dissolved oxygen content would deplete by 2mg/day:

\[ \text{Xml} \times \left( \frac{y_1}{2000\text{ml}} \right) = 2\text{mg} \]

The following filtered waste samples were then prepared for BOD testing:

<table>
<thead>
<tr>
<th>Waste Stream</th>
<th>Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMP mill</td>
<td>5ml and 10ml (per 2L of dilution water)</td>
</tr>
<tr>
<td>Alkaline stage</td>
<td>5ml and 10ml (per 2L of dilution water)</td>
</tr>
<tr>
<td>Acid stage</td>
<td>20ml and 40ml (per 2L of dilution water)</td>
</tr>
<tr>
<td>KM Brownstock</td>
<td>8ml and 16ml (per 2L of dilution water)</td>
</tr>
<tr>
<td>Paper Mach./Coaters</td>
<td>10ml and 20ml (per 2L of dilution water)</td>
</tr>
<tr>
<td>Combined</td>
<td>5ml and 10ml (per 2L of dilution water)</td>
</tr>
<tr>
<td>Glucose-Glutamic Acid Standard</td>
<td>2% dilution</td>
</tr>
<tr>
<td>Seeded Blanks</td>
<td></td>
</tr>
</tbody>
</table>

BOD testing was performed in the following manner:

1. 30L of room temperature distilled water was aerated for half an hour.
2. The following nutrients were added to distilled water on the order of 1ml/L (or 30ml):
   Phosphate Buffer Solution, Magnesium Sulfate Solution, Calcium Chloride Solution, Ferric Chloride Solution, and Seed Solution.

(The seed used in this experiment was acclimated to this particular waste stream by combining 500ml of a seed solution from a local mill with 500ml of the combined influent, since it contained a portion of all waste streams, and aerating the mixture overnight.)
3. The correct amounts of each waste sample, as stated previously, were then pipetted into a 2L graduated cylinder and filled to the 2L mark with the prepared dilution water.

4. The contents of the 2L graduated were then used to fill six BOD bottles. The bottles were then stoppered, capped, and the initial dissolved oxygen (DO) measurement was taken on one of the bottles.

5. A 2% dilution of glucose-glutamic acid standard was then made by diluting 20ml of the standard with 1L of the dilution water. This solution was poured into three BOD bottles that were stoppered, capped, and the initial DO was measured. The BOD\textsubscript{5} of this sample should be 198 + or - 30.5mg/L. This value can be used to critique the accuracy of the remaining results.

6. The dilution water that was left over (seeded blank) was used to fill another six BOD bottles that were stoppered, capped, and the initial DO was measured.

7. Once the initial DO was measured on all of the samples, the bottles were then incubated at a constant temperature.

8. Daily DO measurements were taken on each of the waste streams and the seeded blanks. The glucose-glutamic acid standard was left undisturbed until day 5 when the dissolved oxygen was measured in order to determine the BOD\textsubscript{5}. After each of the BOD bottles were taken from the incubator and the DO was read, the six bottles of each waste were reaerated in a flask for approximately ten to fifteen minutes. Again, the waste was poured into the BOD bottles which were stoppered, capped, and an initial DO measurement was taken on one of the samples. They were then returned to the incubator. These wastes were monitored daily for thirteen days.
WINKLER TITRATION

The dissolved oxygen meter must be calibrated before any DO measurements can be performed. This was done daily by means of Winkler Titration. Winkler Titration is performed in the following manner:

1. Aerate 1500ml of distilled water at room temperature for 10 minutes.
2. Fill three BOD bottles with the aerated water and stopper. To each of 2 of these bottles,
3. Add 1ml manganous sulfate solution below surface. Rinse pipette in distilled water, shake dry.
4. Add 1ml alkaline iodide azide reagent below surface, rinse pipette, and shake dry.
5. Stopper and mix by inverting several times.
6. Let precipitate settle to half the bottle.
7. Add 1ml concentrated H₂SO₄ (carefully dispense below the surface of the water).
8. Stopper and mix by inverting until precipitate is gone.
9. Fill the special volumetric flask used for this procedure to the blue line, 201ml, with this solution, and pour into the porcelain dish. Titrate to a pale straw color with 0.025N sodium thiosulfate solution. Before all the pale straw color has disappeared, and about 1ml of starch indicator solution, producing a blue color. Continue with the titration until the blue color is gone.
10. Repeat procedure for second bottle.
11. Average the titrant volumes used for the two titrations.
12. For a 200ml sample titration (as done here), mg/L DO = average ml titrant used for the titration.
13. Place the DO meter probe into the third BOD bottle containing the aerated water, and calibrate the meter to the dissolved oxygen value previously calculated.

STATISTICAL ANALYSIS

BOD values for each of the waste streams were calculated using the following equation:

$$BOD_n = \frac{[(D_{n-1} - D_n) - (B_{n-1} - B_n)]}{P}$$

Where:

- $BOD_n = \text{BOD of waste stream on day } n \text{ (mg/L)}$
- $D_{n-1} = \text{DO of diluted sample on previous day}$
- $D_n = \text{DO of diluted sample on day } n$
- $B_{n-1} = \text{DO of seeded blank on previous day}$
- $B_n = \text{DO of seeded blank on day } n$
- $P = \text{dilution factor (ml of sample added to flask divided by flask volume)}$

Once the daily BOD values are found for each waste stream, the cumulative BOD values can be calculated. These cumulative BOD values as well as their respective days can be entered in the BODCGA BASIC computer program in order to find the BOD rate constant value ($k$) and ultimate BOD value ($L$) for each waste stream. Since two dilutions of each waste were used, the averages of the values were reported.
RESULTS & DISCUSSION

OVERALL COMPARISON

The raw data from this experiment can be found in Appendix A and sample calculations for each of procedures outlined in this experiment can be found in Appendix B. The results containing average values of the unfiltered COD, filtered COD, filtered BOD, and k-values can be seen in figure 1.

<table>
<thead>
<tr>
<th>Waste Stream</th>
<th>Unfiltered COD (mg/L)</th>
<th>Filtered COD (mg/L)</th>
<th>BOD₅ (mg/L)</th>
<th>Ultimate BOD (mg/L)</th>
<th>k-value (day⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMP mill</td>
<td>4350</td>
<td>4291</td>
<td>2101</td>
<td>2494.7</td>
<td>.3693</td>
</tr>
<tr>
<td>KM Alkaline</td>
<td>2428</td>
<td>2420</td>
<td>475</td>
<td>579.7</td>
<td>.2283</td>
</tr>
<tr>
<td>KM Brvnstk.</td>
<td>1195</td>
<td>1099</td>
<td>433.3</td>
<td>646</td>
<td>.2216</td>
</tr>
<tr>
<td>KM Acid</td>
<td>1106</td>
<td>1032</td>
<td>227.1</td>
<td>372.7</td>
<td>.1881</td>
</tr>
<tr>
<td>Combined</td>
<td>973</td>
<td>201.1</td>
<td>201.1</td>
<td>299.4</td>
<td>.239</td>
</tr>
<tr>
<td>P.M./Coater</td>
<td>713</td>
<td>126</td>
<td>25.6</td>
<td>75.2</td>
<td>.1181</td>
</tr>
</tbody>
</table>

Figure 1. Averaged totals from all experiments

The graph entitled “Comparison of BOD and COD Values for All Process Streams” as seen in Figure 2 on the following page gives a good overview of the results from this experiment. From this graph it can be seen that the RMP Mill has significantly higher COD and BOD values than the other waste streams. Refiner mechanical pulping involves shredding and defibering wood chips by means of a refiner with rotating discs. The fibers are then combined with water to make a slurry. Since there are no other significant additives to the fibers at this point, it can be deduced that the majority of the waste stream from the RMP mill is composed of fibers and fines. It can be further deduced from this
Comparison of BOD and COD Values for All Process Streams

Process Streams

- RMP Mill
- KM Alkaline
- KM Brownstock
- KM Acid
- Combined
- Paper
- Machine/Coaters

Values (mg/L)

- Unfiltered COD
- Filtered COD
- UBOD
- BOD5
observation that fibers and fines have a considerable amount of COD and BOD associated with them.

Investigating the same graph, it can be seen that the KM Alkaline waste stream is the next largest generator of COD and BOD. The KM Brownstock and KM Acid waste streams exhibited BOD values only slightly lower than that of the KM Alkaline waste stream. The kraft process acts to delignify wood chips by the means of a strongly alkaline solution of sodium hydroxide. After digestion, the wood chips are discharged from a digester into a blow tank where they are disintegrated into fibers (2). The chips are then washed with water. This water, which likely contains a certain amount of the sodium hydroxide used in the kraft process and some fines or fibers, then becomes the KM Brownstock waste stream. Once the pulp has been screened and cleaned, it must undergo bleaching to achieve the high brightness necessary at this mill. Two stages of bleaching, alkaline and acid, are employed at this mill. The first in this bleaching sequence is the acidic chlorination of the pulp. This employs blending the pulp with a chlorine-water mixture. The pulp is again washed at this point to ensure that no acid is carried over to the alkaline (caustic) stage (this may neutralize some of the caustic) (2). The filtrate from this washing, termed the KM Acid waste stream, likely contains the chlorine used in the acid bleaching stage. The next step in the bleaching process, alkaline extraction, acts to remove the chlorine and oxidized lignin by solubilization (2). From this information, it can be presumed that the filtrate from this stage, KM Alkaline waste stream, contains a fair amount of caustic, lignin and residual chlorine. Since chlorine is present in both the KM Alkaline and KM Acid waste streams, the larger COD values attributed to the KM Alkaline waste stream must not be due to the presence of the chlorine. It can be further
assumed that the high COD values associated with the KM Alkaline waste stream are due to the caustic used in the process or the lignin removed from the process.

The amount of BOD that can be attributed to the paper machines and coater waste streams appears to be almost negligible when compared to that of the other waste streams. However, it does show a significant amount of unfiltered COD. At the papermachine, the pulp slurry as well as any additives that could have been used for a particular type of paper is applied to the wire. At this point, a large amount of water is removed from the pulp in order for the sheet to form. Any additives that were in the pulp slurry that were not retained during sheet formation, as well as any fines that may have passed through the screen, could be present in the paper machine waste stream. Some additives may include sizing agents, fillers, dyes, retention aids, biocides, and other chemicals. It is not known what additives were present in this particular wastewater. The paper machine waste stream was then combined with that of the coaters. The contents of the coater wastewater could include pigments such as clay, calcium carbonate, titanium dioxide, starch, polymers, silicates, etc., all of which improve the surface properties of the final sheet of paper. Unfortunately, it is not known exactly what was present in this particular sample.

Looking at the BOD and COD values from the combined waste streams, it seems as though mixing the streams caused a decrease in the unfiltered COD. This could be due to chemical reactions between the respective waste streams or dilution from the paper machines/coater waste streams. A measure of the unfiltered COD for the combined waste streams was not taken because it had already undergone clarification.
COD TEST RESULTS

The values from the COD tests can be seen in Figure 1 on page 12. The reliability of these results can be analyzed by considering the KHP values obtained when testing was performed. The known value of the KHP indicator was 500mg/L. The experimentally-determined COD value for the KHP indicator was found to be 520mg/L (4% error). This indicates that the results from the COD testing can be considered quite reliable.

The graph titled “Comparison of Unfiltered and Filtered COD Values” can be found in Figure 3 on the following page. From this graph, it can be seen the RMP mill is the major source of COD, both filtered and unfiltered, in the mill. It can also be seen from this graph that there is not a large difference between the filtered and unfiltered samples within each waste stream (RMP mill, KM Alkaline, KM Brownstock, and KM Acid). This indicates that the wastes present in the stream that are accountable for the COD are not being filtered out. In other words, the majority of the COD present in these waste streams is dissolved in the solution. When looking at the COD values from the paper machines/coater waste stream, it can be seen that the unfiltered COD value is more than twice that of the filtered COD value. This indicates that the waste associated with the majority of the COD is in suspended form and can be settled out by filtration or clarification.

BOD TEST RESULTS

The results of the BOD testing can be found in Figure 1 on page 12. The accuracy of these tests can be analyzed by considering the BOD₅ value of the glucose-glutamic acid standard. The BOD₅ of this standard was known to be 198 ± or - 30.5mg/L. The experimentally-determined value of the standard was found to be
Comparison of Unfiltered and Filtered COD Values

Figure 3:
200mg/L. This indicates that the data from the BOD tests can be considered quite accurate.

It is apparent from the graph titled “Comparison of BOD₅ and Ultimate BOD Values”, Figure 4 on the following page, that the major source of BOD is the RMP mill. As expected, for all waste streams, the ultimate BOD is slightly higher than that of BOD₅. Oxidation is only about 60% complete at this time. Therefore, the BOD₅ value will be approximately 60% of the ultimate BOD value, which is the oxygen demand of the waste after about 99% of the material has been oxidized.

The low BOD values for the paper machines/coater waste stream is cause for speculation. When investigating what type of materials could be present in the waste stream, it was speculated that biocides or another type of additive could have caused the waste stream to be toxic. This would have poisoned the seed, causing the BOD to appear smaller than it actually is. The oxygen demand of the waste would have been reduced because the seed was not alive to break down the waste, thus demanding oxygen. It is also possible that this waste stream was low in BOD because the materials that had a higher oxygen demand were removed by filtration. This seems to be a more likely reason since the COD value was so much higher for the unfiltered sample than the filtered sample of the same waste.

TREATABILITY

The treatability of a particular waste stream is proportional to BOD rate constant known as the k-value associated with that stream. It is related to how quickly a waste exhibits its oxygen demand and is dependent on the nature of the waste, the ability of the organisms in the system to utilize the waste, and the temperature of the system. The
Comparison of BOD5 and Ultimate BOD Values

![Bar chart showing BOD values for different process streams. The chart compares BOD5 and Ultimate BOD (UBOD) for RMP, KM Bronst, KM Alk, KM Acid, Combined, Paper, and Mach./Costers processes.]
oxygen uptake will vary with time and with different reaction-rate constant values for the same ultimate BOD (1). It is more advantageous to have a waste stream with a higher k-value because that indicates that the waste exhibits its oxygen demand quicker, thus allowing for more complete biological treatment. The k-values for each waste stream, as seen in Figure 1 on page 12 were determined by entering the cumulative BOD values with their respective days into a BASIC program called BODCGA. The printouts from the BODCGA program can be found in Appendix C and a graphical representation, titled “BOD Rate Constants for Each Process Stream,” can be found in Figure 5 on the following page. From this graph, the waste streams can be ranked in order of highest k-value to lowest as follows: (1) RMP mill, (2) combined (3) KM Alkaline, (4) KM Brownstock, (5) KM Acid, (6) Paper machine/coaters. These results indicate that the RMP mill waste stream, while exhibiting the highest BOD and COD values, is the most treatable. The combined waste streams are also seen to be highly treatable. In contrast, the waste stream from the paper machines/coaters, though it is lower in BOD and filtered COD values than the other waste streams, is less treatable. This is good news for the paper mill since the stream that contributes the most (RMP mill) is the most-readily treatable and the combined waste stream, as it enters secondary treatment, is also highly treatable. If the waste stream from the RMP mill had a low k-value, such as that of the paper machines/coater, then it would be more difficult to handle and treat the waste.
Figure 5:

**BOD Rate Constants for Each Process Stream**

![Bar chart showing BOD rate constants for different process streams: RMP, Combined, Km Bovnst, KM Acid, Paper Mach / Coaters. The x-axis represents the process streams, and the y-axis represents the k-value (day⁻¹). RMP has the highest k-value, followed by Combined, Km Bovnst, KM Acid, and Paper Mach / Coaters.]
CONCLUSIONS

The results from this experiment lead to a number of conclusions. By determining k-values of individual waste streams within a mill, it is possible to estimate their treatability. In this particular mill, the waste stream from the RMP mill was seen to have the highest BOD and COD values. However, the RMP mill waste stream also showed the highest k-value, indicating a higher treatability than the other waste streams. Another conclusion that can be made from this experiment is that clarification has the biggest impact on the COD of the paper machines/coater waste streams than other waste stream. Therefore, the material present in the paper machines/coater waste stream that exhibit the high COD must be suspended in the mixture, thus able to be removed during filtration. The results from this experiment will help the mill to more effectively deal with the waste streams and meet new regulations regarding these streams.

RECOMMENDATIONS

For further research, it would be helpful to investigate the RMP mill and paper machine/coater waste streams more thoroughly since these were seen to give the highest and lowest BOD, COD, and k-values. As opposed to using the BOD tests to find the k-values of each waste stream, it may be helpful to set up a bench-top bioreactor. This would more closely simulate the action of the biological treatment in the mill.
LITERATURE CITED

1. Metcalf & Eddy, Inc., Wastewater Engineering: Treatment, Disposal, and Reuse

2. Gary A. Smook, Handbook for Pulp and Paper Technologists (Vancouver, Angus
APPENDIX A

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</tbody>
</table>

Waste: PM/Coaters (10ml/2L)

<table>
<thead>
<tr>
<th>Bottle #:</th>
<th>228A</th>
<th>25</th>
<th>259A</th>
<th>58A</th>
<th>187B</th>
<th>23A</th>
</tr>
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<tbody>
<tr>
<td>Day</td>
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<tr>
<td>Final DO</td>
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<tr>
<td>Av. Final(Dn)</td>
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<td>Initial DO(Dn-1)</td>
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<td>Delta D</td>
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<td>B(n-1)</td>
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<tr>
<td>Delta B</td>
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<td>BODn</td>
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<tr>
<td>Cum. BOD</td>
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Waste: Combined (5ml/2L)

<table>
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<th>Bottle #:</th>
<th>317A</th>
<th>39B</th>
<th>152A</th>
<th>316B</th>
<th>277</th>
<th>260</th>
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<td>Final DO</td>
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<tr>
<td>Av. Final(Dn)</td>
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<tr>
<td>Initial DO(Dn-1)</td>
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<td>Delta D</td>
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<td>B(n-1)</td>
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<tr>
<td>Delta B</td>
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<tr>
<td>Cum. BOD</td>
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<td>Day</td>
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<tr>
<td>18-Mar</td>
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<td>7.6</td>
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<td>7.9</td>
<td>7.9</td>
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<td>7.7</td>
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<td>7.7</td>
<td>7.7</td>
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<tr>
<td>21-Mar</td>
<td>7.5</td>
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<td>7.4</td>
<td>7.4</td>
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<td>22-Mar</td>
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<td>8.1</td>
<td>8.1</td>
<td>8.1</td>
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<td>23-Mar</td>
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<td>8.3</td>
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<td>8.3</td>
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<tr>
<td>24-Mar</td>
<td>7.7</td>
<td>7.7</td>
<td>7.7</td>
<td>7.7</td>
<td>7.8</td>
<td>7.7</td>
</tr>
</tbody>
</table>
APPENDIX B

SAMPLE CALCULATIONS
Determination of correct dilution:

\[ y_t = L(1-e^{(-kt)}) \]

Where: \( y_t = \) amt. of BOD exerted at time \( t \), mg/L

\[ L = \text{ultimate BOD, mg/L} \]

\[ k = \text{reaction rate constant, day}^{-1} \]

\[ t = \text{time, days} \]

For KM Brownstock; with \( \text{BOD}_5 = 1723 \text{ mg/L} \), \( k = .2 \text{ day}^{-1} \), \( t = 5 \text{ days} \)

\[ \text{BOD}_1 = 2725.7(1-e^{(-.2*1)}) = 494.1 \text{ mg/L} \]

\[ X \text{ ml (dilution)} \times \left( \frac{494.1 \text{ mg/L}}{2000 \text{ mg/L}} \right) = 2 \text{ mg/L} \]

\[ X = 8 \text{ ml} \quad \frac{8}{2000} = .004 = .4\% \text{ dilution} \]

\[ X \text{ ml (dilution)} \times \left( \frac{494.1 \text{ mg/L}}{2000 \text{ mg/L}} \right) = 4 \text{ mg/L} \]

\[ X = 16 \text{ ml} \quad \frac{16}{2000} = .008 = .8\% \text{ dilution} \]

For glucose-glutamic acid standard:

\[ .02 = 2\% \text{ dilution} = \left( \frac{X}{1000L} \right) \]

\[ X = 20 \text{ ml} \]

Calculation of \( \text{BOD}_n \):

\[ \text{BOD}_n (\text{mg/L}) = \frac{((\text{D}_n-1) - \text{D}) - ((\text{B}_n-1) - \text{B})}{P} \]

Where: \( \text{D}_n-1 = \) initial dissolved oxygen of diluted sample, mg/L

\( \text{D}_n = \) average final dissolved oxygen of diluted sample, mg/L

\( \text{B}_n-1 = \) initial dissolved oxygen of seeded blank, mg/L

\( \text{B}_n = \) average final dissolved oxygen of seeded blank, mg/L

\( P = \) decimal volumetric fraction of sample used

For KM brownstock (16ml) at day 13:

\[ \text{BOD}_{13} = \frac{(8.4 - 7.62) - (8.3 - 7.8)}{16/2000} = 35 \text{ mg/L} \]
For glucose-glutamic acid:

\[
\text{BOD}_5 = \frac{(8.0 - 3.1) - (8.7 - 7.8)}{20/1000} = 200 \text{ mg/L}
\]

Calculation of COD:

\[
\text{COD (mg O}_2/\text{L}) = \frac{(A - B) \times M \times 8000}{\text{ml of sample}}
\]

Where:  
A = ml FAS used for blank  
B = ml FAS used for sample  
M = molarity of FAS

Molarity of FAS = \[
\frac{1.5 \text{ ml } K_2Cr_2O_7 \times 0.2079}{\text{ml FAS used in titration}}
\]

\[
= \frac{1.5 \times 0.2079}{3.36} = 0.0928
\]

For unfiltered KM brownstock:

\[
\text{COD} = \frac{(3.32 - 1.71) \times 0.0928 \times 8000}{1} = 1195 \text{ mg/L}
\]
TITLE$="KM Brownstock (8ml)"
ND= 8

<table>
<thead>
<tr>
<th>TIME</th>
<th>OBOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>165</td>
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<tr>
<td>3</td>
<td>425</td>
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<tr>
<td>4</td>
<td>555</td>
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<tr>
<td>5</td>
<td>590</td>
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<td>6</td>
<td>600</td>
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<tr>
<td>7</td>
<td>600</td>
</tr>
<tr>
<td>8</td>
<td>630</td>
</tr>
</tbody>
</table>

TIME ( 1 ) = 1 : OBOD ( 1 ) = 75 : TIME ( 2 ) = 2 : OBOD ( 2 ) = 165
TIME ( 3 ) = 3 : OBOD ( 3 ) = 425 : TIME ( 4 ) = 6 : OBOD ( 4 ) = 565
TIME ( 5 ) = 7 : OBOD ( 5 ) = 590 : TIME ( 6 ) = 8 : OBOD ( 6 ) = 600
TIME ( 7 ) = 9 : OBOD ( 7 ) = 600 : TIME ( 8 ) = 13 : OBOD ( 8 ) = 630

if any mistake, move your cursor and modify
After modification is done, type CONT
break in 5220

if not strike ENTER
enter file name ... ?

Enter first guess of k ... ? .1
second guess ... ? .2
1  .2558002
2  .2326591
3  .2344712
4  .2345675

TERATION CONVERGED
K  =   .2345675
UBOD  =   697.6318
SUM OF SQUARES  =  23201.05
TITLE$="KM Brownstock (16ml)"
ND= 8

TIME( 1 ) = 1 : OBOD( 1 ) = 68.7 : TIME( 2 ) = 2 : OBOD( 2 ) = 168.7
TIME( 3 ) = 3 : OBOD( 3 ) = 298.7 : TIME( 4 ) = 6 : OBOD( 4 ) = 443.7
TIME( 5 ) = 7 : OBOD( 5 ) = 468.7 : TIME( 6 ) = 8 : OBOD( 6 ) = 488.7
TIME( 7 ) = 9 : OBOD( 7 ) = 501.2 : TIME( 8 ) = 13 : OBOD( 8 ) = 536.2

If any mistake, move your cursor and modify
After modification is done, type CONT
Break in 5220
Ok

If not strike ENTER
Enter file name ... ?

Enter first guess of k ... ? .1
second guess ... ? .2
1
2
3

ITERATION CONVERGED
K = 0.2085523
UBOD = 594.3373
SUM OF SQUARES = 4441.072

TO continue, Strike a key
TITLE$="KM Acid (20ml)"
ND=8

TIME( 1 )=1 : OBOD( 1 )=50 : TIME( 2 )=2 : OBOD( 2 )=84
TIME( 3 )=3 : OBOD( 3 )=168 : TIME( 4 )=6 : OBOD( 4 )=258
TIME( 5 )=7 : OBOD( 5 )=270 : TIME( 6 )=8 : OBOD( 6 )=280
TIME( 7 )=9 : OBOD( 7 )=288 : TIME( 8 )=13 : OBOD( 8 )=332

If any mistake, move your cursor and modify
After modification is done, type CONT
Break in 5220
Ok

If not strike ENTER
Enter file name ... ?
Enter first guess of k ... ? .1
second guess ... ? .2

1 .1716872
2 .1770836
3 .1774242
4 .1774188

ITERATION CONVERGED
K = .1774188
UBOD = 371.4827
SUM OF SQUARES = 1375.515

TO continue, Strike a key
TLE$="KM Acid (40ml)"
= 8

ME( 1 ) = 1 : OBOD( 1 ) = 55 : TIME( 2 ) = 2 : OBOD( 2 ) = 87
ME( 3 ) = 3 : OBOD( 3 ) = 199 : TIME( 4 ) = 6 : OBOD( 4 ) = 267
ME( 5 ) = 7 : OBOD( 5 ) = 284 : TIME( 6 ) = 8 : OBOD( 6 ) = 297
ME( 7 ) = 9 : OBOD( 7 ) = 309 : TIME( 8 ) = 13 : OBOD( 8 ) = 342

any mistake, move your cursor and modify
after modification is done, type CONT
break in 5220

not strike ENTER
after file name ... ?

enter first guess of k ... ? .1
second guess 
... ? .2

.1987042
.1990419
.1990428

ERATION CONVERGED
K = .1990428
UBOD = 373.9631
SUM OF SQUARES = 2461.372

TO continue, Strike a key
TLE$="KM Alkaline (5ml)"
I= 8
ME( 1 ) = 1 : OBOD( 1 ) = 86.7 : TIME( 2 ) = 2 : OBOD( 2 ) = 166.7
ME( 3 ) = 3 : OBOD( 3 ) = 254.7 : TIME( 4 ) = 6 : OBOD( 4 ) = 518.7
ME( 5 ) = 7 : OBOD( 5 ) = 526.7 : TIME( 6 ) = 8 : OBOD( 6 ) = 526.7
ME( 7 ) = 9 : OBOD( 7 ) = 526.7 : TIME( 8 ) = 13 : OBOD( 8 ) = 526.7

begin any mistake, move your cursor and modify

iterate modification is done, type CONT
reak in 5220

\not strike ENTER
\iter file name ... ?

\iter first guess of k ... ? .1
  second guess ... ? .2

\l .2249626
\? .2163914
\} .2167474
\{ .2167554

\TERATION CONVERGED
  K = .2167554
  UBOD = 618.3791
  SUM OF SQUARES = 15377.84

TO continue, Strike a key
TITLE$="KM Alkaline (10ml)"

ID = 8

TIME(1) = 1 : OBOD(1) = 140
TIME(2) = 2 : OBOD(2) = 260

TIME(3) = 3 : OBOD(3) = 408
TIME(4) = 6 : OBOD(4) = 620

TIME(5) = 7 : OBOD(5) = 644
TIME(6) = 8 : OBOD(6) = 664

TIME(7) = 9 : OBOD(7) = 680
TIME(8) = 13 : OBOD(8) = 720

If any mistake, move your cursor and modify
After modification is done, type CONT
break in 5220
ok

If not strike ENTER
Enter file name ...?

Enter first guess of k ...? .1
second guess ...? .2
1 .2639046
2 .2375449
3 .2397342
4 .2398548
5 .2398548
ITERATION CONVERGED
K = .2398548
UBOD = 774.3156
SUM OF SQUARES = 3471.114

TO continue, Strike a key
ITEM$="RMP (5ml)"
D= 8

TIME ( 1 ) = 1 : OBOD ( 1 ) = 1000 : TIME ( 2 ) = 2 : OBOD ( 2 ) = 1224.8
TIME ( 3 ) = 3 : OBOD ( 3 ) = 1584.8 : TIME ( 4 ) = 6 : OBOD ( 4 ) = 2104.8
TIME ( 5 ) = 7 : OBOD ( 5 ) = 2272.8 : TIME ( 6 ) = 8 : OBOD ( 6 ) = 2352.8
TIME ( 7 ) = 9 : OBOD ( 7 ) = 2384.8 : TIME ( 8 ) = 13 : OBOD ( 8 ) = 2504.8

If any mistake, move your cursor and modify
iteration modification is done, type CONT
reak in 5220

not strike ENTER
enter file name ... ?
enter first guess of k ... ? .1
second guess ... ? .2

.7480215
.323479
.3623266
.3687915
.3683504
.3683539

ERATION CONVERGED
K = .3683539
UBOD = 2465.085
SUM OF SQUARES = 77641

TO continue, Strike a key
RMP (10ml)

\[
\begin{align*}
\text{TIME(1)} &= 1 : \text{OBOD(1)} = 943.3 \\
\text{TIME(2)} &= 2 : \text{OBOD(2)} = 1255.3 \\
\text{TIME(3)} &= 3 : \text{OBOD(3)} = 1711.3 \\
\text{TIME(4)} &= 6 : \text{OBOD(4)} = 2151.3 \\
\text{TIME(5)} &= 7 : \text{OBOD(5)} = 2319.3 \\
\text{TIME(6)} &= 8 : \text{OBOD(6)} = 2387.3 \\
\text{TIME(7)} &= 9 : \text{OBOD(7)} = 2427.3 \\
\text{TIME(8)} &= 13 : \text{OBOD(8)} = 2591.3
\end{align*}
\]

If any mistake, move your cursor and modify
After modification is done, type CONT
Break in 5220

If not strike ENTER
Enter file name ... ?

Enter first guess of k ... ? .1
   second guess ... ? .2
\[
.7816908 \\
.3216072 \\
.3629066 \\
.3707942 \\
.3701796 \\
.3701858
\]

\text{ITERATION CONVERGED}
\[
\begin{align*}
K &= .3701858 \\
\text{UBOD} &= 2524.237 \\
\text{SUM OF SQUARES} &= 48742.1
\end{align*}
\]

TO continue, Strike a key
TLE$="PM/Coaters (20ml)"
= 7

ME( 1 ) = 1 : OBOD( 1 ) = 3.33 : TIME( 2 ) = 2 : OBOD( 2 ) = 3.33
ME( 3 ) = 5 : OBOD( 3 ) = 27.33 : TIME( 4 ) = 6 : OBOD( 4 ) = 27.33
ME( 5 ) = 7 : OBOD( 5 ) = 31.33 : TIME( 6 ) = 8 : OBOD( 6 ) = 31.33
ME( 7 ) = 12 : OBOD( 7 ) = 31.33 : TIME( 8 ) = 0 : OBOD( 8 ) = 0

any mistake, move your cursor and modify
ter modification is done, type CONT
reek in 5220

not strike ENTER
ter file name ... ?
ter first guess of k ... ? .1
second guess ... ? .2
K = .1672523
.1729222
.1733334
.1733266
ERATION CONVERGED
K = .1733266
UBOD = 40.16945
SUM OF SQUARES = 124.4373

TO continue, Strike a key
If any mistake, move your cursor and modify
After modification is done, type CONT
Leak in 5220
Ok

If not strike ENTER
Enter file name ... ?

Enter first guess of k ... ? .1
second guess ... ? .2
6.980623E-02
.0593351
3
.0529075
4
5.237503E-02
5.235776E-02

ITERATION CONVERGED
K = 5.235776E-02
UBOD = 114.0777
SUM OF SQUARES = 665.8658

TO continue, Strike a key
any mistake, move your cursor and modify
any modification is done, type CONT
back in 5220

not strike ENTER

er file name ... ?

er first guess of k ... ? .1

second guess ... ? .2

.1547604
.1612063
.1619082
.1618935

RATION CONVERGED
K = .1618935
UBOD = 306.4048
SUM OF SQUARES = 601.5295

TO continue, Strike a key
TITLE$="Combined (10ml)"

\[ \begin{align*}
\text{TIME}(1) &= 1 : \text{OBOD}(1) = 60 \quad \text{TIME}(2) = 2 : \text{OBOD}(2) = 120 \\
\text{TIME}(3) &= 3 : \text{OBOD}(3) = 208 \quad \text{TIME}(4) = 6 : \text{OBOD}(4) = 260 \\
\text{TIME}(5) &= 7 : \text{OBOD}(5) = 260 \quad \text{TIME}(6) = 8 : \text{OBOD}(6) = 260 \\
\text{TIME}(7) &= 9 : \text{OBOD}(7) = 260 \quad \text{TIME}(8) = 13 : \text{OBOD}(8) = 296
\end{align*} \]

If any mistake, move your cursor and modify
After modification is done, type CONT
Press in 5220

not strike ENTER

Enter file name ... ?

Enter first guess of k ... ? .1
second guess ... ? .2

.4938849
.2821158
.3081231
.3167385
.3161121
.3161221

OPERATION CONVERGED
K = .3161221
UBOD = 292.2511
SUM OF SQUARES = 2015.655

TO continue, Strike a key