

Summary on Assay for Leather Processing Effluents Treatment with NS 20, Maintain D in Bogota, Colombia

A new alternative for the treatment of effluent waters from the Leather Processing Industry was tested at several facilities in Colombia. The parameters for identification of pre-treatments operations were done to adjust the conditions of effluents for optimal pH, filtration and flocculation. The products used in this study were NS 20, Accelobac[®] 5000, Maintain D[®] and a mixture of them. The two products selected for larger removal of the total COD after a 24 hour period were NS 20 and Maintain D[®]. Once those products were selected the concentration ratios for each of them were 80; 20 per application. The variables measured during the study were temperature, product quantity and aeration. The optimal temperature for the product total microorganisms growth acceleration was 45°C.

There are about 350 leather processing microbusinesses in Bogota, Colombia. The industry generates leather finished materials for the manufacture of: shoes, upholstery and other leather goods. Hazardous chemicals are used during the overall processing. These chemicals include: strong bases, surfactants, chromium, and sodium sulphur. Due to the nature of the leather itself; meaning fat, proteins and other organic substances these are other contaminants that are added to the list of effluents contents. The majority of these effluents are improperly discharged in waterways, specifically The Tunjuelito River. Worries have generated a variety of proposals and possible solutions for these problems. However, none of them offer a biological treatment solution.

This study proposes an innovative way of treating the water effluents of leather industry by using biological products. These biological products are added to the primary treatment of filtration and neutralization. They contain 5 different strains which produce lipases and proteases. The direct application of the products in the primary treated waters doesn't require the design of a biological reactor.

There is a concentration of about 90 % of leather processing industries in San Benito neighbourhood, near the Tunjuelito River. The elevated contamination in this area represents danger to the soils, air and waterways. Among other negative impact there is the risk of chemical exposure for the workers and residents. There is no proper training for the workers that manage the residues and the businesses owners are not open to deal with the problem. The industries won't comply with the minimal safety regulations. Around 50 % of the businesses don't have a proper treatment system for the effluents. There is no control for storage or treatment for the solid residues. Among the potential health risks are the possibility of carcinogenic substances like chromium and sulphur release to the environment.

There are several steps involved in the leather processing. The raw leather will undergo: soaking, liming, division, tanning, and draining and thickness reduction. The finishing steps include drying, colouring and finally ironing. The process steps that are responsible for the majority of effluents residues are: soaking (this initial step produces effluents containing: bacteria, enzymes, surfactants sodium sulphur and caustic soda in most cases. The tanning process uses formic acid and sulphuric acid, acid water and

dissolved salt chromium. The finishing processes generate fats, dissolved salts, waxes, syntans, and pigment traces residues.

The steps for the primary treatments of the effluents include the separation and homogenization of effluents. These effluents are recovered in concrete tanks. Polyethylene tanks were also used for the effluent recovery and the total formation and sedimentation solids. Aluminium sulphate is applied after decanting the primary sludge and this sludge will be consequently treated for composting purposes. The primary treatment includes the clarification sedimentation and decanting processes which constitute the primary sludge.

The total environmental impact for the tanning process is the most pollution generator compared to the others steps involved in the leather processing. This pollution is aggressive because it contains a large quantity of pollutants and solid residues which cause severe problems to waterways, and nearest people.

The primary treatment process involves the solids removal by sieving or gravity separation. Sometimes aiding molecules are used to help the solid sediments at a faster rate. Among other techniques there is flotation or filtration. Each one tries to separate the solids from the liquids by mechanical means.

The secondary treatment is realized by aerobic and anaerobic processes where the organic matter is metabolized by different bacteria strains. The activated sludge has to contain high organic matter concentration. The two main objectives are the oxidation and aeration and finally flocculation. This system permits the separation of the total biomass of the treated effluent.

Assay Methods

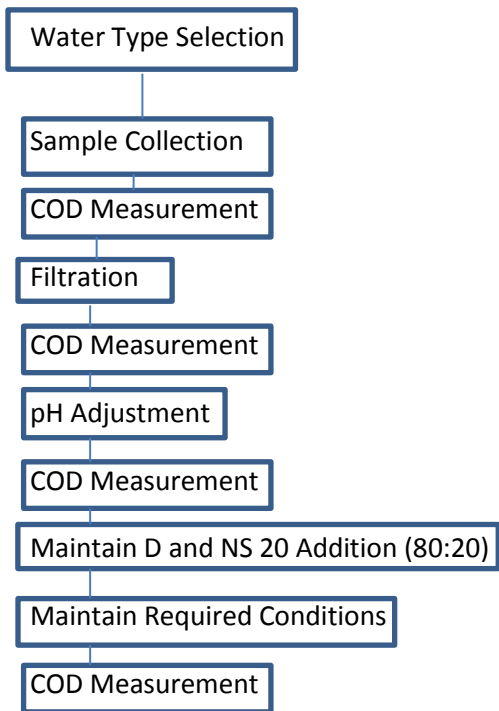
The first step is the sample collection from the grease trap which is immediately treated. Three variables were tested: temperature, agitation by aeration and anaerobic conditions. The concentration was always 100 ppm, and the product dosage was doubled because of the low retention period and the large quantity of chemicals in the effluents. While the volume and pH for all tests remained the same the temperature and the sample concentration change for each sample.

Objective

The main objective was to prove the functionality of the product and the total COD removal. In the realization of these tests the temperature maintained was 18°C and the water collected from different sources.

The COD removal percentage was reported for each sample.

Flowchart 1: Experimental Design Methods





Test 1: This assay was done with the purpose of proving the efficacy of the products.

Image 1: Three water effluent samples collected from the liming, tanning and colouring processes.

Table 1: Parameters for Concentration

PARAMETER	VAL
Blank (mL)	24
Concentration FAS	0.24

Results for this test are included in tables 2, 3, 4.

Table 2: Preliminary Test: NS 20

NS 20 PRODUCT		HOUR	DQO (ppm)	% REMOVAL
Initial Conditions	Value	0	3628	-
Biological Product Concentration (ppm)	97.09			
Water Type:		4	2627	27.59
Liming	80%			
Colouring	20%	24	673	81.44
pH (units)	8.7			
V (L)	10.3			

Table 3: Preliminary Test: Maintain D®

MAINTAIN D PRODUCT		HOURS	COD	% REMOVAL
Initial Conditions	V	0	1255	-
Product Concentration (ppm)	8			
Water Type: Primary Treatment		4	1005	19.92
	1			
pH (units)	5			
V (L)	1	24	760	39.45

Table 4: Preliminary Test: Accelobac® 5000

ACCELOBAC PRODUCT		HOURS	COD	% REMOVAL
Initial Conditions	V	0	1255	-
Product Concentration (ppm)	8			
Water Type: Primary Treatment		4	1177	6.22
	1			
	0			
pH (units)	5	24	785	37.45
V (L)	1			

Image 1: Geotextile treated with Maintain D® and NS 20



Image 3: Preliminary Test on treated and control water samples



Blank (mL) = 24.7, [] FAS (M) = 0.2577, COD(ppm) [0 h] = 1155, pH = 5.21, T (°C) = 17.5				
HOURS	PRODUCT	NS	NS/MAINTAIN D® (80:20)	CONTROL
4	COD (ppm)	743	660	908
	% Removal	35.67	42.86	21.39
7	COD (ppm)	743	578	908
	% Removal	35.67	49.96	21.39
24	COD (ppm)	743	578	908
	% Removal	35.67	49.96	21.39

Table 5: Preliminary Test 2. Results by COD % removal for each sample

The sample tests were done by using NS y NS/MAINTAIN D® (80:20) mixture and control water with no product added.

Note: that the product sample were done after filtration, another test was done before the filtration process to observe further changes.

Image 4: The samples tested after 24 hr. period



Blank (mL) = 24.7, [] FAS (M) = 0.2577, COD (ppm) [0 h] = 2846, pH = 5.14, T (°C) = 18.5			
HOURS	PRODUCT	NS	NS/MAINTAIN D (80:20)
24	DQO (ppm)	1128	1034
	% Removal	60.37	63.67

Table 6: Preliminary Test 3 Results by COD % removal for each simple with no filtration

- I. **Discussion.** It was found after performing the tests that in the majority of the cases, the primary treatment waters used for this testing already comply with minimal law parameters for COD %, since the value found was below 2000 mg/L. However the purpose of this assay was to determine the efficacy of these products on removing COD.

According to the results for the three biological products, Maintain D® and the Maintain D®/NS 20 mixture were the most efficient ones. The product of less effectiveness was the Accelobac 5000®.

Note: The waters cannot be filtered after product addition, this will ensure that the product won't be removed and left the waters untreated.

*In this case the water was filtered prior the product addition.

The final results evidence that the product with more activity for COD removal was Maintain D®/NS 20

Image 5: Residual water without treatment



Image 6: Residual waters after treatment with Biological Products



Results for water with most liming residue concentration: The water used for the assay (image 5) was a combination of liming-tanning processes in a (80:20) ratio. A total of 2 mL of H₂SO₄ 98% solution was used to increase the acidic pH to 7 (neutral), flocculation was observed in the water before the products were added. The concentration of product was 100 ppm for each 5 L recipient.

A duplicate of the test were performed using five different products. Results are listed in the following table.

Blank (mL) = 24.7, [] FAS (M) = 0.2513, COD (ppm) [0 h] = 4866, pH [Control] = 10, T (°C) = 18.5											
HOURS	PRODUCT	MAINTAIN D		ACCELOBAC		N		NS/MAINTAIN		NS/ACCELOBAC	
2	COD (ppm)	4263	4182	4343	4263	4102	4062	3780	3740	3780	3780
	% Removal	12.39	14.06	10.75	12.39	15.70	16.52	22.32	23.14	22.32	22.32
4	COD (ppm)	3559	3599	4001	4001	3840	3820	3519	3499	3659	3680
	% Removal	26.86	26.04	17.78	17.78	21.09	21.50	27.68	28.09	24.80	24.37
6	COD (ppm)	3177	3157	3539	3499	3378	3398	3137	3097	3217	3217
	% Removal	34.71	35.12	27.27	28.09	30.58	30.17	35.53	36.35	33.89	33.89
8	COD (ppm)	2694	2654	3197	3177	3117	3157	2493	2453	2855	2815
	% Removal	44.64	45.46	34.30	34.71	35.94	35.12	48.77	49.59	41.33	42.15
24	COD (ppm)	1689	1669	2694	2654	2272	2292	1488	1468	2091	2091
	% Removal	65.29	65.70	44.64	45.46	53.31	52.90	69.42	69.83	57.03	57.03

Table 7: Initial test. Water with higher liming residue concentration

Graph 1: Initial Test % Removal vs. Time. For Water with Higher Liming Residue Concentration

100 ppm of biological product

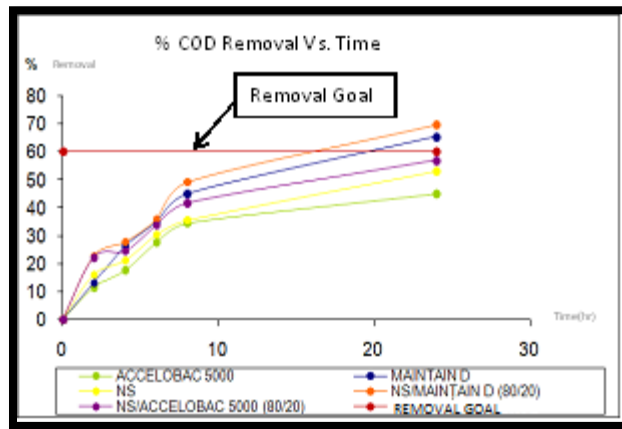


Image 7 & 8: Agitation and Aeration Testing

To generate more aeration of the treated water an aeration motor was employed.



Water with higher liming residue concentration

A mixture of liming-tanning waters (80:20) was collected for testing. 2mL of H₂SO₄ 98% solution was used to increase the pH to 7(neutral). The biological products were added in the water at a concentration of 100 ppm and each 5 L container was aerated by agitation.

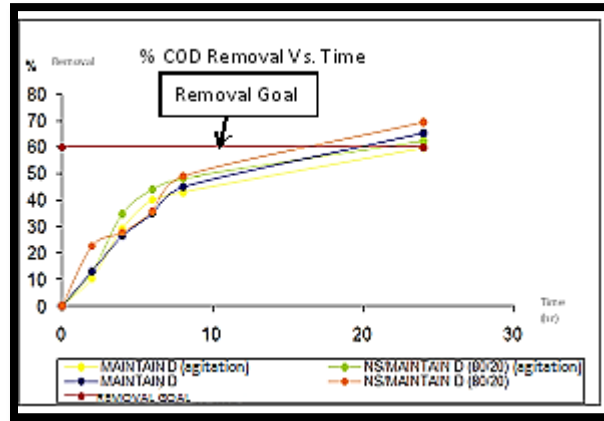
Water Type		
Water with no filtration	COD (ppm)	5543
Filtered Water	COD (ppm)	5219
	% Removal	5.85
Water with ph Adjustment	DQO (ppm)	4873
	% Removal	12.09

Table 8: COD % removal before treatment with biological products, with the highest liming residue concentration

Blank (mL) = 24.8, [] FAS (M) = 0.2538, COD (ppm) [0 h] = 4873, pH [Untreated Water] = 10, T (°C) = 17.5					
HOURS	PRODUCT	MAINTAIN D		NS/MAINTAIN D (80:20)	
2	COD (ppm)	4346	4366	4264	4224
	% Removal	10.81	10.40	12.50	13.32
4	COD (ppm)	3452	3432	3188	3168
	% Removal	29.16	29.57	34.58	34.99
6	COD (ppm)	2924	2904	2742	2721
	% Removal	40.00	40.41	43.73	44.16
8	COD (ppm)	2782	2762	2518	2518
	% Removal	42.91	43.32	48.33	48.33
24	COD (ppm)	1950	1970	1828	1848
	% Removal	59.98	59.57	62.49	62.08

Table 9: Results for COD % removal with Maintain D and NS 20/ Maintain D (80:20) mixture

Graph 2: Agitation Tests with % Removal vs. Time for water with the highest liming residue concentration and 100 ppm of biological product



Results for water with higher tanning residue concentration: A mixture of water with a total liming-tanning-colouring processes proportion (15-70-15) was used for the test. To increase the pH to 7 1 mL of H₂SO₄ 98% solution was added and lastly the product in a 100 ppm concentration and it was submitted for agitation by aeration of 5 L.

Table 10: Agitation Test: COD % before treatment with biological products on water with higher tanning processing residue concentration.

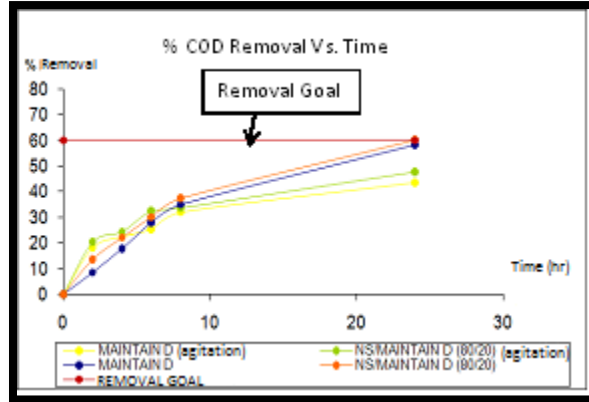
Water Type		
Unfiltered Water	COD (ppm)	5259
Filtered Water	COD (ppm)	4975
	% Removal	5.4
Water with pH Adjustment	COD (ppm)	4406
	% Removal	16.22

The tests were realized in duplicate using the two products that yield the best results and the results are shown in the following table, the following graphic also shows the COD % removal.

Table 11: Agitation Test: Water with higher tanning process residue concentration

Blank (mL) = 24.8, [] FAS (M) = 0.2538, DQO (ppm) [0 h] = 4406, pH [Untreated Water] = 8.5, T (°C)					
HOURS	PRODUCT	MAINTAIN D		NS/MAINTAIN D (80:20)	
2	COD (ppm)	4285	4305	4183	4183
	% Removal	18.52	18.14	20.46	20.46
4	COD (ppm)	4061	4082	3960	3980
	% Removal	22.78	22.33	24.70	24.32
6	COD (ppm)	3939	3919	3554	3533
	% Removal	25.10	25.48	32.42	32.82
8	COD (ppm)	3594	3574	3493	3472
	% Removal	31.67	32.04	33.58	33.98
24	COD (ppm)	2985	2965	2742	2742
	% Removal	43.24	43.62	47.86	47.86

Graph 3: Agitation Tests: % Removal vs. Time for water with higher concentration of tanning process residue and 100 ppm of biological product



Concentration Tests

These tests were realized with the objective of evaluate if the microorganism’s behaviour was affected by decreasing the concentration by half, which would also lower the cost by half. The tests were done with a unique concentration of 50 ppm since the decrease between 50 and 100 ppm doesn’t represent a significant cost reduction. Concentrations higher than 100 ppm where not evaluated either since the biological products cost will increase the costs in the facilities.

Results for water with higher proportion of liming residue:

The water used for this test was a combination of liming-tanning processes (80:20), the required procedures were done to bring elevate de acidic pH to 7, 2mL of H2SO4 98% solution, thus obtained a flocculation, thereafter the biological product was added at the corresponding 50 ppm concentration in each of the 5 L containers.

To better determine the COD removal the COD was measured prior application of biological products. The following table provide the initial measurements:

Table 12: Concentration Tests for COD before treatment with biological products. Results shown below are for water with higher liming residue concentration.

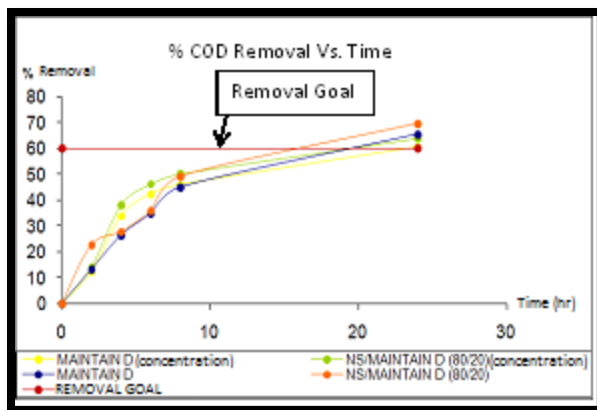
Water Type		
Unfiltered Water	COD (ppm)	5543
Filtered Water	COD (ppm)	5219
	% Removal	5.85
Water with pH Adjustment	COD (ppm)	4873
	% Removal	12.09

The tests were realized in duplicate using the two products that yield better results on the initial tests, those results are shown in the following table and the following graphic shows the COD % removal.

Table 13: Concentration Tests for water with higher liming concentration.

Blank (mL) = 24.8, [] FAS (M) = 0.2538, DQO (ppm) [0 h] = 4873, pH [Untreated Water] = 10, T					
HOURS	PRODUCT	MAINTAIN D®		NS/MAINTAIN D® (80:20)	
2	COD(ppm)	4285	4264	4183	4183
	% Removal	12.07	12.50	14.16	14.16
4	COD (ppm)	3229	3209	3005	3026
	% Removal	33.74	34.15	38.33	37.90
6	COD (ppm)	2802	2802	2640	2599
	% Removal	42.50	42.50	45.82	46.67
8	COD (ppm)	2620	2640	2417	2437
	% Removal	46.23	45.82	50.40	49.99
24	COD (ppm)	1929	1909	1767	1747
	% Removal	60.41	60.82	63.74	64.15

Graph 5: Concentration Tests for total % Removal vs. Time. Results shown below are for water with higher proportion of liming 50 ppm of biological product.



Results for water with higher concentration of tanning residue:

The water used was a combination of liming-tanning processes (20-80), a required procedure for pH adjustment was done in which the pH was elevated to 7 by adding 5 mL of H2SO4 98% solution, after that the product was added in a concentration of 50 ppm in each 5 L container.

To determine the COD removal in each operation a measurement was taken prior product application on unfiltered, filtered and adjusted pH waters. Results are shown in the following table.

Table 14: Concentration Tests for COD before treatment with biological products. Results are shown below for water with higher tanning processing residue concentration.

Water Type		
Unfiltered	COD (ppm)	4792
Filtered	COD (ppm)	4752
	% Removal	0.83
With PH Adjustment	COD (ppm)	4549
	% Removal	5.07

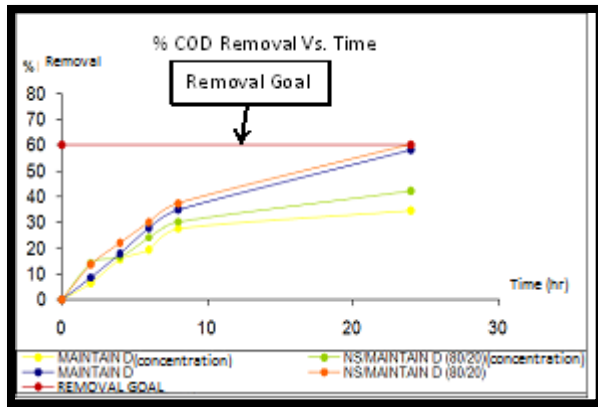
The tests were done in duplicate applying both products and these results are shown in the following table. Graphic 6 show the obtained removal.

Table 15: Concentration tests for water with higher tanning concentration

Blank (mL) = 24.8, [] FAS (M) = 0.2538, DQO (ppm) [0 h] = 4549, pH [Untreated Water] = 13, T (°C) = 18					
HOURS	PRODUCT	MAINTAIN D®		NS/MAINTAIN D® (80:20)	
2	COD (ppm)	4244	4264	3899	3899
	% Removal	6.70	6.27	14.29	14.29
4	COD (ppm)	3838	3838	3797	3777
	% Removal	15.63	15.63	16.53	16.97
6	COD (ppm)	3655	3676	3432	3452
	% Removal	19.65	19.19	24.55	24.12
8	COD (ppm)	3310	3290	3188	3168

8	% Removal	27.24	27.68	29.92	30.36
24	COD (ppm)	2985	2965	2640	2620
24	% Removal	34.38	34.82	41.97	42.40

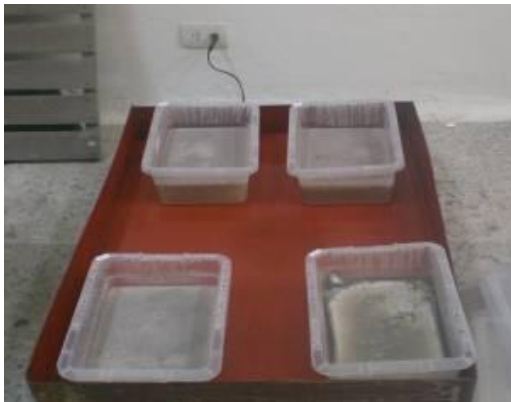
Graph 6: Concentration Tests for total % Removal Vs. Time on water with higher tanning processing residue with 50 ppm of biological product



Temperature Tests

The containers with the water to be treated were heated until they reached a temperature of $45^{\circ}\text{C} \pm 4^{\circ}\text{C}$, The temperature which remained constant was monitored every hour

Image 9: Temperature



Water with higher liming residue concentration

The water used was a combination of liming and tanning processes (80:20), the required procedure was done to increase the acidic pH in the waters to 7 by adding 2 mL of H₂SO₄ 98% solution, thus there was a flocculation, the correspondent biological product was added into the mixture afterwards in a 100 ppm concentration. The analysis was done on the 5 L heated (45°C ± 4°C) containers.

To better determine the COD removal for unfiltered, filtered and pH adjusted water without the biological product added. Results shown in the following table:

Table 16: Temperature tests for COD before treatment with biological products. Results are shown below for water with higher liming residue concentration.

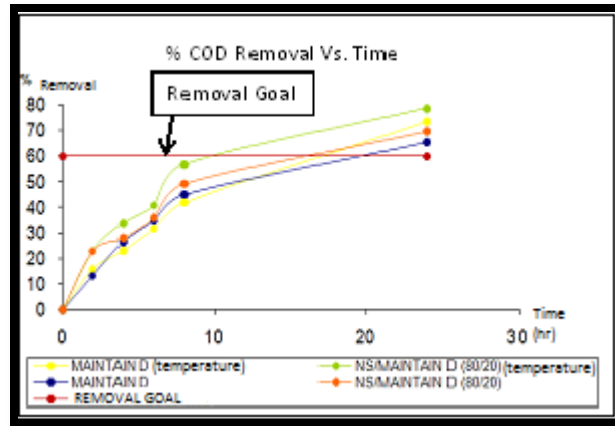
Water Type		
Unfiltered Water	COD (ppm)	6868
Filtered Water	COD(ppm)	6707
	% Removal	2.34
Adjusted pH Water	COD (ppm)	4808
	% Removal	30.00

The test was done with the two products that yield the best results in the initial testing. The following table and graphic show the results for this assay

Table 17: Temperature Test. Water with higher liming residue concentration

Blank (mL) = 25. [] FAS (M) = 0.2525. DOO (ppm) [0 h] = 4808. pH [Untreated Water] = 10					
HOUR	PRODUCT	MAINTAIN D®		NS/MAINTAIN D® (80:20)	
2	COD (ppm)	4061	4040	3717	3697
	% Removal	15.54	15.97	22.69	23.11
4	COD (ppm)	3677	3717	3192	3172
	% Removal	23.52	22.69	33.61	34.03
6	COD (ppm)	3293	3273	2849	2828
	% Removal	31.51	31.93	40.75	41.18
8	COD (ppm)	2788	2788	2061	2081
	% Removal	42.01	42.01	57.13	56.72
24	COD (ppm)	1273	1253	1010	1031
	% Removal	73.52	73.94	79.00	78.56

Graph 7: Temperature Test. % Removal vs. Time. Water with higher liming concentration, 100 ppm of biological product was added.



Results for water with higher liming residue concentration: The water tested was a combination of liming-tanning processes (15-85), the acidic pH was elevated to 7 by adding 10 mL of H₂SO₄ 98% solution, followed by the addition of the biological product in the 5 L container.

To better determine COD removal % in each operation the data for unfiltered, filtered and pH adjusted water was reported in the following table:

Table 18: Temperature tests for COD % before addition of biological product. Results are shown below for water with higher tanning residue concentration.

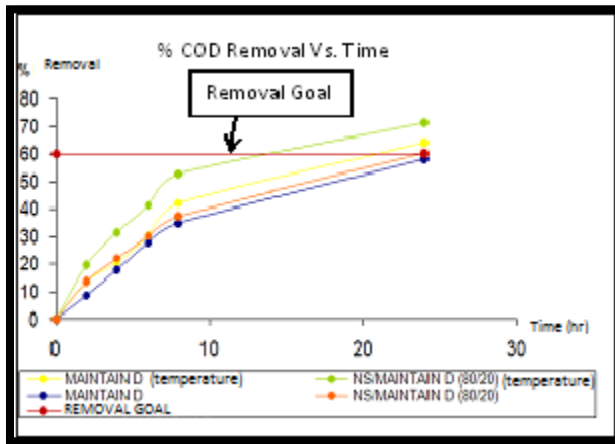
Water Type		
Unfiltered	COD (ppm)	6011
Filtered	COD (ppm)	5825
	% Removal	3.09
With pH Adjustment	COD (ppm)	4976
	% Removal	17.22

The tests were performed in duplicate using both products that shown the best results in the initial test. Data is shown in the following table, followed by the graphic shows the COD removal % in each case.

Table 19: Temperature Tests. Water with higher tanning residue concentration

Blank (mL) = 25, [] FAS (M) = 0.2525, COD (ppm) [0 h] = 4976, pH [Untreated] = 14					
HOURS	PRODUCT	MAINTAIN D®		NS/MAINTAIN D® (80:20)	
2	COD (ppm)	4283	4323	4000	3980
	% Removal	13.93	13.13	19.61	20.02
4	COD (ppm)	3960	3939	3394	3414
	% Removal	20.42	20.84	31.79	31.39
6	COD (ppm)	3455	3475	2909	2909
	% Removal	30.57	30.16	41.54	41.54
8	COD (ppm)	2869	2889	2344	2364
	% Removal	42.34	41.94	52.89	52.49
24	COD (ppm)	1637	1616	1414	1435
	% Removal	67.10	67.52	71.58	71.16

Graph 8: Temperature testing % Removal vs. Time Water with higher tanning residue concentration for 100 ppm biological product.



TEST FOR ANAEROBIC CONDITIONS

To establish anaerobic conditions it was necessary to close hermetically the containers, for this purpose various lids were used. A hole was made on each lid which was sealed with a hose and melted silicone to avoid air coming into the container and to release the gas produced by the microorganisms into a container filled with water. A one-time COD sample was taken after 24 hour period to avoid any oxygen entrance into the containers.

Image 10: Test Aerobic Conditions



Results for water with higher liming concentration: Water used was a combination from liming and tanning (80:20), the procedure involved to increase the pH to 7 by adding 2 mL of H₂SO₄ 98% solution, after it was added the correspondent biological product in a 100 ppm concentration under anaerobic conditions on each 5 L container.

To determine the COD removal due to each operation a measurement was realized and data is shown in the following table.

Table 20: Water testing results for anaerobic conditions assay. COD levels before biological treatment for water with higher liming concentration

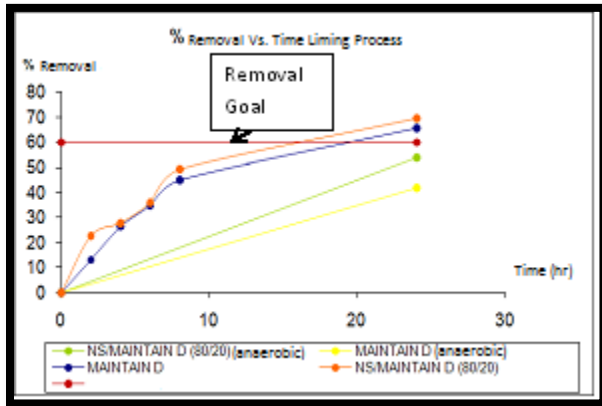
Water Type		
Unfiltered	COD (ppm)	6868
Filtered	COD (ppm)	6707
	% Removal	2.34
Adjusted pH	COD (ppm)	4808
	% Removal	30.00

The tests were done duplicate applying the two best products in the initial testing. Results are shown in the following table. The following graph shows the COD removal % for each treatment.

Table 21: Test for anaerobic conditions. Water with higher liming concentration

Blank (mL) = 25, [] FAS (M) = 0.2525, COD (ppm) [0 h] = 4808, pH [Untreated Water] = 10, T (°C) =					
HOURS	PRODUCT	MAINTAIN D®		NS/MAINTAIN D® (80:20)	
24	COD (ppm)	2788	2808	2222	2222
	% Removal	42.01	41.60	53.79	53.79

Graph 9: Test for anaerobic conditions. Removal vs. Time Water with higher liming concentration 100 ppm of biological product



Water with higher tanning concentration: The water applied was a combination of liming-tanning (15-85) the procedure involved raising the pH to 7 by adding 10 mL of H₂SO₄ 98% solution, the biological product was added after in a 100 ppm concentration and under anaerobic conditions on each 5 L container.

To determine the COD % removal each sample was measured accordingly and results are shown in the following table.

Table 22: Test for anaerobic conditions. Total % COD before treatment with biological products on water with higher liming proportion.

Water Type		
Unfiltered	COD (ppm)	6011
Filtered	COD (ppm)	5825
	% Removal	3.09
pH Adjustment	COD (ppm)	4976
	% Removal	17.22

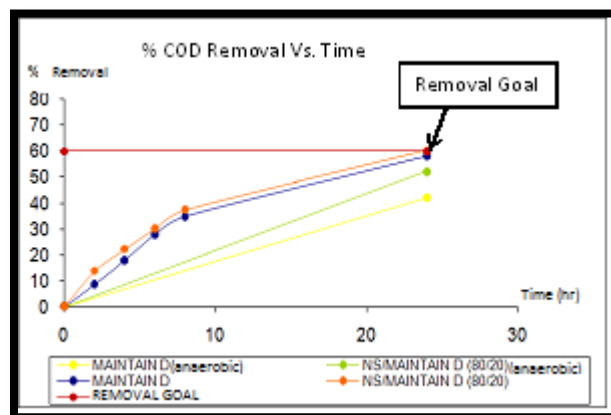
The test was realized applying the best two products based on initial results.

Table 23: Test under anaerobic conditions for water samples with higher tanning residue concentration

Blank (mL) = 25, [] FAS (M) = 0.2525, COD (ppm) [0 h] = 4976, pH [Untreated Water] = 14, T (°C)

HOURS	PRODUCT	MAINTAIN D®		NS/MAINTAIN D® (80:20)	
24	COD (ppm)	2889	2869	2384	2364
	% Removal	41.94	42.34	52.09	52.49

Graph 10: Anaerobic Conditions for water with higher liming proportion 100 ppm of biological product.



Analysis and Results Discussion

Initial Testing

According to the COD testing it was determined that the best suitable products with better performance were the blend (80:20) MAINTAIN D® Y NS/MAINTAIN D®. As showed in the graph 1 and 2. This two products help decrease de COD below the minimum obligatory levels which are 2000 mg/L and they achieved percentages superior to the removal goal. Therefore, posterior tests were done with these two products only.

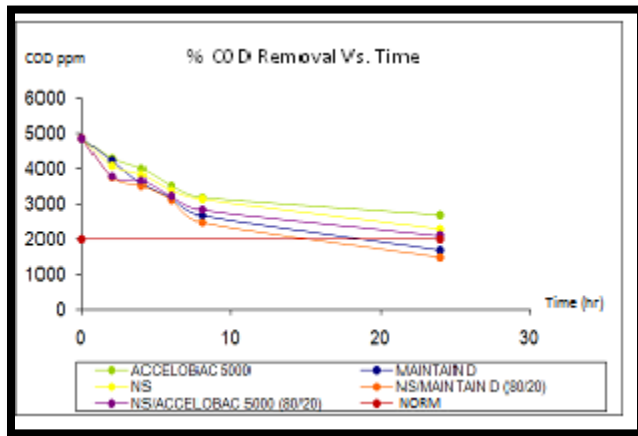
The microorganisms present in NS 20 have shown more resistance to heavy metals compared to other products. This was seen when they continue to degrade contaminant compounds even at higher concentrations (100 mg/L) of heavy metals in water. This product is also designed to degrade a variety of contaminants and toxins; it also metabolizes other chemicals like mineral oils surfactants, lipid acids, carbohydrates, lignin, and alcohols among others.

The microorganisms present in MAINTAIN D® are specially formulated to produce higher quantities of the enzymes lipase, protease and amylase which make this product suitable for degradation of organic waste of leather tanning processing waters.

The obtained results in this test confirmed that the properties and characteristics of these two products are the most suitable for the leather processing water environment.

Results for water with higher liming processing residue concentration: In the following graphs it can be observed the behaviour of the biological products for liming water and it's a fact that by using MAINTAIN D® and NS/MAINTAIN D® (80:20), they will reduce the contaminants below the concentrations permitted by law.

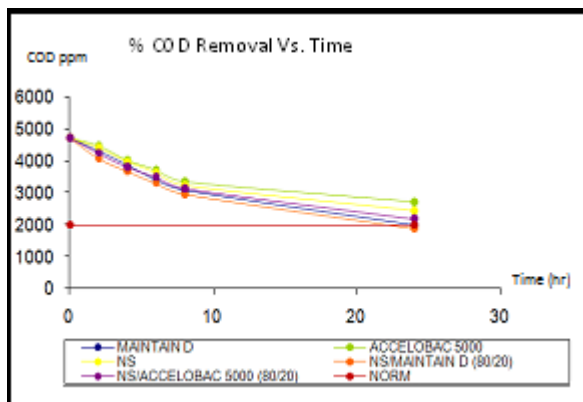
Graph 1: Initial testing on Liming Residue water for COD % vs. Time



Water with higher tanning processing residue concentration

In the next graph it is shown the biological product behaviour for liming residue water demonstrating that MAINTAIN D® y NS/MAINTAIN D® (80:20), reduce the contaminant below the concentrations permitted by law.

Graph 2: Initial testing for total % COD vs. Time for water with higher tanning processing residue proportion and 100 ppm biological products.



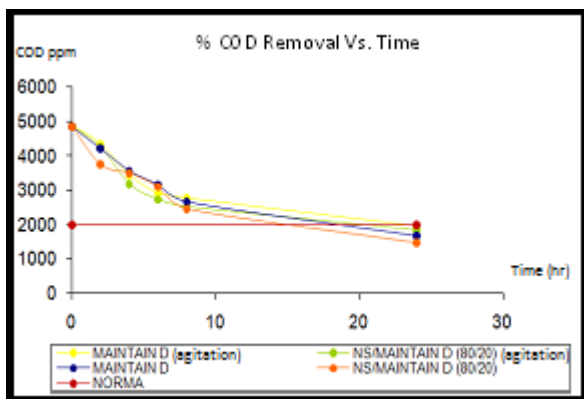
- These results showed the product effectiveness taking into consideration that a clarifying primary treatment wasn't performed.

These results showed that when agitation it's applied in the waters isn't a viable option since the required COD diminution wasn't accomplished. (< 2000 mg/L), these results are generated because the agitation makes difficult the sedimentation of the biomass that it's formed as the microbial metabolic product. This is a factor that increases the organic charge measured in the COD testing.

Water with higher liming residue concentration

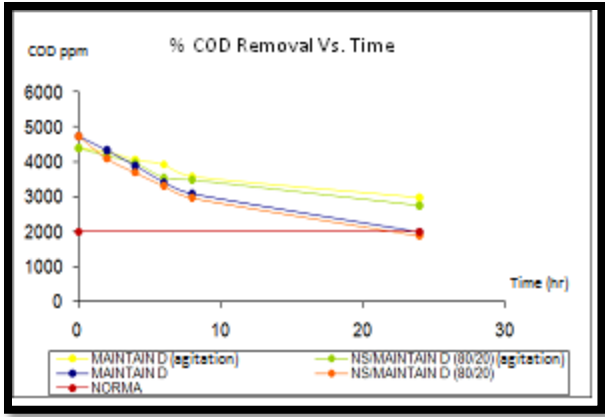
According to the testing on COD it's observed a better performance for the product NS/MAINTAIN D® (80:20), this reduction below the permitted levels by law (DQO < 2000 mg/L), is shown in the next graph; however the reduction isn't the same when there's no agitation applied.

Graph 3: Agitation Test. COD vs. Time for water with higher liming residue concentration. 100 ppm of biological product



Water with higher tanning residue concentration According to the testing on COD it is observed a better performance for the products NS/MAINTAIN D® (80:20), however there's no reduction below the permitted levels by law. (DQO < 2000 mg/L), this could be caused by the high chromium amount present in the waters. For better results it will be necessary to do a chemical precipitation of chromium and applying the primary treatment with aluminium sulphate 10% In addition, the constant agitation doesn't allow that the biomass formed or the organic matter achieves sedimentation which increase de COD.

Graph 4: Agitation Test COD vs. Time for water with higher concentration of tanning residue with 100 ppm of biological product.



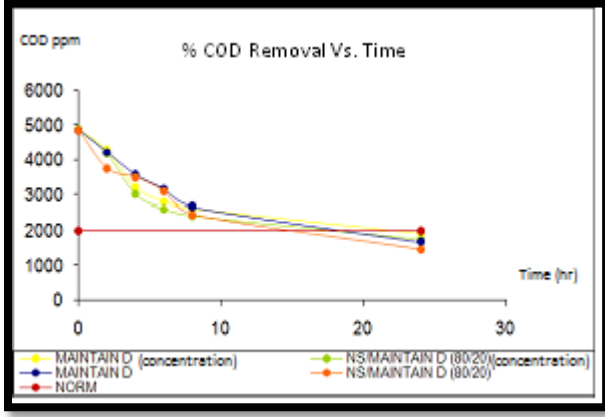
CONCENTRATION TEST

By this analysis it was observed that the product concentration that was used in all the others tests were appropriate considering that by decreasing the concentration the desired removal rate or speed isn't achieved

Water with higher liming concentration

According with the test on COD it was observed a better performance by the products NS/MAINTAIN D (80:20), a reduction below the allowed levels by law was observed (COD < 2000 mg/L) (see graph #5), however the reduction isn't the same than when a higher concentration of product is applied.

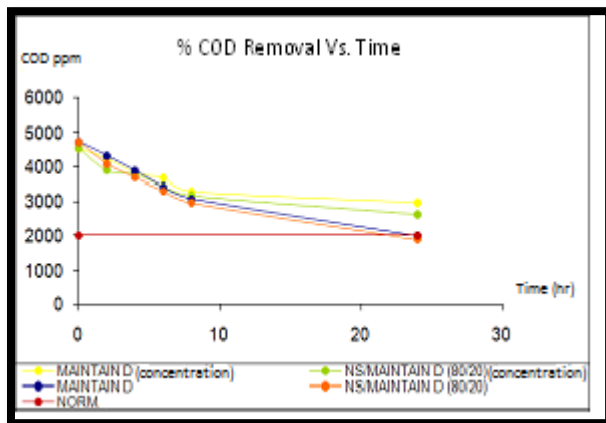
Graph 5: Concentration Test for COD vs. Time for water with higher liming residue and 50 ppm of biological product



Water with higher tanning residue concentration

According with the COD test it was observed a better performance by the products NS/MAINTAIN D (80:20), however, the reduction achieved isn't below the accepted levels by law (DQO < 2000 mg/L), as is shown in the next graph this can be due to the high chromium content in the water and the tanning residue water percentage on this test. . For better results it will be necessary to do a chemical precipitation of chromium and applying the primary treatment with aluminium sulphate 10% In addition, the constant agitation doesn't allow that the biomass formed or the organic matter achieves sedimentation which increases the COD.

Graph 6: Concentration Test COD vs. Time for water with higher tanning residue concentration 50 ppm of biological product



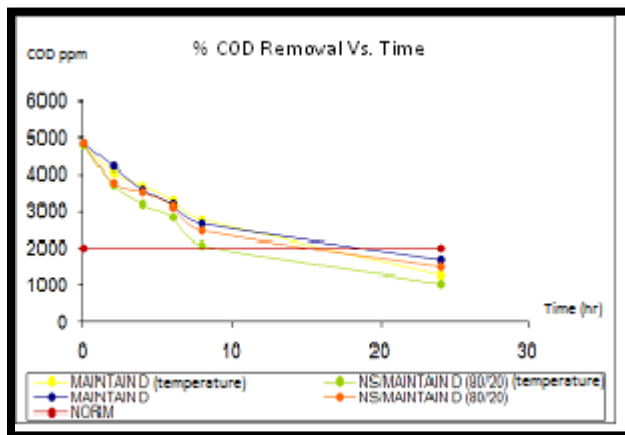
TEMPERATURE TEST

This test was done considering the technical recommendations of applying a temperature of 49°C for the proper biological product performance, a significant reduction was obtained for the COD compared to those results where none treatment is applied.

Water with higher liming residue concentration

According to the test son COD, it was observed a better performance for the products NS/MAINTAIN D (80:20), a reduction lower than the permitted levels (COD < 2000 mg/L), as show on the following graph by applying the adequate temperature.

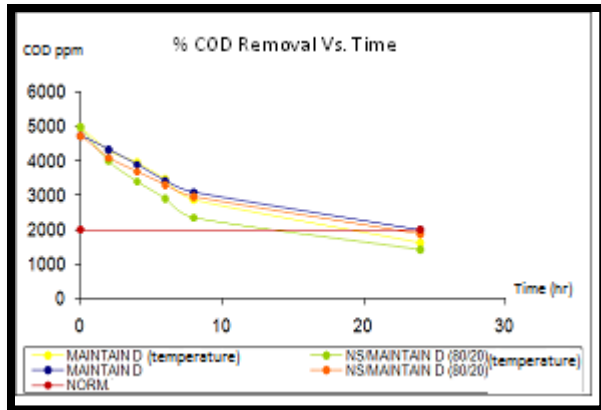
Graph 7: Temperature Test COD vs. Time Water with higher liming residue concentration and 100 ppm of biological product



Water with higher tanning residue concentration

According to the COD test, it was observed a better performance by the products NS/MAINTAIN D (80:20), with a reduction below the permitted levels by law (COD < 2000 mg/L), as shown in the following graph, by applying the adequate temperature better results were achieved.

Graph 8: Temperature Test. COD vs. Time Water with higher tanning residue concentration 100 ppm of biological product



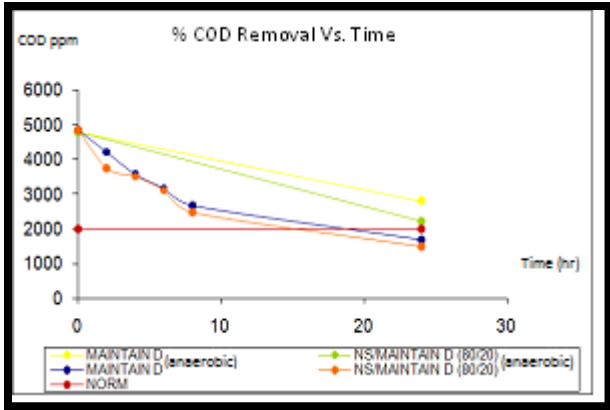
ANAEROBIC CONDITIONS TEST

This test was realized with the objective of comparing if the aerobic facultative and anaerobic facultative bacteria present in the products improve their performance under anaerobic conditions, however the majority of the microorganisms present are strictly aerobic, which means that they wouldn't survive this condition and that will affect the product performance during the treatment of residual leather processes waters by selective methods.

Water with higher liming concentration

According to the test on COD it was observed a better performance by the products NS/MAINTAIN D[®] (80:20), however, a reduction below accepted levels by law wasn't achieved (COD < 2000 mg/L), as shown in the next graph this was due to the lack of oxygen necessary for the growth of the microorganisms contained in the biological products.

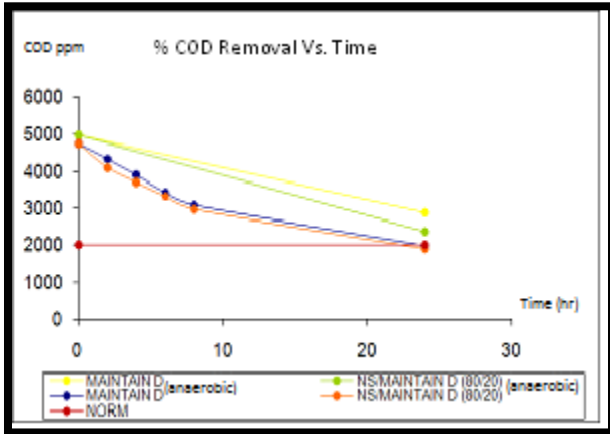
Graph 9: Anaerobic conditions Tests for % COD Removal vs. Time for water with higher liming residue concentration and 100 ppm of biological product



Water with higher tanning residue concentration

According to the test on COD, it was observed a better performance by the products NS/MAINTAIN D (80:20) however; a reduction below the accepted levels by law wasn't achieved. (COD < 2000 mg/L), as shown in the next graph this is due to the lack of oxygen necessary for proper microbial growth.

Graph 10: Anaerobic conditions test for % COD Removal vs. Time. For water with higher tanning residue concentration and 100 ppm of biological product



DISCUSSION

By the experimental methods developed it was observed that the microorganisms have a better performance in the effluents that contain a higher proportion of water from the liming processes. This is due to the organic matter quantity found in this water and lower toxic quantity than the tanning processes water. The tanning processes water contains a total chromium amount that exceeds the 100 ppm (maximum tolerated quantity by microorganisms) which makes that the microorganisms work a lot slower since they can't metabolize the toxic compounds and this cause them to multiply a slower rates as well.

To reduce the chromium concentration and impede that the microbial growth is affected, is necessary to realized a primary treatment on the tanning residue waters which consists on flocculation and coagulation by applying a sulphate aluminium solution 10% in a concentration of 1600 ppm. However, it must be maintained a neutralization operation, since the effluents are acidified slightly, it must be applied caustic soda 50% before applying the biological products this will prevent the microbial growth to be slowed down. On all the tests it was observed a biomass formation in the form of settled sludge which is a metabolic product of the generated enzymes during the organic matter degradation process, therefore isn't advisable the water agitation during treatment since the generated biomass will increase the total COD and BOD once is agitated.

To realize the residual water characterization in a certified laboratory a sample of a combination of liming-tanning (80:20) was collected and the residual water treatment was done with a concentration of y se de NS/MAINTAIN-D (80:20) mixture following the same procedure described in the experimental methods. The results obtained in this characterization showed an initial COD of 6.852 mg/L and a final COD of 1.868 mg/L which represents a removal percentage of 72.2 % this value is very close to the one obtained during the initial test with water that had higher concentration of liming residue which was 69.63%.

Percolated Filter Design

To design the percolated filter is necessary that this filter comply with the following specifications to properly manage the high organic matter concentration contained on leather processing effluent waters:

- Filter Media: Filling in black propylene honeycomb shape. With a specific surface of = 90 m²/m³

External Diameter = 187 mm

Height = 50 mm

Unitary Weight = 105 g

Surface Area for each element = 0.164 m² Element quantity by m³ = 500

- Caudal = 0.42 m³/h
- Initial COD = 5000 ppm
- Desired COD = 1500 ppm
- Initial BOD = 2500 ppm
- Desired BOD = 750 ppm

$$L_D / L = 10^{-3.3 \cdot K \cdot D}$$

CONCLUSIONS

- By the experiment findings it was determined that the COD of the water that comes from the liming processes is between 4.700 to 7.000 mg/L and the water that comes from the tanning processes is 4.700 y 6.000 mg/L. These results were confirmed by the several analyses done at the certified lab facilities. It was also demonstrated the high concentration of: sulphur, suspended and sedimented solids, BOD fats and oils that are contained on liming processes water.
- According to the technical specifications of the biological products it is necessary to conditioning the effluents before application, whit that perspective the pre-treatment operations that should be done are: filtration and pH adjustment to a value close to 7
- It was identified that the adequate conditions for application of the biological products are pH of 7 and a temperature of 45°C ± 4°C at a concentration of 100 ppm to achieve the highest percentage of organic

matter removal which is approximately 80% for the retention period that the process requires which is 24 hours.

- According to the experimental design it was determined that the biological product that achieved a higher percentage of COD removal is NS/MAINTAIN D in proportions of 80:20, this achieved a removal of 79% at a temperature around $45^{\circ}\text{C} \pm 4^{\circ}\text{C}$ for the liming process water.
- The implementation in the waste water treatment plant doesn't generate the expected savings (20% according to the Internal Rate Opportunity TIO); this is because the internal rate for the project is about 15%. However, the proposal represents a total saving budget of \$24.687.150,33 which corresponds to the value that is no longer paid for fines and 30 day closing, in addition to the generation of additional income of \$6.679.421,02. Also with this proposal it's pretended the creation and promotion of environmental conscience regarding the waterways resources conservation in the municipality.
- The percolated filter designed by engineer means brings three important advantages: recirculation of treated waters, good aerations conditions and a total efficiency of 60%. This means that the COD reduction value obtained will be inferior with the biological product application only.