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BOD and COD Loading Effects of Repeatedly Recycled Paper Fibers.

Ken Stager

April 7, 1996

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ABSTRACT:

BOD and COD are two very important and highly regulated aspects of the paper industry. The first is the biochemical oxygen demand, BOD, and it is simply the amount of oxygen that bacteria need to digest the nutrients in a wastestream. The second is the chemical oxygen demand, COD, and is the amount of oxygen required to fully oxidize all the material present in an effluent sample using hot concentrated chemicals.

One aspect of recycling that has not been discerned is the effect of repeatedly recycling paper fibers on the BOD and COD of the effluent. This is important because the government, and the general public, are forcing higher and higher levels of recycle in a furnish. If a fiber exerts a higher BOD or COD as it is recycled than a virgin fiber, the resulting effluent will be naturally higher in BOD and COD. This in itself would not be very important of the EPA were not lowering the BOD and COD effluent limits as the years go by. Therefore, an effluent that may be naturally higher in BOD and COD will be regulated down to an even lower limit. This costs a significant amount of money to reach these new goals.

Virgin Kraft Softwood was repeatedly recycled in a loop consisting of slurrying the pulp to a target freeness, draining the pulp on a screen and catching the effluent, testing the effluent for BOD and COD, pressing the fiber web, and drying the web. The dried fibers were then run through the same loop. This process was completed six times. From this BOD and COD data was collected.

Many problems occurred with the BOD and many of the data points were faulty. The COD faired better, and a discernible trend was observed. The BOD and COD went down as the number of recycles increased. This could be due to residual chemicals and the easy to break off fiber chunks getting washed away in the first few recycles. Many of the problems related to the DO meters. The first DO meter broke and was not able to be repaired. The second gave varied readings and was very difficult to calibrate. The last problem was contamination of starch from felt pressing pad. This caused a possible increase in the BOD and COD loading from that contaminant.

Closing of the recycle loop would give a baseline reading for the BOD and COD due to keeping the chemicals and the fines in the loop. A good dependable DO meter would solve the dissolved oxygen problem.

INTRODUCTION:

The more the paper industry recycles, the more fibers they will have that are going through their multiple number of recycle. Thus, if the fiber is being recycled over and over again, it might, in some models, contribute a higher BOD and COD load to the effluent. The BOD is the amount of oxygen that is used up for bacteria to digest the nutrients in the effluent in a time span of five days. The COD is the amount of oxygen deficit that would occur for all of the materials present in the effluent to be oxidized. This is more complete since all of the material is oxidized, not just the nutrients the bacteria can digest. This is especially relevant since the EPA is continuing to lower the allowable effluent limits. This experiment should give some indicator whether the number of times a fiber is recycled is proportionally related to the BOD and COD load it exerts. If this thesis were to show that there is a correlation, it would be beneficial for the paper industry (who's effluent limit guidelines are currently under review) because it would quantitatively show that, as our industry recycles more and more of its fibers, the over all BOD and COD loads will naturally increase for the whole industry since they are dealing with a pool of fibers that are getting more and more degraded as they pass through the recycle loop over and over again. If this were substantiated, it is relevant for the paper industry to ask the EPA to take this into consideration when dictating what BOD and COD limits are acceptable for the years to come.

The only variable that was manipulated was the number of times the fibers are recylced since their is very little previous research done that would have correlated with this specific topic. The fibers underwent a process of repulping, made into a large web(sheet), dried, then repulped. The consistency, temperature, and pulping time have been held as constant as possible for each separate run. Thus, the only variable that should have been affected would be the natural degradation of the fibers themselves. Much of the industry uses Softwood Kraft in their furnishes, so that was selected as the fiber.

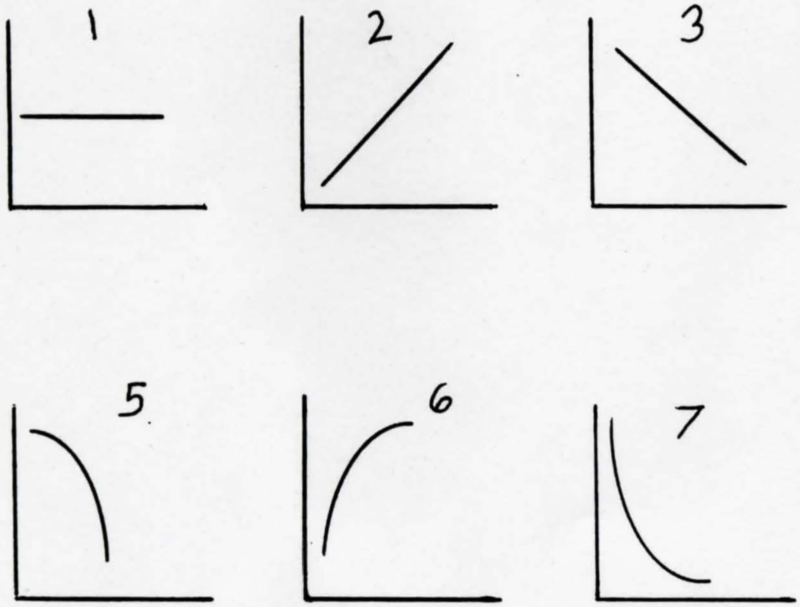
BACKGROUND AND THEORETICAL:

No research has been done on the topic of BOD and COD loading versus the number of recycle. Strength and optical properties, as they are affected by recycling, have been researched extensively. This can be attributed to the paper industry wanting to know how the recycling will affect the properties their papers are specifically designed for. Therefore, the next logical sequential step in the process is to see how the effluent is affected.

The main problem is making sure their are no differences between runs. Variations in freeness, consistency, and sampling could easily affect the BOD and COD readings. Therefore, great care must be taken to make the pulp runs as similar as possible. Refining to the same freeness should equalize the fines loading. Care in measurement should guarantee the same consistency. Lastly, collecting all of the whitewater and taking a representative sample should keep the sample usable.

When considering what may happen to the BOD and COD as one recycles a fiber, many different behaviors may occur. Table A.1 Possible Behaviors shows what some of curves could look like if the exerted BOD or COD (y-axis) versus the number of times recycled (x-axis). The first is explained as a fiber yielding at a constant rate, so basically the same BOD or COD at every recycle. The second is a fiber yielding at a constant increasing rate. This is explained by the fiber degrading more and more every recycle, but in a linear fashion. The third is a fiber yielding at a constant decreasing rate explained by the fiber having all of the easily removed pieces breaking off in a linear way. The fourth is more complicated with the fiber loading increasing in a exponential manner. This would be explained by a fiber holding strong for a few recycles, but eventually reaching a failure point causing a significant increase near the end. The fifth is explained by the fiber holding out well and finally all of the easily broken pieces are gone so the loading drops off significantly. The sixth is a variant of the fourth except the fiber immediately starts to disintegrate and plateaus off. The seventh is the fiber decreasing dramatically as all of the BOD and COD loading material is quickly washed out. Also, any number of combinations of these are possible. But, since no exact modal of the paper fiber exists, one cannot predict infallibly the results of the degradation of the fiber.

Table A.1 Possible Behaviors

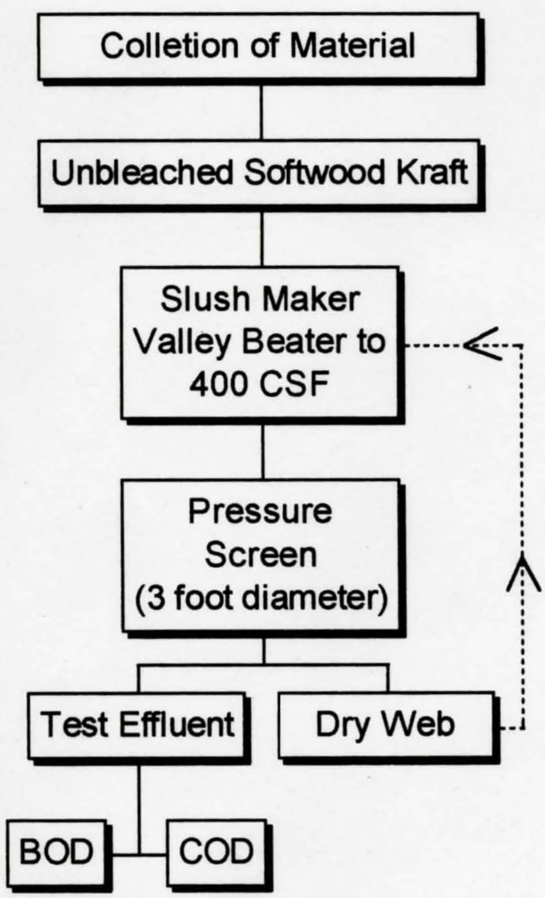


EXPERIMENTAL PROCEDURES:

The unbleached Kraft pulp was repulped in the laboratory slusher. The pulp was then drained through a 36 inch diameter screen in a single batch. The pulp was at the consistency to give 69 lbs per thousand square feet, a typical weight board This should have guaranteed a small variation in consistency will be minimized with respects to the whitewater. After this, the large sheet of pulp was cut into smaller sections for pressing and drying. All of the whitewater was collected and a representative sample had triplicates of BOD and COD run on it using the Standard Methods for the Examination of Water and Wastewater methods described on pages 5-1 to 5-10. After that, the web was repulped again using the slusher and the same process of draining on the large wire and BOD and COD tests was run again. This process was repeated six times. The BOD and COD results were averaged and plotted against the recycle number. Figure One, Experimental Design, shows the exact step by step process used in this thesis.

Figure One:

Experimental Design



PRESENTATION OF RESULTS AND DISCUSSION:

The complete raw data for the SW Kraft BOD and COD is located in Appendix A: Raw Data. The sample calculations for the BOD and COD are located in Appendix B. Table A shows the BOD and COD values for the experiment in relation to their recycle number.

Table A: BOD and COD

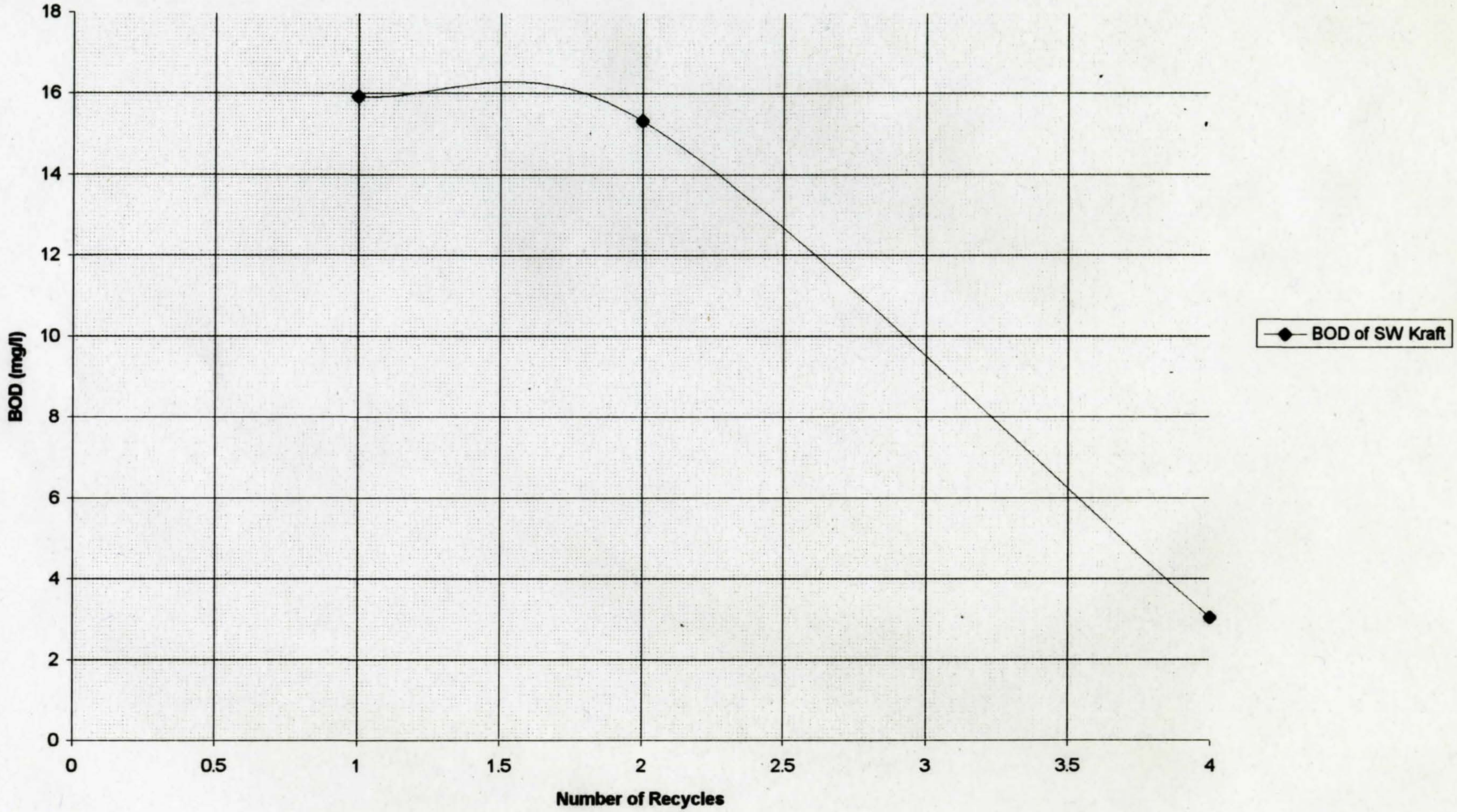
Recycle Number	BOD(mg Oxygen/Liter)	COD (mg Oxygen/Liter)
1	15.93	149
2	15.33	43
3	*****	42.4
4	3.04	26.7
5	*****	33.3
6	*****	36.7

***** means a negative value occurred causing the data point to be invalidated

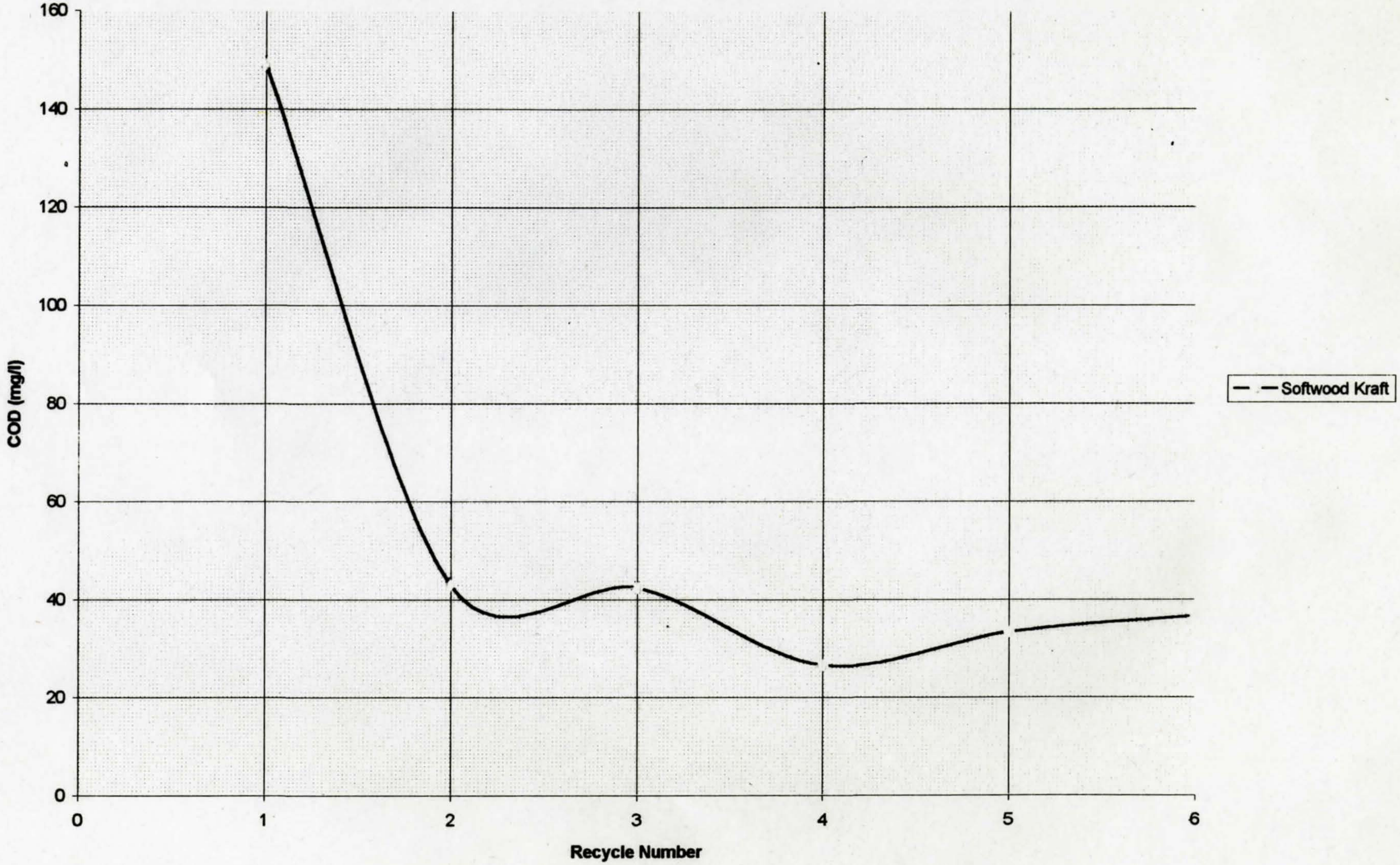
Recycles number 3,5, and 6 had negative values for the BODs. This essentially means something went wrong with that specific batch and the data point had to be thrown out. The possible reasons for that will be discussed later.

Graph One shows the BOD versus number of recycles, and a clear trend is possibly evident. However, since the trend is mostly dependent on the third data point, the downward tendency might be suspect since a faulty third reading could throw off a fairly uniform flat line. When Graphs Two and Three are considered, showing the COD versus number of recycle, the BOD trend may prove correct. Since the first data point for the COD is significantly higher than the rest of the data points, it is easier to remove that point and look at the remaining points for recycles 2 through 6 as is shown in Graph Three.

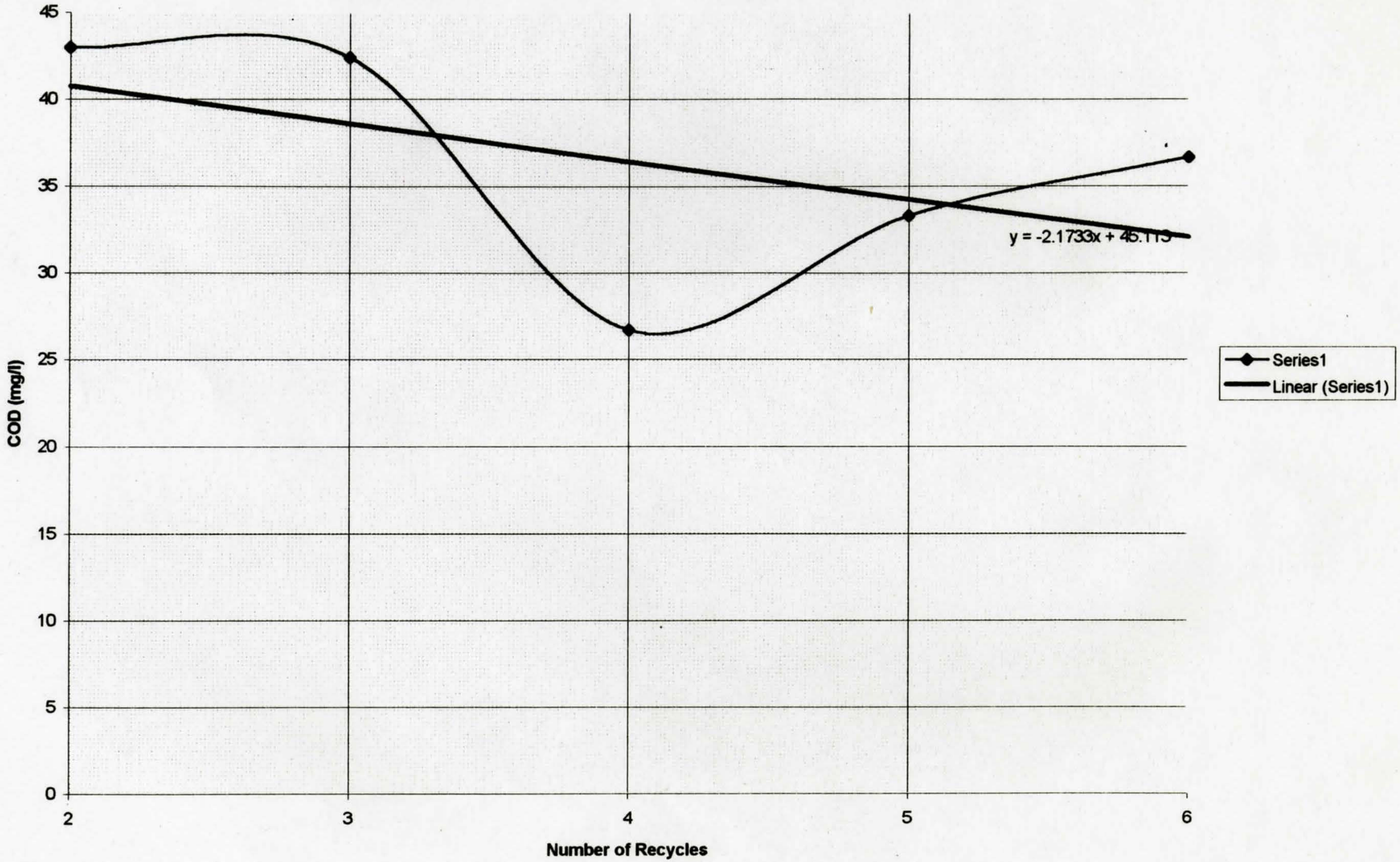
<u>GRAPH ONE</u>: BOD of SW Kraft versus Number of Recycles



GRAPH TWO: COD of Softwood Kraft Fibers versus Number of Recycles



GRAPH THREE: COD Values for SW Kraft versus Number of Recycles



If a linear trend line is inserted into Graph Three, the equation would be the one labeled on the graph. When a Chi-Squared test is performed on the data, the test yields a value of .437 which is well below the critical Chi-Squared value for any distribution. This essentially means that the linear trendline is acceptable for the values within a 95% assurance rate. Therefore, the data points have a definite declining trend.

This downward trend can be explained by a few differing possibilities. The first is that the residual chemicals in the fibers cause a high COD loading rate in the initial step and this decreases in successive recycles as the chemicals are washed out. The second explanation could be the small pieces of the fiber structure break out of the fiber easily in the beginning. Then, after each successive recycle, fewer and fewer pieces are available for breaking out causing a decrease in the BOD and COD. However, since the data points are scattered and the collected data in littered with "bad" and thrown out points, it is very difficult to verify a solid trend.

Many problems were encountered in this experiment. The main six are as follows:

1: DO meter probe coil broke in the summer

2: Time constraints

3: New DO meter has difficult calibration method

4: Design flaw in consideration to the effluent stream

5: Contamination of felt pressing pads

6: New DO meter has sporadic performance

The first problem occurred during summer when the DO meter being used broke and no replacement parts were available. This caused a significant delay, in the caliber a two months, so a time crunch was then encountered. The next was the new DO meter used barometric pressure and room air to calibrate. This was a significant change from the old DO meter, so mistakes may have been made calibrating the machine for the few first trials.

Also, to even out the possible difference in COD and BOD due to residual chemicals, the loop should be closed by using the whitewater from the previous recycle as the dilution water for the next trial. This would then cause the chemicals to remain in the system and form a baseline. Also, much of the fines were washed away after each recycle with the whitewater. Therefore, fiber loss was observed after each recycle.

The next problem was contamination coming from the felt pressing pads. At the time, another individual was performing his thesis project that concerned surface applied starch coatings. These coatings tended to impregnate the felt press pads and would impart a small amount of coating onto the SW web being pressed for this experiment. This added starch could have upset the BOD and COD amounts.

Lastly, the new DO meter has significant problems with repeatable performance. Variations as much as +/- .5 mg/l oxygen were observed on the same sample. This would cause significant variance in the BOD readings.

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SUMMARY OF RESULTS AND CONCLUSIONS:

The BOD and COD loading of the fibers seemed to decrease as they were repeatedly recycled. Because the data points varied significantly, no concrete mathematical equation could be fit to the data set. However, the COD was able to show a slight downward trend.

It can be concluded that the fibers apparently "seal" up and do not exert as much BOD and COD as they are recycled over and over. Because of this, it can be concluded that a pool of fibers that is being recycled will then lower the overall BOD and COD of the final furnish. However, much of the recycle of today has many additives in the waste paper. These additives would exert a higher BOD and COD. With better concrete data, it would be possible to determine the proportional BOD and COD of a specific recycle furnish if all the additives were known, the additives BOD and COD values were known, and the percent of each fiber in the different number of recycle. By this, a simple proportion would yield the theoretical BOD and COD values.

RECOMMENDATIONS:

Many of the problems faced in this project could be easily avoided with hindsight. A closing of the effluent loop would yield a constant baseline for COD and BOD. Also, familiarization with a properly functioning DO meter would decrease the chances of misreading and miscalibrations. Purchasing new felt pads and keeping them exclusively for an individual thesis would keep out contamination problems. Lastly, sticking to a rigid time schedule would take out the human procrastination factor allowing for repeating of specific areas if necessary.

LITERATURE CITED:

NCASI, TB670, Spring, 1994.

Standard Methods for the Examination of Water and Wastewater, 18th Edition, pages 5-1 to 5-10.

APPENDIX A: Raw Data, BOD and COD Values

		COD DATA				
Kraft	Recycle #	ml for blank 1	ml for blank 2	ml for 1st sample	ml for 2nd sample	COD
	1	7.85	7.95	8.6	8.6	149
	2	8.8	8.75	8.45	8.45	43
	3	8.8	8.75	8.4	8.55	42.4
	4	9	8.8	8.7	8.7	26.7
	5	8.85	8.8	8.55	8.6	33.33333
	6	8.85	8.8	8.65	8.55	36.66667

KRAFT BOD																	
Recycle 1			Recycle 2			Recycle 3			Recycle #4			Recycle #5			Recycle #6		
Blanks #	DOi	DO5	Blanks #	DOi	DO5	Blanks #	DOi	DO5	Blanks #	DOi	DO5	Blanks #	DOi	DO5	Blanks #	DOi	DO5
102A	8.63	8.4	72A	10.4	8.1	102A	10.4	8.1	123A	11	7.8	278	8.98	6.67	278	8.98	6.67
42D	8.63	8.5	319A	10.4	7.9	42D	10.4	7.9	317A	10.9	7.9	319	8.99	6.61	319	8.99	6.61
Avg.	8.63	8.45	Avg.	10.4	8	Avg.	10.4	8	Avg.	10.95	7.85						
2% Effluent #			6% Effluent #			6% Effluent #											
10A	8.61	8.1	62A	10.1	7.5	47D	9.6	8.2	6% Effluent #			3ml Effluent			3ml Effluent		
293A	8.58	8.1	341A	10.2	6.3	9B	9.6	8.3	346A	10.8	7.8	10	8.98	8.6	34	8.98	7.3
Avg.	8.595	8.1	Avg.	10.15	6.9	Avg.	9.6	8.25	106B	10.7	7.7	12	9	8.35	44	8.97	6.92
BOD5	15.93		BOD5	16.27		BOD5	-15.39		Avg.	10.75	7.75	13	8.99	8.29	46	8.95	7.28
			8% Effluent #			8% Effluent #			BOD5	1.053							
			308A	10.1	6.9	39B	9.5	8.2	8% Effluent #			5 ml Effluent			5 ml Effluent		
			347B	10.1	7.3	67A	9.5	8.1	318A	10.7	7.6	20	8.98	7.98	69	8.95	6.8
			Avg.	10.1	7.1	Avg.	9.5	8.15	350A	10.7	7.7	22	9	7.81	81	8.97	7.1
			BOD5	0.961		BOD5	-11.02		Avg.	10.7	7.65	26	8.97	7.51			
			10% Effluent #			10% Effluent #			BOD5	2.094							
			43A	10	7	214A	9.5	8.1	10% Effluent #								
			340C	10.1	6.1	41B	9.5	8.2	259A	10.7	7.6						
			Avg.	10.05	6.55	Avg.	9.5	8.15	328A	10.7	7.5						
			BOD5	13.53		BOD5	-7.97		Avg.	10.7	7.55						
			12% Effluent #			12 % Effluent #			BOD5	3.763							
			46A	10	5.9	62A	9.5	7.9	12% Effluent #								
			59B	10	6	58A	9.5	7.9	32B	10.6	7.1						
			Avg.	10	5.95	Avg.	9.5	7.9	42B	10.6	7.4						
			BOD5	16.21		BOD5	-4.21		Avg.	10.6	7.25						
									BOD5	5.256							

APPENDIX B: Sample Calculations

COD sample calculation

COD(mg/l)=[(a-b)*m*8000]/ml of sample

a=ml FAS for Blank

b=ml FAS for Sample

m=molarity of FAS Solution

ex: 2 ml of sample

a=8.38, b=7.47, m=.05

cod=[(8.38-7.47)*.05*8000]/2=182 mg/l

BOD sample calculation

BOD(mg/l)=[(d1-d2)-(b1-b2)f]/p

d1=DO of sample after initial dilution

d2=DO of sample after 5 days incubation

b1=DO of blank initially

b2=DO of blank after 5 days incubation

f=ratio of seed in diluted sample to seed in seed control

p=decimal volumetric fraction of sample used

ex: recycle number one

b1=8.63, b2=8.45, d1=8.595, d2=8.1, f=(.049/.05), p=.02

BOD (mg/l)=[(8.595-8.1)-(8.63-8.450*.98]/.02=15.93