CHARACTERIZATION AND TREATMENT OF SPENT VEGETABLE TAN LIQUORS

by

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I. INTRODUCTION

"Tanning is an industry deriving from prehistoric times, and to those familiar with them, the wastes from the industry present many Neolithic characteristics, notably a disagreeable appearance, a bad smell, and a high degree of intractability." [18]

Location of early tanneries was in the vicinity of watercourses from which process water was obtained and into which the disposition of wastes and effluents from the tanneries were and still are released. The characteristics of these waterborne waste are high Biochemical Oxygen Demand, high solids, including large quantities of soluble organic material, suspended solids, color, odor, and a high Chemical Oxygen Demand. Because of these characteristics the waste has obtained the classification of one of the "Four Horsemen of Pollution",[7] thus ranking tanneries as one of the heaviest polluters of all industries.

The tanning industry remains an art more than a science even though great steps have been made toward a standardization of the processes. Still,analysis of the tanning process is primarily a plant to plant problem with each plant incorporating at least a slight differentiation from any "standard" process. A continued change in the process chemicals used in the process affords an effluent that cannot be considered constant in characteristics.

Cattlehides, sheepskins, and goatskins are the major hides used in tanneries in the United States with cattlehides ranking first in the tonnage of hides used. The difference in the waste effluent from a tannery treating any one of the above hides differs little more than a normal plant to plant variation. The type of tanning process used does, however, affect the waste characteristics to a great extent. The three processes now in use by tanneries in the United States are termed vegetable, mineral, and chrome tan processes. Of these, chrome tan is responsible for most of the volume in the industry with vegetable tan processes producing the bulk of the remaining volume.

Most of the research and pilot studies concerning the treatment of the tannery wastes have been conducted in India, Japan, and Germany. Recent research endeavors performed here in the United States indicate a growing need and requirement for a satisfactory and economical means for treating this waste. These studies have included both chemical treatment consisting primarily of the coagulation of both the composite and separated waste with the salts of aluminum, iron, and with lime, and biological treatment processes including activated sludge, anaerobic lagoons and trickling filters. Aeration of both settled and unsettled raw waste has been explored.

Of the major pollutional characteristics of the waste, the color of the spent vegetable tannins is often singled out as particularly esthetically objectionable, and in the eyes of the general public, this color is an indication of pollution. This waste, entering a stream containing a high content of iron, will turn the water black. Chemical coagulation especially with the iron salts has not been efficient in color removal. Activated sludge has shown possibilities along this line but only with extended periods of aeration contact. In addition the high dilutions required make the feasibility of the activated sludge process for color removal questionable. Another pollutional characteristic of this waste is the high Biochemical Oxygen Demand exerted on the stream. The need for an economically feasible treatment process is readily visualized, for without such a process the receiving waters will tend to become polluted beyond the extent of recovery of the stream. A typical high Biochemical Oxygen Demand tannery waste must receive treatment to lower the oxygen demand of the waste to a point where the stream can efficiently assimilate the waste.

Over the last several years, research has concentrated on the segregation of the tannery waste. Different forms of both biological and chemical treatment have persisted over these years, but few combinations of these processes have been explored. Activated sludge treatment has been the most efficient of the biological treatment methods, whereas chemical coagulation with ferric chloride also gave good results.

The research undertaken consisted of an investigation of chemical treatment of the waste either preceded by or followed by a form of biological treatment. The chemical treatment consisted of coagulation of the segregated spent vegetable tannin liquor utilizing combinations of aluminum sulfate and a synthetic liquid cationic electrolyte produced by the Nalco Chemical Company. Biological processes used were confined to pre-aeration of the waste and post-aeration of the supernatant from the chemical treatment. The purpose of this study was to determine if the use of the high charged polymer was feasible for effecting the degree of treatment required and if the aeration would have a significant effect on the efficiency of the process with respect to the lowering of the Chemical Oxygen Demand of the effluent.

II. LITERATURE REVIEW

Tannery waste treatment, one of the most complex problems in the field of industrial waste treatment due to the high pollutional characteristics of the spent waste, is made even more complex by the wide variation of processes and materials used by the individual plants. Therefore, each plant tends to have a unique treatment problem. Even the segregated spent vegetable tannin liquors differ widely because of the great variation in the materials, both quantitatively and qualitatively, used to prepare the vegetable tannins, and the variation in the processing of the hides before reaching the tannin vats.

The tanning process in general consists of removing the epidermis and fatty tissue of the hide and treating the corium (the protein collagen, $C_{102}H_{149}N_{31}O_{38}$) and transforming it into an insoluble, tough, highly durable, and flexible material. The processes involved include the beamhouse operation in which the hair, fatty tissue, and undesirable protein are removed from the hide and the corium is prepared for the tan house, followed by the tanning process in which the actual conversion to leather takes place. The following is a typical flow sheet of a vegetable tanning process illustrating sources of waste. (Figure 1).

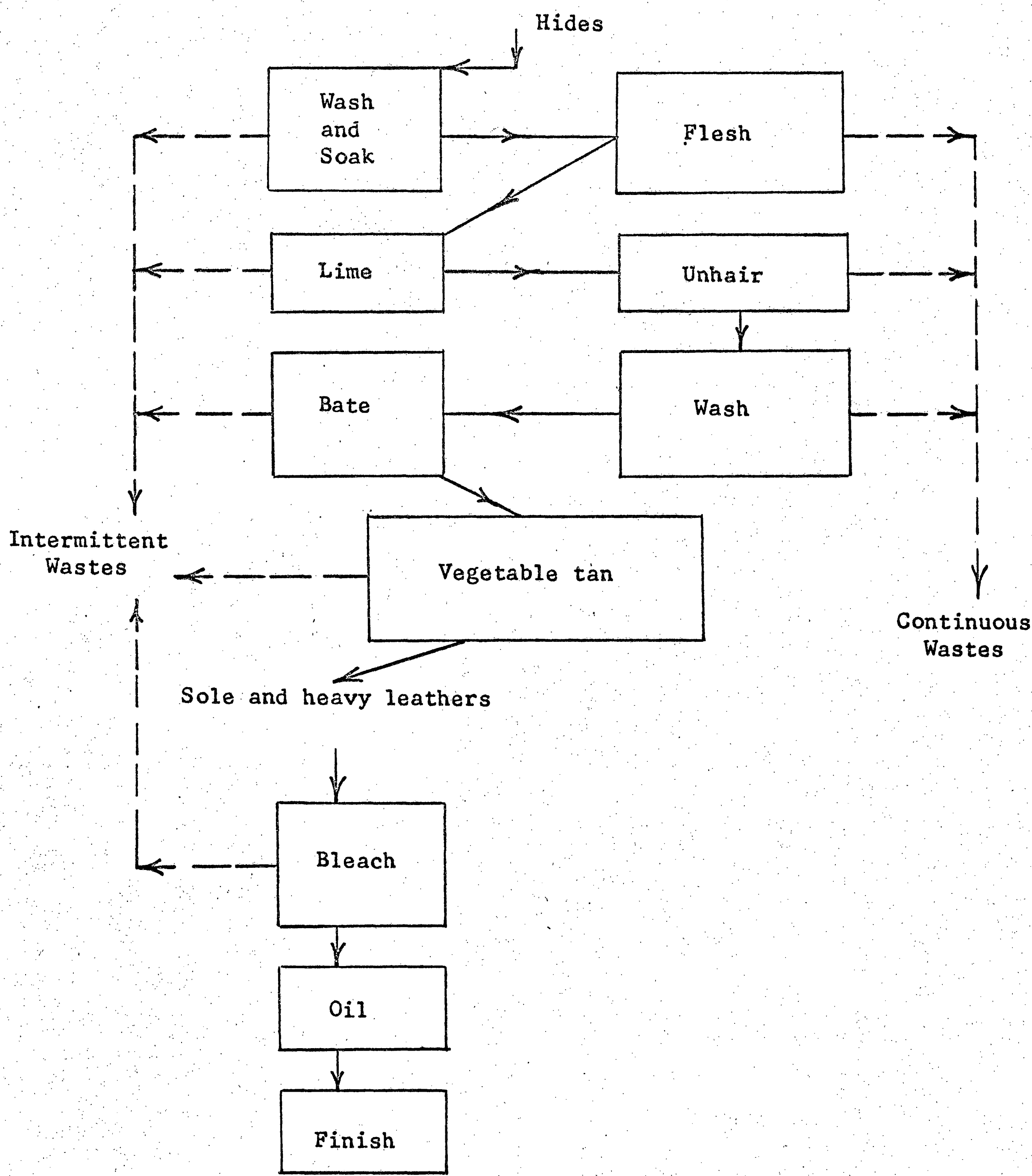

Figure 1. Flow Sheet of Sole and Heavy Leather vegetable Tanning Process

The vegetable tannins generally consist of complex glucosides of tannic acid obtained from chestnut and hemlock barks, quebracho wood, myrobalan, cutch or mangrove bark, and extract from certain fruits. The waste tan liquors constitute the strongest portion of the tannery waste in terms of organic pollution load and Biochemical Oxygen Demand. The spent vegetable tannins carry only 6 to 8% of the total plant waste volume but from 45 to 50 per cent of the total Biochemical Oxygen Demand loading as well as the majority of the color.

"If the spent tan can be eliminated in some manner, a long step has been taken in reducing the pollutional strength of the waste. Since the weaker wastes are, in general, the continuously discharged wastes and the stronger wastes are the intermittent discharges, a segregation based on this principle is feasible." (18) The composite spent vegetable tan waste strength varies according to constituent material but a general range is reported as follows:

Total Solids	-	18,400	---	34,255 ppm
Suspended Solids	-	1,200	---	6,000 ppm
Soluble Solids	-	17,110	---	33,400 ppm
Volatile Solids	-	15,400	---	29,176 ppm
$B.O.D._5$	-	800	---	3,000 ppm
Color	-	4,000	---	5,000 ppm
pH	-	5.2	---	5.5

Several methods for segregated treatment of the intermittent waste have been proposed as a result of research, including both chemical and biological treatment processes.

Chemical precipitation has consisted mainly of coagulation of the spent tan liquor using sulfuric acid, sodium hydroxide, and carbon dioxide for pH control with coagulation enacted by lime, alum, and iron salts in combination with mechanical flocculation. Howalt and Cavett [12] aerated the intermittent wastes from a vegetable tan plant at pH 5.5, and then mixed the product with the continuous waste from the plant containing a high lime content which served as a coagulant. From this system a settable coagulant with good color and total solids reduction was obtained. Chemical coagulation with regulation of pH to a level of about 11.5 was also tested. Lime was used and the calcium tannate precipitated along with excess lime left a dark brown supernatant. A significant reduction in color and suspended solids but less favorable removal of Biochemical Oxygen Demand was obtained. Toyoda, Yarisawa, Futami, and Kikkawa [25] in tests on spent tan liquors showed that alkalization by sodium hydroxide yielded a very small effect, whereas, acidification by hydrochloric acid or sulfuric acid and alkalization by lime to a pH 11.5 showed an especially good result. Coagulation by iron salts, especially ferric chloride showed considerable promise. Some early studies by Reuning [17] used evaporation of the spent tannins as a means of treatment.

Principle means of secondary treatment tested have been in connection with a mixture of tan liquors with sludge from domestic sewage aerated for 24 hours followed by sedimentation, trickling filters, sand beds, and sludge drying on sand beds.[5] Recent studies have largely been related to aerobic treatment, primarily activated sludge. Biological methods have been confined primarily to pilot plant studies because of the difficulty in treating the straight tanning waste.

Aerobic activated sludge treatment studies of tannery wastes have been conducted by Chakrabarty, Khan, and Chandra.[3] Tannery waste was found to be amenable to treatment by the activated sludge process in admixture with sanitary sewage, the amount of which varied with the nature and concentration of the wastes. Thabaraj, et al.,[23] found that at an aeration solids concentration between 2000 to 4000 mg/l, the Biochemical Oxygen Demand of the presettled and diluted vegetable tannery waste could be reduced from 988 mg/l to 684 mg/l with 6 hours aeration, to 370 mg/l with 12 hours aeration, to 162 mg/l with 18 hours aeration, and to 34 mg/l with 24 hours aeration.

The studies preformed by Chakrabarty, et al.,[3] consisted of using a sludge seed acclimated to tannin waste and a well mixed composite sample of the spent vegetable tannin waste. The residual concentration of tannin in the spent tan liquor had a normal range of from 0.62 - 1.2% on a weight volume relationship. The average oxygen requirement in the treatment of tannery waste was found to be about 98.6 mg/hr./gm volatile solids at the start of the aeration period. From these studies it was found that a significant concentration of tannin in the substrate increased the oxygen requirement greatly. Since the spent tannins consist primarily of benzene ring compounds containing either two or three hydroxyl groups, catechol or pyrogallol respectively, and since these compounds are strong reducing agents, it was surmised that a considerable amount of the oxygen was utilized by these compounds. A dilution of the waste in a range from 60 to 90% with domestic sewage was used for the aerobic activated sludge treatment.

Aerobic biological treatment processes of the waste have been found to reduce significantly the Biochemical Oxygen Demand of the waste, whereas, some type of chemical coagulation and precipitation treatment will afford significant reductions in the color and solids concentration of the waste. With a reduction in solid content by chemical precipitation, the air requirements necessary for aerobic biological treatment of the waste can possibly be lowered to a point where an efficient and reasonably economical means of treatment by this type of process can be developed.

III. TAN HOUSE PROCEDURE AND WASTE COMPOSITION

The tanning waste chosen for this study was the spent vegetable tan liquors acquired from the Leas and McVitty Corporation tannery in Pearisburg, Virginia. This waste was selected because of its characteristically high pollutional strength and color properties as well as the treatment problems associated with satisfactory disposal of these liquors to streams. The need for better treatment techniques is apparent from a review of the current state of the art. The approximate composition of the tannins studied was obtained from the Leas and McVitty plant officials at the Pearisburg Plant.

Composition Of Waste

This waste consists primarily of the spent tannins of which the major constituent is a benzene ring compound that is polyhydroxyl in nature with the three hydroxyl compound, pyrogallol, being especially prevalent. This compound is a poisonous, bitter, white crystalline phenol, $C_6H_3(OH)_3$, obtained chiefly by the action of heat on gallic acid. The source of the gallic acid in the vegetable tannins is the bark of certain trees and the extract of fruit. This extract displays acidic properties and is sometimes called pyrogallic acid. The tan waste is composed of the spent liquors derived from the following raw materials:

1. quebracho bark - obtained from a tree, the Quebrachia lorentzii of the sumac family, is bright red in color and rich in tannins.
2. chestnut bark - a tree of the beech family
3. whetle - the bark and extract from a Brazilian tree
4. valonia - the dried acorn cups of the valonia oak tree, a Turish oak
5. ligno sulfonates - a lignin ester of sulfonic acid
6. rinse waters

Tanning Procedure

The tanning liquors are obtained by placing the source material constituents previously mentioned in large boilers to which heat is applied. During this time the gallic acid present in the compounds is converted to pyrogallol. The specific gravity of the solution is used as a check on the preparation of the solution by a barkometer, a special type of hydrometer used by the industry. Once the barkometer reading is compared satisfactorily to results obtained by previous experience, the tanning solution is considered ready for use. At this point the solution is high in the polyhydroxyl benzene ring compound, pyrogallol, a reducing agent that is oxidized by oxygen obtained from the air during the tanning process.

The tanning operation in which the prepared hides are placed in intermittent contact with the tan liquors is a countercurrent operation taking from one to two weeks. The hides are placed on arms known as rockers and then placed in the tannin vats. The hides proceed from the weakened solution known as the tail liquors to the stronger liquors until the degree of tannage desired is obtained. These tail liquors or spent liquors are the waste from the actual tanning process. It is the purpose of this research to study feasible methods of treatment for this waste.

IV. METHODS AND MATERIALS

Experimental Materials

A. Reagents

1. Aluminum Sulfate. ($Al_2(SO_4)_3 \cdot 14H_2O$), C.P. (Fisher). Used in a 1.0 Normal solution as a coagulant in combination with the cationic electrolyte.

2. Cationic Electrolyte. Nalcolyte 607 coagulation chemical, (Nalco). Used as the primary coagulant in combination with variable quantities of aluminum sulfate.

3. Dextrose. anhydrous, ($C_6H_{12}O_6$), (d-glucose), certified reagent. (Fisher). Used for obtaining a standard curve for Chemical Oxygen Demand.

4. Ferric Chloride. ($FeCl_3 \cdot 6H_2O$), lump, C.P. (Fisher). Used in a 1.0 Normal solution as a coagulant in preliminary coagulation studies.

5. Ferroin Indicator Solution. (1, 10 - Phenanthroline Ferrous Sulfate Complex), (Fisher). Used for indicator in conventional Chemical Oxygen Demand determinations.

6. Ferrous Ammonium Sulfate. ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$), granular, certified reagent, (Fisher). Used in conventional Chemical Oxygen Demand analysis as a titrant.

7. Lime, high calcium hydrate, ($Ca(OH)_2$), chemical grade, (National Gypsum Company). Used in a 1.0 Normal solution in a preliminary study as a possible coagulant.

8. Mercuric Sulfate. ($HgSO_4$), powder, analytical grade, (Baker). Used to eliminate interferences due to chlorides in the tan wastes in both the conventional and Technicon Auto-Analyzer Chemical Oxygen Demand analysis.

9. Potassium Dichromate. ($K_2Cr_2O_7$), fine crystals, certified reagent, (Fisher). Used as an oxidant in the conventional and Technicon Auto-Analyzer Chemical Oxygen Demand analyses.

10. Silver Sulfate. (Ag_2SO_4), powder, reagent grade, (Baker and Adamson). Used as a catalyst in Technicon Auto-Analyzer Chemical Oxygen Demand analysis to assist in oxidizing straight-chain compounds in the tanning waste.

11. Standard pH Buffer. (Monopotassium Phosphate-Sodium Hydroxide Buffer), 0.05 Molar, (pH 7.00 $\pm$ 0.02 @ 25°C) certified reagent, (Fisher). Used as a buffer for standardization of pH meter.

12. Standard pH Buffer. (Potassium Biphthalate Buffer), 0.05 Molar, (pH 4.00 $\pm$ 0.02 @ 25°C) certified reagent, (Fisher). Used as a buffer for standardization of pH meter.

13. Sulfamic Acid. (H_2NSO_2OH), granular, certified reagent, (Fisher). Used in the conventional and Technicon Auto-

Analyzer Chemical Oxygen Demand analysis to eliminate interference due to nitrite in the tanning waste.

14. Sulfuric Acid. concentrated, (H_2SO_4), reagent grade, (Fisher). Used in digestion mixture for Technicon Auto-Analyzer Chemical Oxygen Demand analysis; used in conventional Chemical Oxygen Demand analysis; used in standard Biochemical Oxygen Demand determinations to fix dissolved oxygen concentration.

B. Apparatus

1. Analytical Balance. (Sartorius). Used for determining accurate weight in tests.
2. Beakers. 1000ml, (Corning), Pyrex Brand Glass. Used in coagulation (jar tests).
3. Burettes. 25ml, (Fisher). Used for titrations.
4. Condensers. (Friedrichs), Pyrex Brand Glass with 24/40 Ground-Glass Joints. Used as a part of the reflux apparatus in the conventional Chemical Oxygen Demand analysis.
5. Dessiccators. (Fisher). Used to cool reagents, residues, and their containers to room temperature after drying in the drying ovens and ignition in the muffle furnace.
6. Drying Oven & Electric Muffle Furnace. (Precision). Used to dry reagents and samples from suspended solids and volatile solids tests.

7. Evaporating Dishes. Used in titrations and to hold samples for total solids and volatile solids.
8. Extraction Heating Unit and Support. Six Electrically Heated Units, (Precision). Used as part of the reflux apparatus for conventional Chemical Oxygen Demand analysis.
9. Flat-Bottom Flasks. 500ml, (Corning), Pyrex Brand Glass with Long Neck and 24/40 Ground-Glass Joints. Used as part of the reflux apparatus in conventional Chemical Oxygen Demand analysis.
10. Gas Diffuser Stones. (Fisher). Used for air diffusion in the post and preaeration of the waste and in Biochemical Oxygen Demand dilution water preparation.
11. Glass Fiber Filters. (Reeve Angel). Used in the filtration for the determination of suspended solids.
12. Gooch Crucibles (Coors). Used in the filtration for the determination of suspended solids.
13. Harvard Trip Balance (Ohaus). Used for determining less accurate weights in experiments.
14. Large 20 Liter Pyrex Brand Bottle. (Corning). Used for Biochemical Oxygen Demand dilution water preparation.
15. Magnetic Mixer. (Wilkens-Anderson). Used to mix solutions.
16. Multiple Stirrer. (Phipps and Bird). Used for coagulation (jar test).

17. Oxygen Meter. Y.S.I. Model 51, (Yellow Spring Instrument Company). Used to measure the dissolved oxygen content in the aerated waste and aerated settled waste.

18. pH Meter with Glass Electrodes. (Leeds and Northrup). Used to measure pH of samples.

19. Spectronic 20 Colorimeter/Spectrophometer. (Bausch and Lomb). Used in color determinations of wastes and color removal.

20. Technicon Auto-Analyzer. (Technicon). Used to determine Chemical Oxygen Demand of samples.

Experimental Methods

The purpose of this investigation was to determine if selected cationic polyelectrolytes in combination with variable amounts of aluminum sulfate are applicable as chemical coagulants upon the spent vegetable tan liquors for color and solids removal, and if a reduction in the Biochemical Oxygen Demand of the liquors would be effected by the use of either pre-aeration of the spent waste before coagulation and sedimentation or post-aeration of the coagulated waste supernatant. The spent vegetable tannin was supplied by the Leas and McVitty Corporation from its plant in Pearisburg, Virginia.

Initial tests were performed upon the raw waste to determine its characteristics. Tests run included total solids, volatile solids, suspended solids, pH, conventional Chemical Oxygen Demand analysis, Technicon Auto-Analyzer Chemical Oxygen Demand analysis, oxygen uptake rate (Warburg), conventional Biochemical Oxygen Demand, alkalinity, color, dissolved solids, per cent settleable solids by volume, and chemical coagulation with "jar tests".

Test performed upon the pre-aerated and coagulated waste and the chemical coagulated waste with post-aeration were Technicon Auto-Analyzer Chemical Oxygen Demand, suspended solids, chemical coagulation with "jar tests", and color. The appearance and color of the supernatant and the amount of sludge precipitated were noted in each coagulation test.

A description of the manner in which the various tests were conducted follows:

EXPERIMENT 1: CHARACTERIZATION OF WASTE

A thorough characterization of the waste was initially performed to determine the major pollutional characteristics of the waste in order to provide a basis for determining a method of treatment which would produce a satisfactory effluent at a reasonable cost. Composite waste samples obtained were well mixed by thorough stirring before all experiments were performed.

Total Solids Test: The total solids test was performed as described in *Standard Methods for the Examination of Water and Wastewater* [22] under the method for Residue on Evaporation.

Volatile Solids Test: The volatile solids test was performed as described in Standard Methods for the Examination of Water and Wastewater [22] under the method for determining Total Volatile and Fixed Residue.

Suspended Solids Test: The suspended solids test was performed as described in Standard Methods for the Examination of Water and Wastewater [22] under Total Suspended Matter (Nonfilterable Residue) except that a 2.1 centimeter glass fiber filter was used in place of the asbestos mat in the Gooch Crucible method.

Dissolved Solids Test: The dissolved matter was obtained by the difference between the residue on evaporation and total suspended matter as described in Standard Methods for the Examination of Water and Wastewater [22] under Dissolved Matter (Filterable Residue).

Settleable Solids Test: The settleable solids were determined on a volume basis as described in Standard Methods for the Examination of Water and Wastewater [22] under Settleable Matter.

pH Determination: A Leeds and Northrup glass-calomel electrode pH meter was used to measure the pH values of the sample directly. The meter was standardized with buffer solutions at pH 4.0 and 7.0.

Alkalinity: The alkalinity of the raw waste was determined in accordance with procedures set forth in Standard Methods for the Examination of Water and Wastewater (22) using the pH titration method.

Chemical Oxygen Demand (Conventional): The determination of chemical oxygen demand of the raw waste was in accordance with the method as set forth in Standard Methods for the Examination of Water and Wastewater (22) with an exception being the use of flat bottom flasks in place of erlenmeyer flasks.

Chemical Oxygen Demand (Technicon Auto-Analyzer): Chemical Oxygen Demand tests run on the raw waste were conducted as a check on the results obtained from the conventional chemical oxygen demand analyses. Mercuric sulfate, sulfamic acid, and silver sulfate were added to the other constituent reagents in the same quantities as in the conventional chemical oxygen demand analysis. The method for determining chemical oxygen demand consists of the digestion of the sample by known quantities of potassium dichromate and concentrated sulfuric acid. Colorimetric methods were used to determine the depletion of color due to the oxidation of the organic materials in the sample with results recorded on the chart of a recorder. The chemical oxygen demand of the samples was determined by comparison of their responses with those of known glucose solutions which were used to plot a standard curve. (Figure 3). A flow diagram of the Technicon system for measurement of chemical oxygen demand is shown in Figure 2. The manual accompanying the Technicon Auto-Analyzer gives a more detailed discussion of the operation of the Analyzer for such determinations.

Biochemical Oxygen Demand: Methods used for the determination of the Biochemical Oxygen Demand of the waste were in accordance with the procedures as set forth in *Standard Methods for the Examination of Water and Wastewater* [22] for a seeded dilution water with the following exception. Dilutions of less than one per cent were necessary for the waste to retain an excess of dissolved oxygen in the incubated biochemical oxygen demand bottle. These biochemical oxygen demand determinations were used to obtain a correlation between biochemical oxygen demand and the chemical oxygen demand of the waste such that for further analyses the determination of chemical oxygen demand would be sufficient.

Color Determination: The apparatus used for color determinations of the waste was the Spectronic 20 Colorimeter/Spectrophotometer manufactured by Bausch and Lomb. Information concerning the use of the instrument was obtained from the instruction manual accompaning the instrument. The dominant wave length was determined by the method described in *Standard Methods for the Examination of Water and Wastewater*. [22]

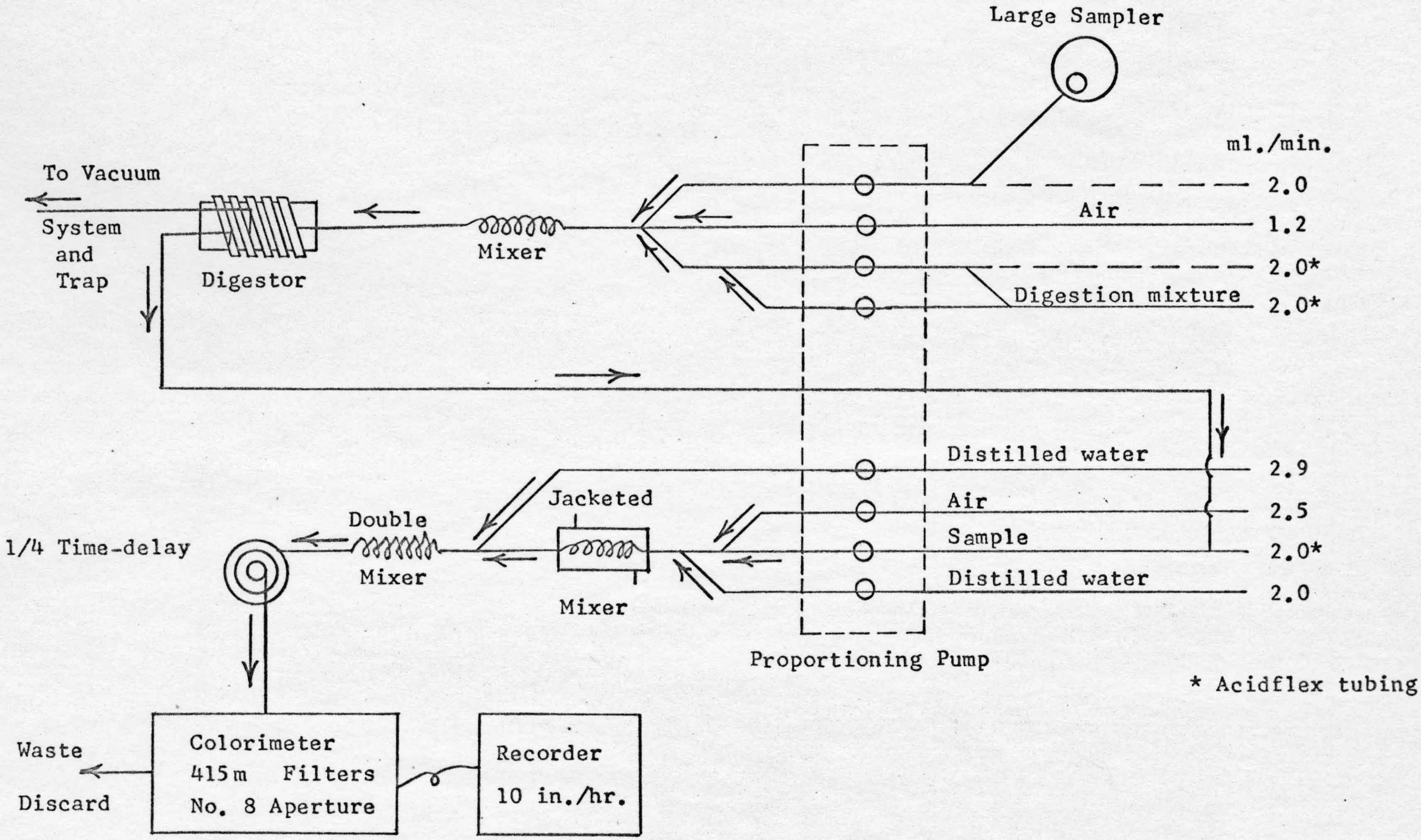

Figure 2. Flow Diagram of Auto-Analyzer For Chemical Oxygen Demand Determination

Warburg Respirometer Test: The five day Biochemical Oxygen Demand value and the oxygen uptake rate of the spent vegetable tan liquors were determined by the use of the Warburg Respirometer manufactured by the Precision Scientific Company. This manometric method was employed to study the rates of oxidation of this industrial waste mixed with an acclimated seed. This method is superior to the standard azide method for dilutions containing much greater concentrations of waste than possible to measure within the dilution limits of the standard azide method. For the determination 10 ml. of activated sludge with a sludge concentration of 4000 mg/l was pipetted into the Warburg flask. To this was added 0.5 ml. of the spent vegetable tan liquor and 9.5 ml. of dilution water. The Thomas graphical method was employed for the determination of the five day Biochemical Oxygen Demand and oxygen uptake rate of the waste from the Warburg data.

Preliminary Tests: Preliminary coagulation tests consisted of the use of lime, ferric chloride, and polyelectrolytes produced by the Nalco Chemical Company. Results of these coagulation studies indicated that these coagulants were of questionable value. Lime produced a dark brown supernatant but required a high coagulant demand for significant color removals. Ferric chloride produced little results. A problem with an iron-pyrogallol complex forming on the addition of the ferric chloride decreased the color removal efficiency. No noticeable effective results were obtained from the use of cationic polyelectrolytes produced by the Nalco Company other than with the polyelectrolyte used in this investigation.

EXPERIMENT 2: TREATMENT OF SPENT VEGETABLE TANNIN

Chemical Coagulation With Aeration Treatment: The investigation of the treatment of spent vegetable tannin waste utilized the processes of chemical coagulation with a cationic electrolytic polymer in variable combinations with aluminum sulfate and either aeration of the spent waste previous to the chemical treatment or of the supernatant from the coagulation-sedimentation process.

The aeration chamber was a two and one-half gallon plastic container. Air supplied to the system passed through cotton plug filters to remove all particulate contaminants. Diffusion of the air through the solution was effected using two porous gas diffuser stones.

A high degree of foaming was noted during the aeration and some problems with overflow of the foam from the container were present. Correction of this situation was accomplished through lowering of the liquid level in the tank. Samples were taken from the tank after 12, 24, and 36 hours aeration. Sample size was approximately three liters.

Coagulation Test: Coagulation tests were performed upon the raw and aerated samples to determine their chemical coagulant demand. Coagulants used for this test consisted of a cationic electrolyte and aluminum sulfate in variable dosages. In all experiments the electrolyte was added to the sample previous to the aluminum sulfate. Aluminum sulfate solutions were prepared every two days while the electrolyte was furnished in a liquid form by the manufacturing company and was thus ready for use.

The procedure followed was that as set forth by Parsons. [16] The coagulant demand of the samples was determined by varying the coagulant dosage in 25 milliliter samples. From these determinations, the range of chemical dosage for the regular coagulation tests were then derived. 500 milliliter samples were then added to each of six beakers accommodated on the coagulant test apparatus. This jar test apparatus was a multiple stirrer device manufactured by Phipps and Bird. The coagulants were added to the beakers in increasing dosages from the left to right while the apparatus was operating at 100 revolutions per minute (rpm). The machine was allowed to run at 100 r.p.m. for one minute after the dose had been applied. The operating speed of the stirring mechanism was then reduced to 45 r.p.m. for thirty minutes. At the end of this time the machine was turned off, the stirring blades removed from the solution and the mixtures allowed to settle for an additional forty five minutes. The pH of the supernatant, amount of color removal and amount of sludge produced was measured. The sludge was measured by the graduations on the side of the beakers. From the above results, the optimum coagulant dosage was determined.

<u>Color Removal Analysis</u>: The per cent of color removal was determined in the manner developed by Laing.[14] The median wave length of maximum light absorption was determined by passing a variable series of light waves through the sample and determining the range in which maximum absorption occured. The median value of this range was observed. A standard curve was determined by passing the median light wave through dilutions of the waste and plotting the absorption versus per cent dilution. The per cent color removal is correlated to this per cent dilution standard curve. The absorption values for the supernatant liquors were determined by passing the median wave length through the liquors. These absorption values were then referred to the standard curve from which the per cent color removal was obtained as correlated to a per cent dilution of the waste.

<u>Other Tests</u>: Other tests including pH suspended solids, and Chemical Oxygen Demand (Auto-Analyzer) were conducted as previously described under Experiment 1.

V. EXPERIMENTAL DATA AND RESULTS

A. Experiment 1: Characterization of Spent Tannin Waste

The objective of this experiment was to characterize the spent tannin liquor waste.

1. Conventional Chemical Oxygen Demand Analysis: The purpose for conducting the conventional chemical oxygen demand analysis was to obtain immediate data concerning the oxygen demand of the waste. The procedure was to obtain a Chemical Oxygen Demand value for the raw spent tannin waste. The samples were analyzed as described in the Methods and Material chapter.

   The results of the conventional Chemical Oxygen Demand analysis on the raw samples indicated the waste possesses a high oxygen demand demonstrated by an experimental chemical oxygen demand of 38,500 mg/l.

2. Technicon Auto-Analyzer Chemical Oxygen Demand Analysis: The purpose of this analysis was to verify the results of the Chemical Oxygen Demand determination obtained from the conventional Chemical Oxygen Demand analysis. The Chemical Oxygen Demand values were found by an automated colorimetric method using the Technicon Auto-Analyzer. The raw samples were analyzed as described in the Methods and Materials

chapter. A standard curve was prepared using glucose solutions of 0, 200, 400, 600, 800, and 1000 mg/l Chemical Oxygen Demand. These standards were digested by known amounts of potassium dichromate and sulfuric acid containing 22 grams of silver sulfate per a pound bottle of concentrated sulfuric acid. The depletion of color due to the oxidation of the glucose was measured colorimetrically in terms of light transmittance. A standard curve was plotted showing the relationship between Chemical Oxygen Demand concentration and the logarithm of the light transmittance. This curve is shown in Figure 3. Since the standard curve has a maximum Chemical Oxygen Demand it was necessary to dilute the unknown samples such that the resulting Chemical Oxygen Demand values would fall in the range between 0 and 1000 mg/l. Chemical Oxygen Demand. From the results of this analysis a correlation between the Chemical Oxygen Demand values from the conventional and the Technicon Auto-Analyzer determinations was made. This correlation afforded the direct use of the results of the Auto-Analyzer results for all further Chemical Oxygen Demand determinations. A raw waste Chemical Oxygen Demand value of 38,000 mg/l was obtained from the Technicon Auto-Analyzer analysis.

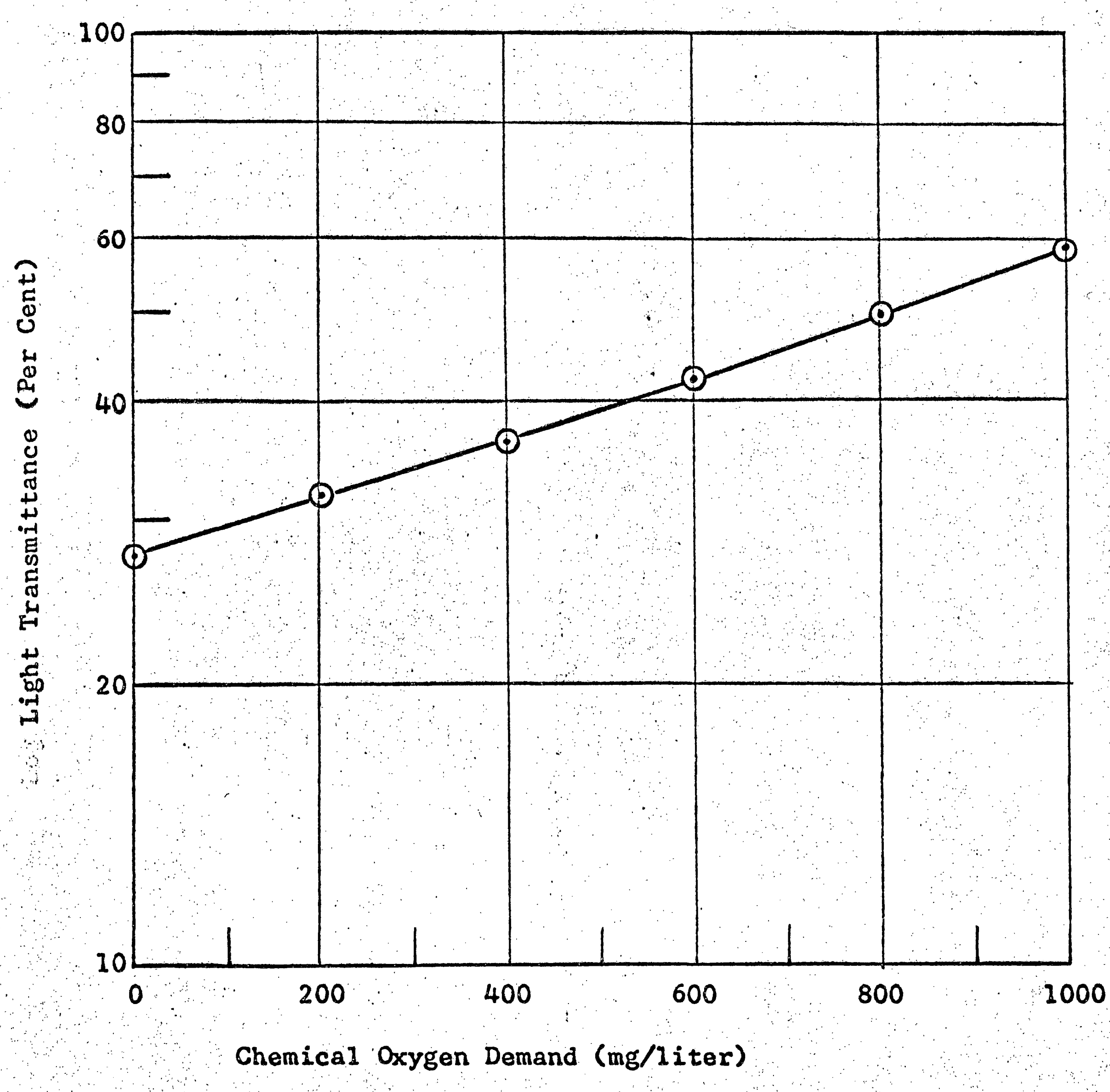

Figure 3. Standard Chemical Oxygen Demand Curve

3. Biochemical Oxygen Demand Analysis: The Biochemical Oxygen Demand tests were performed such that a correlation between Biochemical Oxygen Demand and Chemical Oxygen Demand values for the waste would necessitate only Chemical Oxygen Demand determinations for further analyses. The procedures followed were described in the Methods and Materials chapter.

The results of the Biochemical Oxygen Demand analysis on the raw waste using these procedures is of questionable value. This result is attributed to the very high dilutions necessary in order to obtain a residual of dissolved oxygen in the Biochemical Oxygen Demand bottle after the five days of incubation. These required dilutions were in the range of 0.015 per cent by volume. Inconsistent data from these determinations may be attributed to a failure to perform accurate dilutions at such a high rate. Measured values were in the range of 8,000 to 10,000 mg/l.

4. Warburg Respirometer Test: The purpose for conducting the Warburg Respirometer Biochemical Oxygen Demand analysis was to determine an accurate five day Biochemical Oxygen Demand value for the waste and to determine the oxygen uptake rate constant for the spent tan liquor. The procedure followed was as described in the Methods and Materials chapter.

The results of the Warburg Biochemical Oxygen Demand determinations are given graphically in Figure 4. The Biochemical Oxygen Demand data is given in tabular form in Table 3 in the Appendix C. Figure 16 illustrates the Thomas Graphical Method for determination of the oxygen uptake rate constant and the five day Biochemical Oxygen Demand value. Figure 16 shows that the oxygen uptake rate constant, K, was 0.469. The five day Biochemical Oxygen Demand value obtained using this constant and the Biochemical Oxygen Demand data was found to be 25,600 mg/liter.

5. Total Solids Test: The purpose of this test was to determine the concentration of total solids contained in the raw waste. The procedure followed was described in the Methods and Materials chapter.

The average total solids value of 37,750 mg/l obtained from this series of tests indicated that this was a particular pollutional characteristic that must be dealt with effectively before sufficient treatment of the waste would be accomplished.

6. Volatile Solids Test: The concentration of volatile solids was determined as a preliminary investigation in order to test the theory that the very distinct odor attributed to

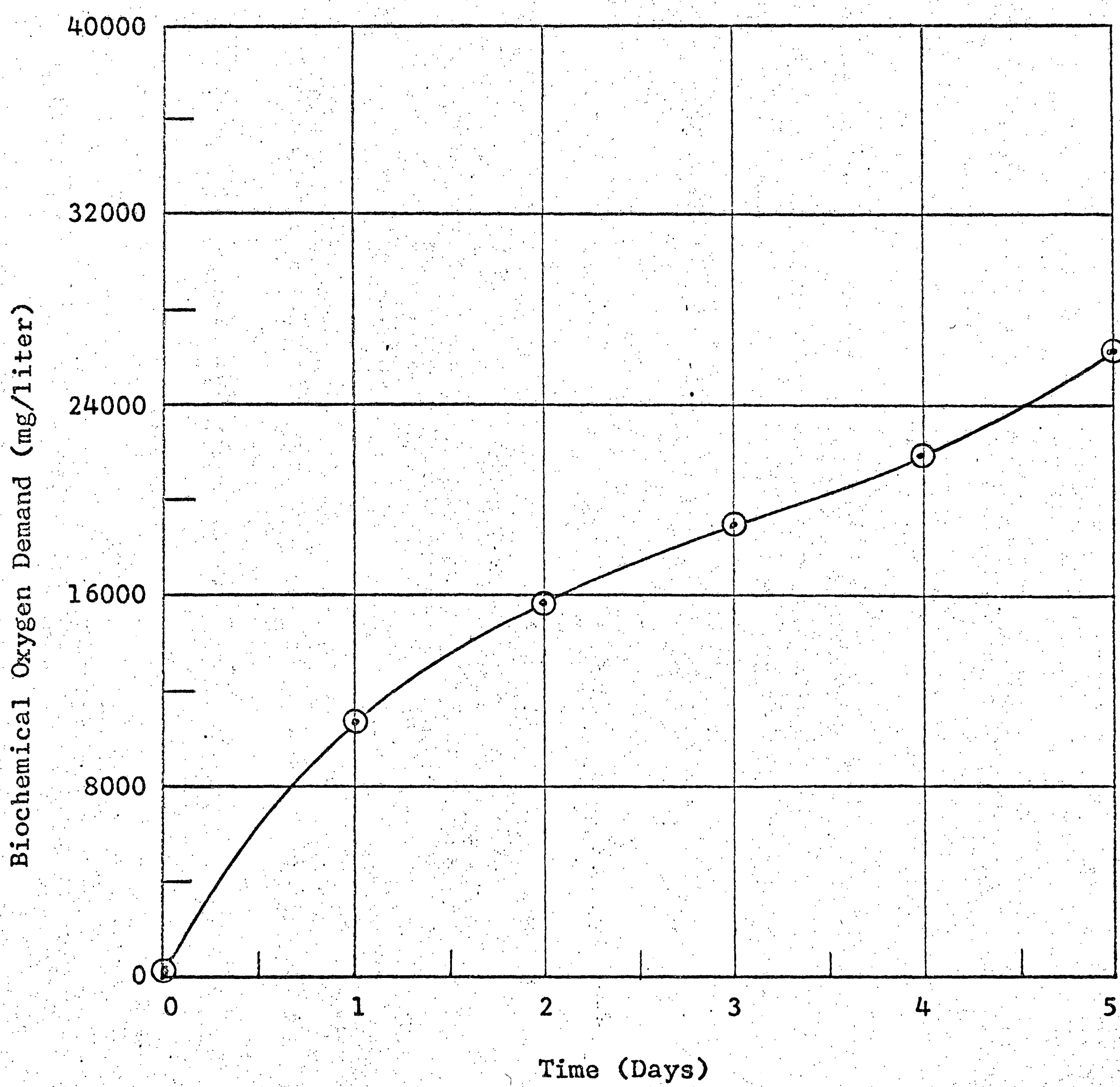

Figure 4. Biochemical Oxygen Determination of Spent Tan Liquor Using Warburg Manometric Techniques

the waste was a result of a high volatile solids concentration inherent with the spent tan liquor waste. The methods followed were described in the Methods and Materials chapter.

A high volatile solids concentration ranging in the vicinity of 16,000 mg/l for the spent waste was determined from this test. From this determination it was concluded that the odor problem experienced with the waste has a definite relation to the high volume of volatile solids present in the waste.

7. Suspended Solids Test: The concentration of suspended solids was determined so that for further analyses of the treatment of the waste with chemical coagulation and aeration the affect of these types of treatment upon the concentration of suspended solids would be determined. A decrease in suspended solids due to chemical coagulation was used as a principle parameter in determining optimum coagulant dose. Methods used were described in Methods and Materials chapter.

An average suspended solids concentration of 2640 mg/l was obtained from tests performed upon the raw waste. This value was then used as a basis to relate further suspended solids data obtained from chemical coagulation and aeration treatment.

8. Dissolved Solids Test: This test was performed on the raw waste to determine the concentration of dissolved solids, and from this analysis to determine if this high concentration of dispersed matter could be coagulated with the addition of highly charged polymers in addition to normal coagulants. Methods used were described in Methods and Materials chapter.

A concentration of 35,000 mg/l dissolved solids was obtained from this test indicating that use of a highly charged coagulant polymer could possibly afford a greater degree of color removal since a large portion of the color was imparted to the waste from these dissolved solids.

9. Settleable Solids Test: The purpose of this test was to determine the concentration of settleable matter in the waste as a per cent of the total volume of waste produced. The untreated samples were analyzed as described in the Methods and Materials chapter.

From the test performed the amount of settable matter was found to be 2 per cent on a volume basis with no significant increase throughout a week of settling. Therefore, from this information it is evident that no significant increase in efficiency of removal due to initial settling of waste would be obtained.

10. Color Analysis: The purpose of conducting the color analysis was to determine the dominant wave length for maximum absorbance of light by the raw waste as a check on the determination of the mean wave length for maximum light absorbance used in tests for determining color removal.

Results of the test indicated that the dominant wave length was 700 mμ which is significantly below the mean wave length of maximum absorbance for all samples. A problem existed in that it was necessary to change the light filter in the Spectronic-20 for wave lengths above 675 mμ. Error could have been introduced into the results at this point due to the necessity to adjust the mechanism after changing the filter. The mean wave length for maximum absorption was determined to be 800 mμ. A standard curve for color analysis is shown in Figure 5.

B. Experiment 2A: Treatment of Spent Tannin Waste with Pre-Aeration Followed by Aluminum Sulfate Coagulation with Nalcolyte 607 Cationic Polyelectrolyte

The objective of this experiment was to determine if pre-aeration of the spent tannin waste followed by chemical coagulation

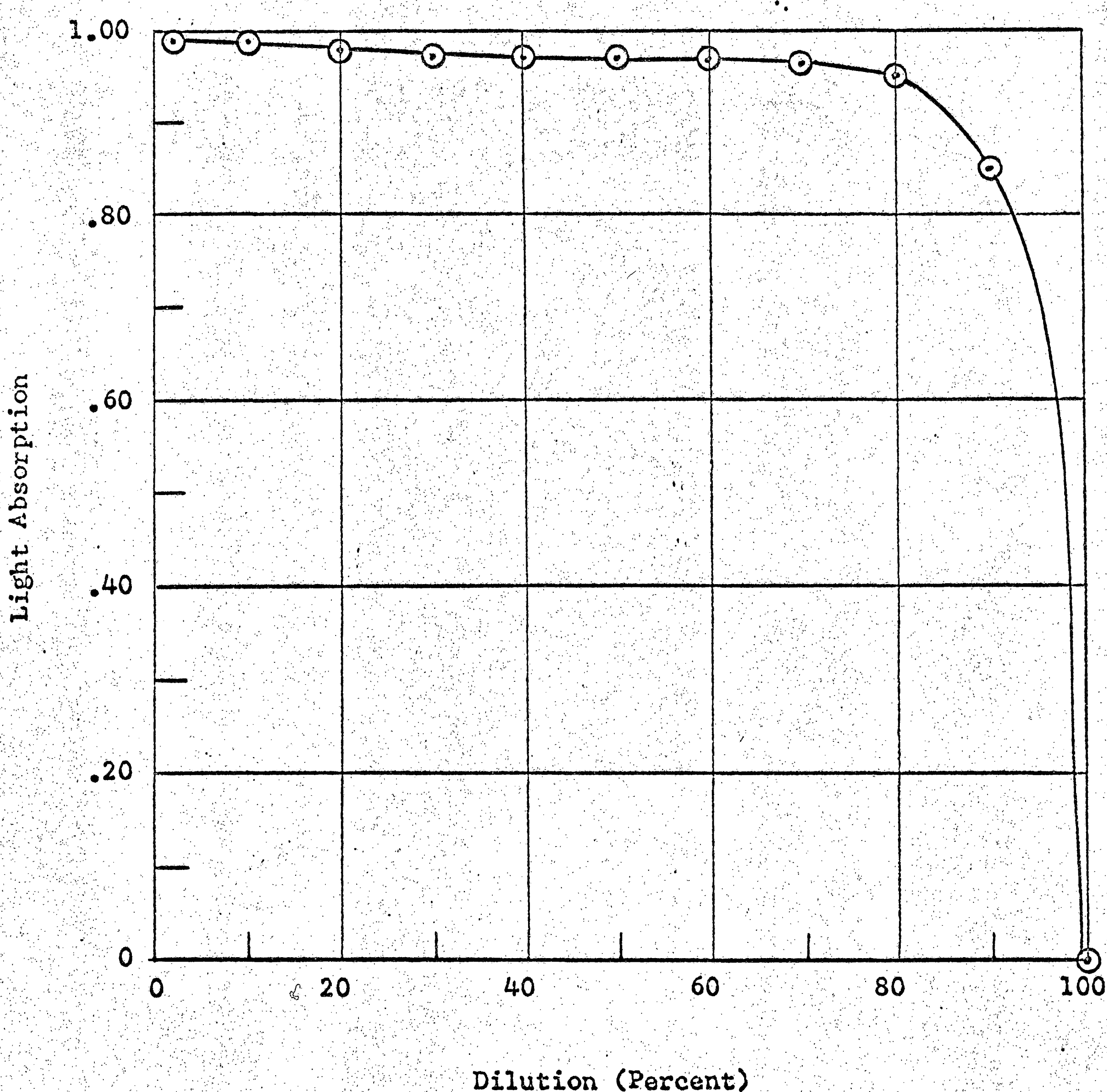

Figure 5. Standard Curve For Color Analysis

using aluminum sulfate in combination with Nalcolyte 607 cationic polyelectrolyte would provide an effective treatment of the spent tan liquor waste.

1. Color Removal Analysis: The amount of color removal was found for each of the preaeration - coagulation samples in order to evaluate the effect of preaeration of the waste on its coagulant demand. The methods employed for coagulation and color removal were as described in the Methods and Materials chapter.

The standard curve obtained for the color removal analysis is shown in Figure 5. The effect of preaeration of the waste on color removal and coagulant demand is shown graphically in Figures 6 and 7. The results shown indicated that preaeration has a definite effect upon the coagulant demand of the waste in order to obtain color removal. With preaeration of the waste up to 12 hours there was a significant decrease in coagulant demand for a corresponding greater percentage of color removal. Further preaeration of the waste up to 24 hours demonstrated little improvement in the color removal - coagulant demand relationship. Preaeration up to 36 hours indicated a deleterious effect on color removal in that a higher coagulant demand was required for a significantly lower percentage of color removal. Of primary significance is that with the longer periods of aeration the hue of the waste changed from a reddish-brown to a darker reddish-black tint. This change was a possible reason for the lower color removal and indicated a chemical or biological change in the tannin waste. The color hue change may be attributed to an iron-pyrogallol complex which will form if iron is present in the waste. Another possible reason for the decrease in color removal with preaeration time may be the higher suspended solids content of waste developed in the longer periods of aeration. Suspended solids cause less light transmittance through a sample, therefore, affording an apparent lower color removal observation.

The results of color removal analysis are tabulated in Table 1 in Appendix B. The results given in this table and shown in Figures 6 and 7 indicated that 12 hours of preaeration effected the greatest reduction in coagulant demand for a given degree of color removal.

2. Suspended Solids Test: The concentration of suspended solids was determined as a second parameter to describe the performance of the preaeration-chemical coagulation system. The suspended solids concentration was used as an indication of the efficiency of removal of the suspended matter in relation to coagulant demand and color removal. Suspended solids data

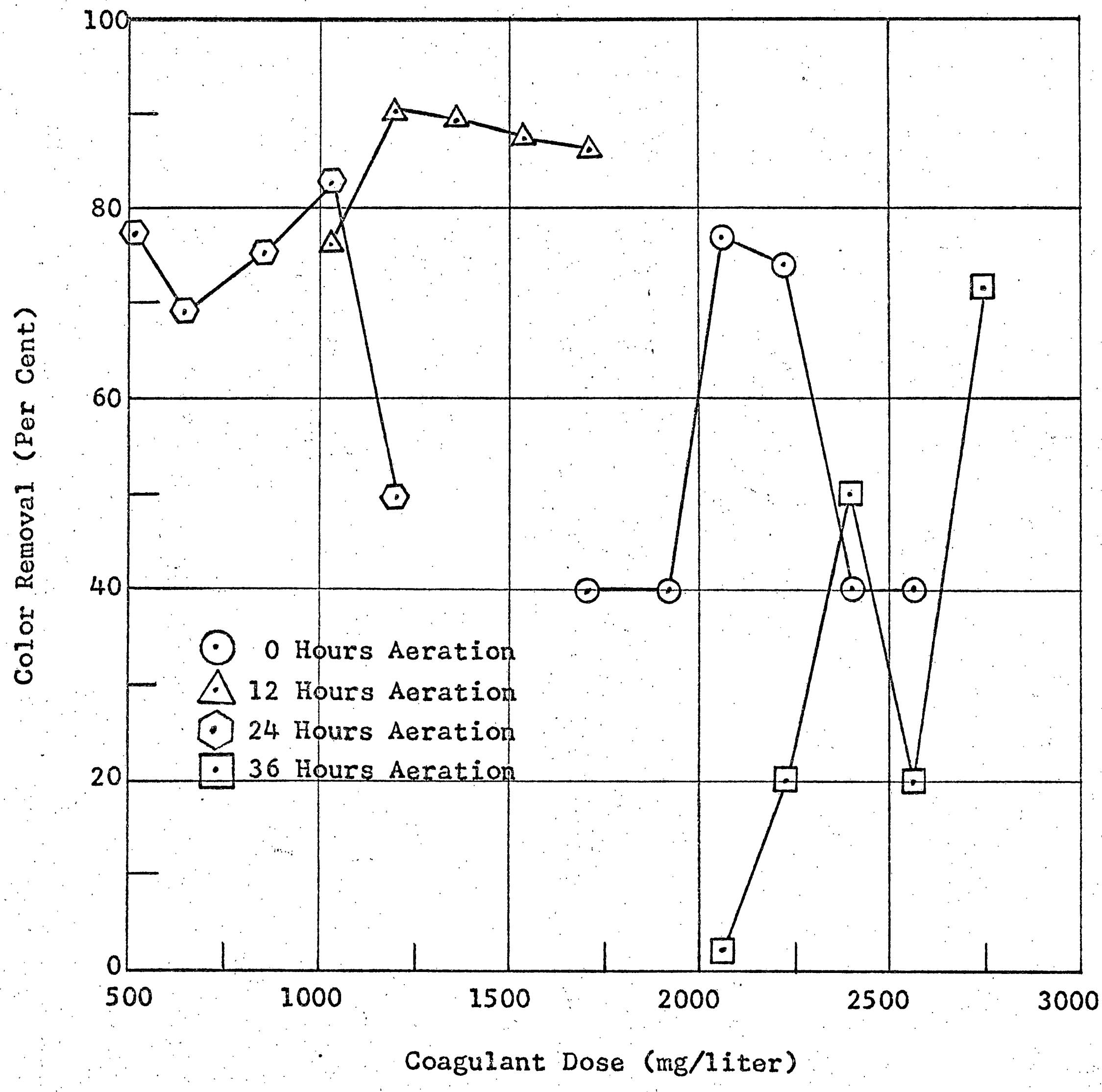

Figure 6. Per Cent Color Removal Analysis for Pre-Aeration and Coagulation System for 3/4 Hour Settling

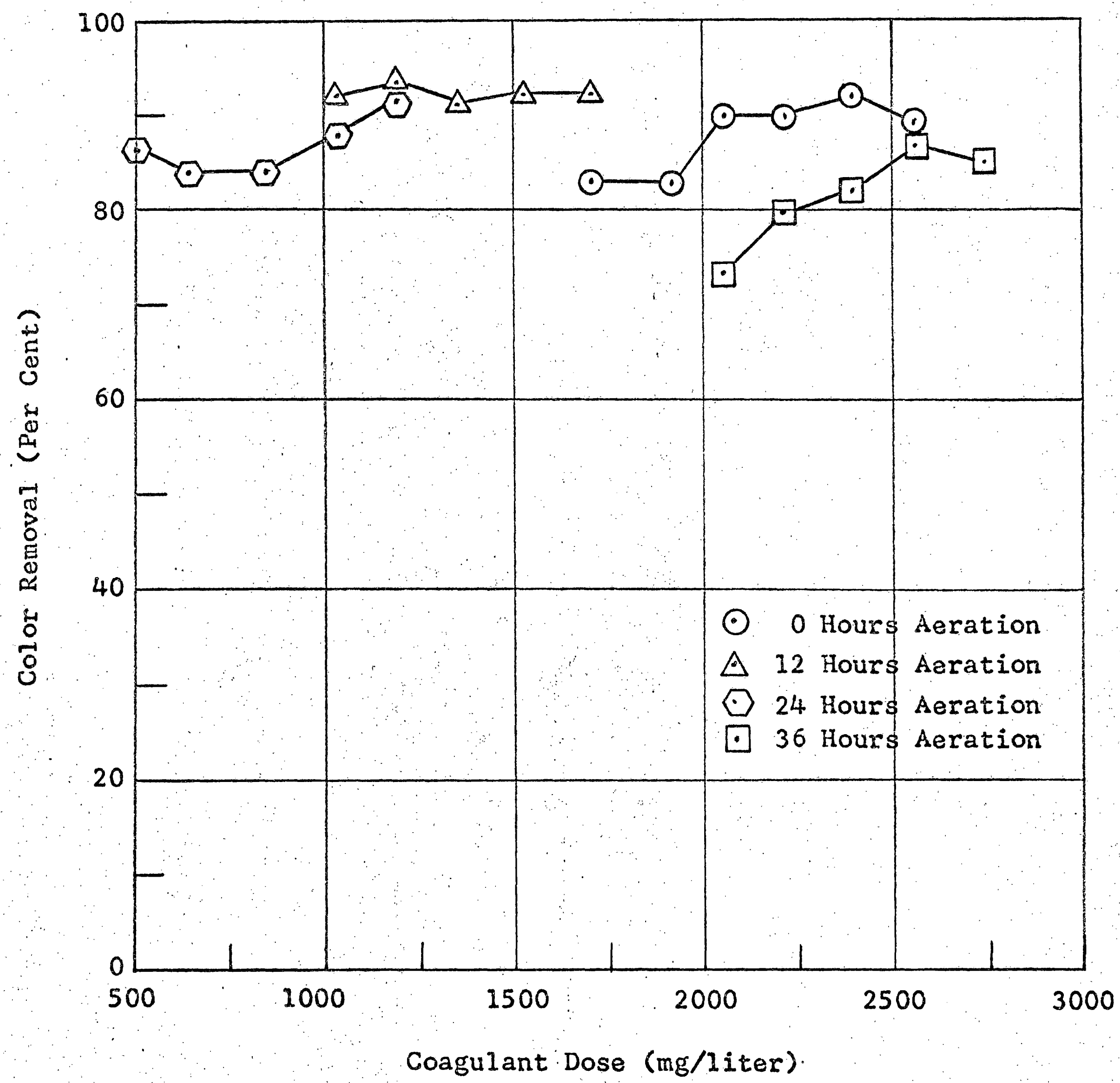

Figure 7. Color Removal Analysis for Pre-Aeration and Coagulation System for 24 Hours Settling

was obtained for 0, 12, 24, and 36 hours of preaeration. Supernatant of the coagulated waste was analyzed. The procedure used is described in the Methods and Materials chapter.

The suspended solids removal results are shown graphically in Figure 8. Of special significance was the increased concentration of suspended solids of the preaerated waste for up to 36 hours preaeration. The aeration system was also found capable of reducing the Chemical Oxygen Demand and Biochemical Oxygen Demand of the spent waste. The observed increase in solids indicated the possibility that biological action on the waste was responsible. For further supporting information, a sample of the waste was autoclaved and then aerated. Samples were taken of the autoclaved waste throughout a period of 120 hours aeration at selected intervals. Suspended solids data collected at intervals throughout the aeration period gave no indication of an increase nor was any reduction in Chemical Oxygen Demand noted throughout the samples as illustrated in Figure 17.

3. <u>Technicon Auto-Analyzer Chemical Oxygen Demand Analysis</u>: The purpose of this analysis was to verify the results of the suspended solids test showing that the preaeration-

chemical coagulation system was capable of reducing the Chemical Oxygen Demand of the waste. The Chemical Oxygen Demand values were found by an automated colorimetric method using the Technicon Auto-Analyzer as arranged in Figure 2. All samples were analyzed as described in the Methods and Materials chapter. A standard curve was prepared using glucose solutions containing 200, 400, 600, 800, and 1000 mg/l Chemical Oxygen Demand. These glucose standards were digested with known amounts of potassium dichromate in combination with sulfuric acid containing 22 grams of silver sulfate per 9 pound bottle. The depletion of color due to the oxidation of the standards was colorimetrically determined in terms of light transmittance. A standard curve was plotted illustrating the relationship between Chemical Oxygen Demand concentration and light transmittance. This curve is shown in Figure 3. It was necessary to dilute the unknown samples so that the resulting Chemical Oxygen Demand values were less than 1000 mg/liter. This dilution was necessary since the standard curve had a maximum Chemical Oxygen Demand value of 1000 mg/liter Chemical Oxygen Demand.

The results of the Technicon Auto-Analyzer Chemical Oxygen Demand analysis on the preaerated-coagulated super-

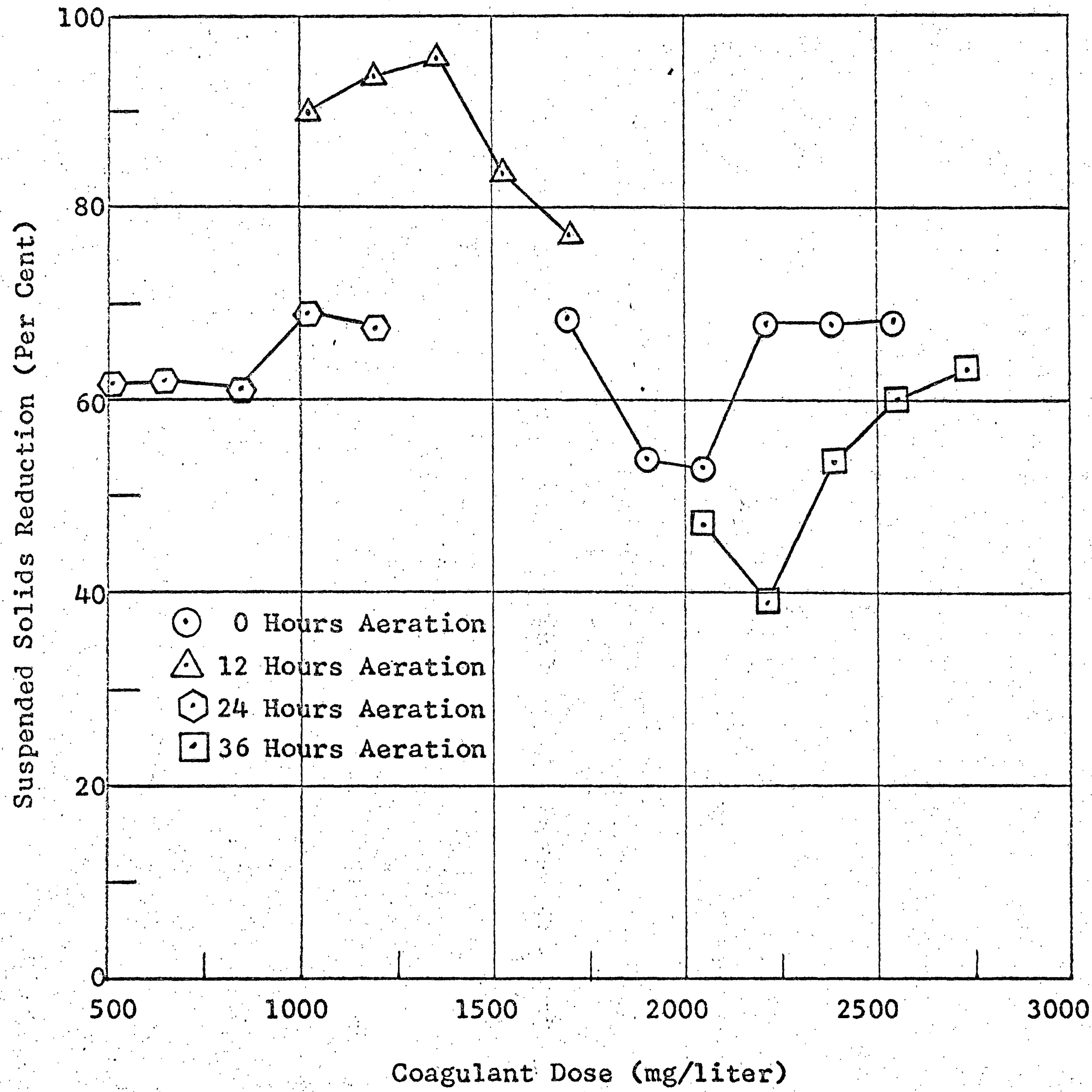

Figure 8. Suspended Solids Analysis for Pre-Aeration and Coagulation System for 24 Hours Settling

natant liquor are shown in Figure 9. This curve indicates that 36 hours preaeration afforded the greatest reduction of Chemical Oxygen Demand.

This was in accord with data collected concerning suspended solids concentration of the preaerated samples in that the greatest increase in suspended solids occured at this point.

C. Experiment 2B: Treatment of Spent Tannin Waste with Aluminum Sulfate and Nalcolyte 607 Cationic Polyelectrolyte Coagulation with Post-Aeration

The object of this experiment was to determine if effective treatment of the spent tannins would be effected by the use of chemical coagulation using aluminum sulfate and Nalcolyte 607 cationic polyelectrolyte in combination with aeration of the supernatant from the coagulation-sedimentation process.

1. Color Removal Analysis from Coagulant Test: The amount of color removal was found for each of the samples from the coagulation and post-aeration series of tests. The methods employed for coagulation and color removal were as described in the Methods and Materials chapter.

The effect of chemical coagulation with aeration of the supernatant from this process is shown graphically in Figure

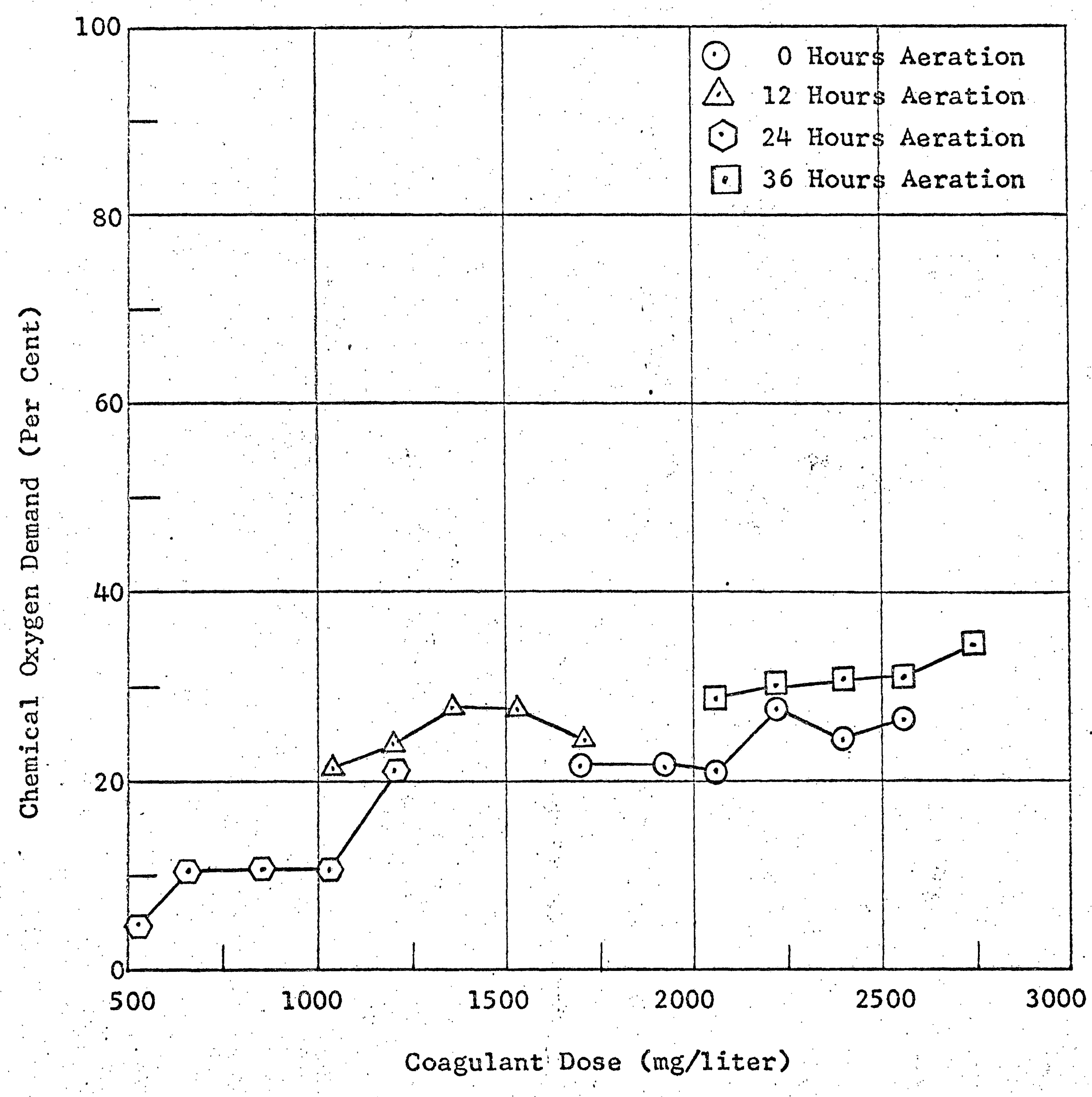

Figure 9. Chemical Oxygen Demand Removal Analysis for Pre-Aeration and Coagulation System for 24 Hours Settling

10. The results illustrated indicated that an increase in color removal could be obtained for up to 12 hours of aeration of the supernatant from the coagulation process. No further beneficial effect was obtained from the extension of the aeration process as illustrated in this figure. A profound color hue change was noted at 12 hours post-aeration with an incremental change up to 36 hours. A color hue change was also noticeable throughout coagulation. The color hue during coagulation changed from a dark reddish brown to a brown color, and from this hue to a progressively darker brown throughout the extent of the aeration process. The color change during the aeration process may be attributed to the formation of an iron-pyrogallol complex which imports a black color to the waste. This change of color due to aeration may be a cause of the lower removals of color after the longer periods of aeration. Also noted with the longer periods of aeration was an increase in suspended solids. These suspended solids would cause less light transmittance through a sample, therefore, yielding an apparent lower per cent of color removal.

The results of color removal analysis are tabulated in Table 2 in Appendix B under chemical coagulation data. The results given in this table and illustrated graphically

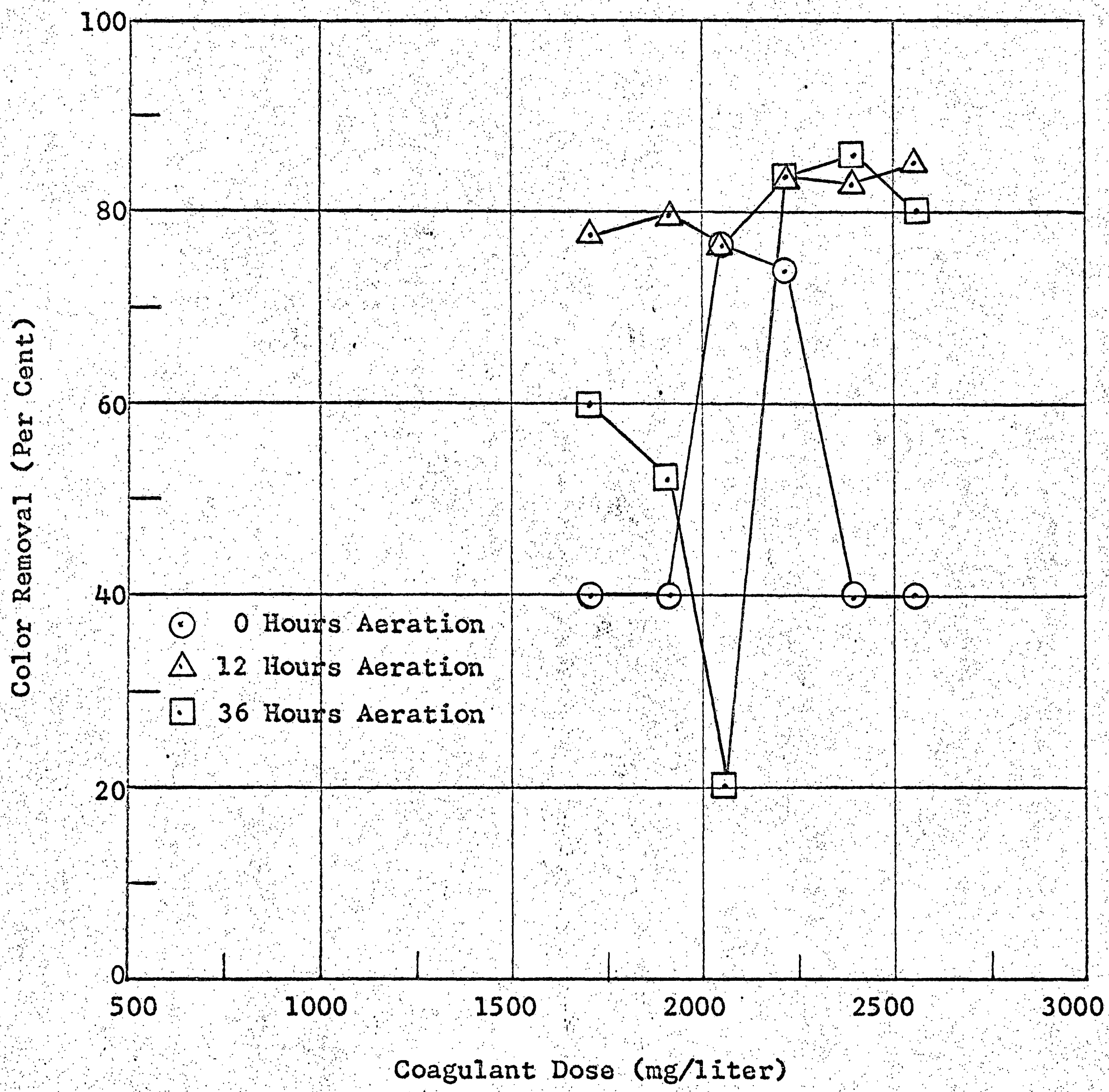

Figure 10. Color Removal Analysis for Coagulation and Post-Aeration System with 3/4 Hour Settling

in Figure 10 indicated that aeration of the supernatant for up to 12 hours yielded the highest per cent of color removal.

2. Suspended Solids Test: The concentration of suspended solids was determined as a second parameter of the performance of the coagulation and post-aeration treatment system. The suspended solids concentration was used as an indication of the efficiency of removal of the suspended matter in relation to coagulant demand, color removal, and aeration time. Suspended solids data was obtained for 0, 12, and 36 hours of aeration of the supernatant from the chemical coagulation process. Samples were collected for each of these aeration times after 45 minutes settling. The procedure followed was described in the Methods and Materials chapter.

The suspended solids removal results are illustrated graphically in Figure 11 and tabulated in Table 2 in Appendix B. An increase in suspended solids was noticed throughout the extent of the aeration period. This observation indicated that either a chemical or biological stripping of the pyrogallol compound in the waste was taking place. For supporting information a study of an autoclaved and aerated spent waste was conducted to

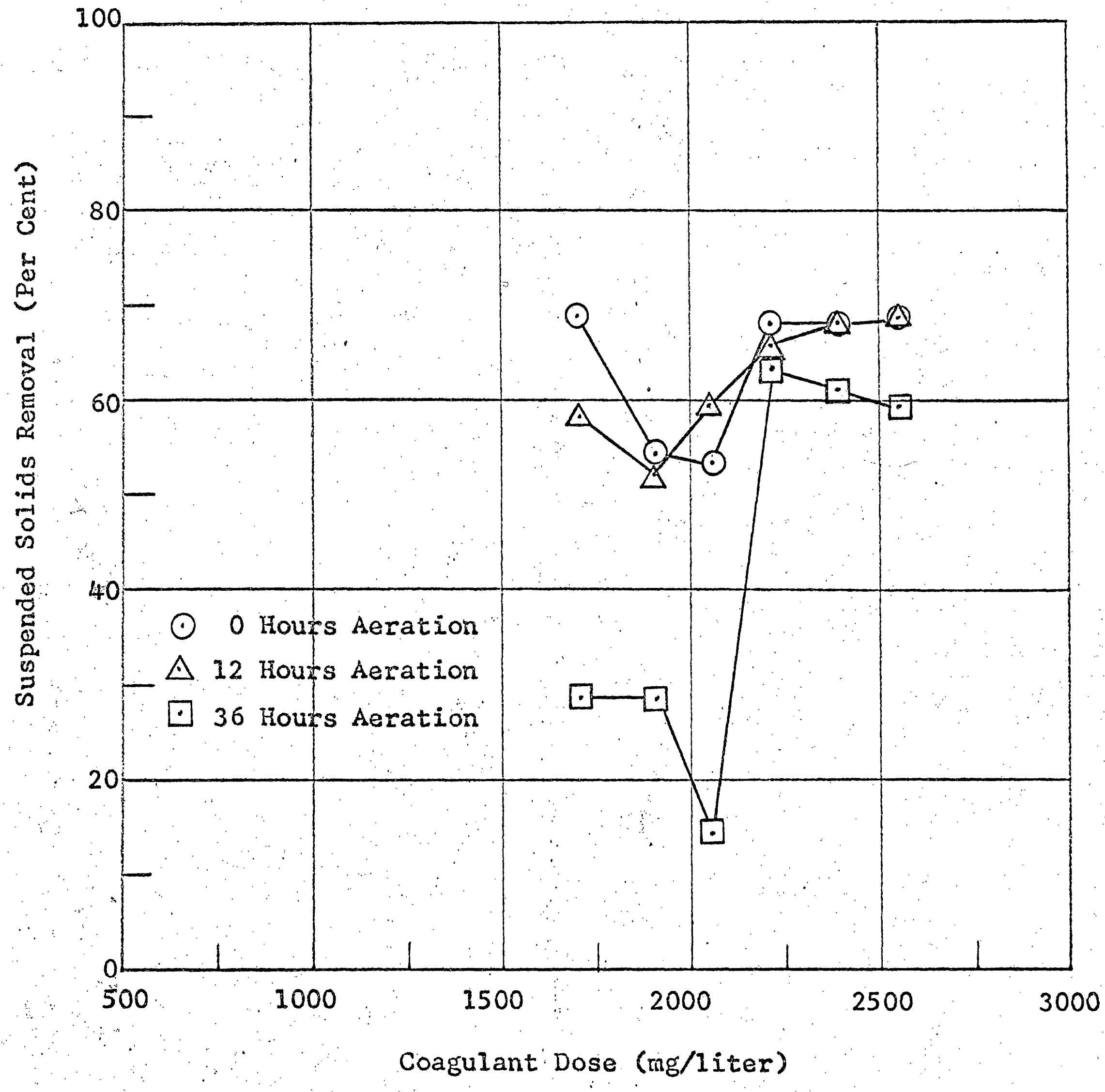

Figure 11. Suspended Solids Removal Analysis for Coagulation and Post-Aeration Treatment System with 3/4 Hours Settling

support the theory that the stripping was biologically accomplished. Samples taken throughout the 120 hours aeration period indicated that no suspended solids increase or reduction in Chemical Oxygen Demand was accomplished as illustrated in Figure 17.

3. Technicon Auto-Analyzer Chemical Oxygen Demand Analysis: The purpose of this analysis was to verify the results of the suspended solids test indicating that the coagulation and post-aeration treatment system was capable of reducing the Chemical Oxygen Demand of the waste. All samples were analyzed as described in the Methods and Materials chapter.

The standard curve was prepared as described in "Experiment 2A". The standard curve is illustrated in Figure 12. The results of the Chemical Oxygen Demand analysis using the Auto-Analyzer are illustrated in Figure 13 and are given in tabulated form in Table 2 in Appendix B. From Table 2 and Figure 13, indication was given that an increase of Chemical Oxygen Demand removal was effected throughout the extent of the aeration period.

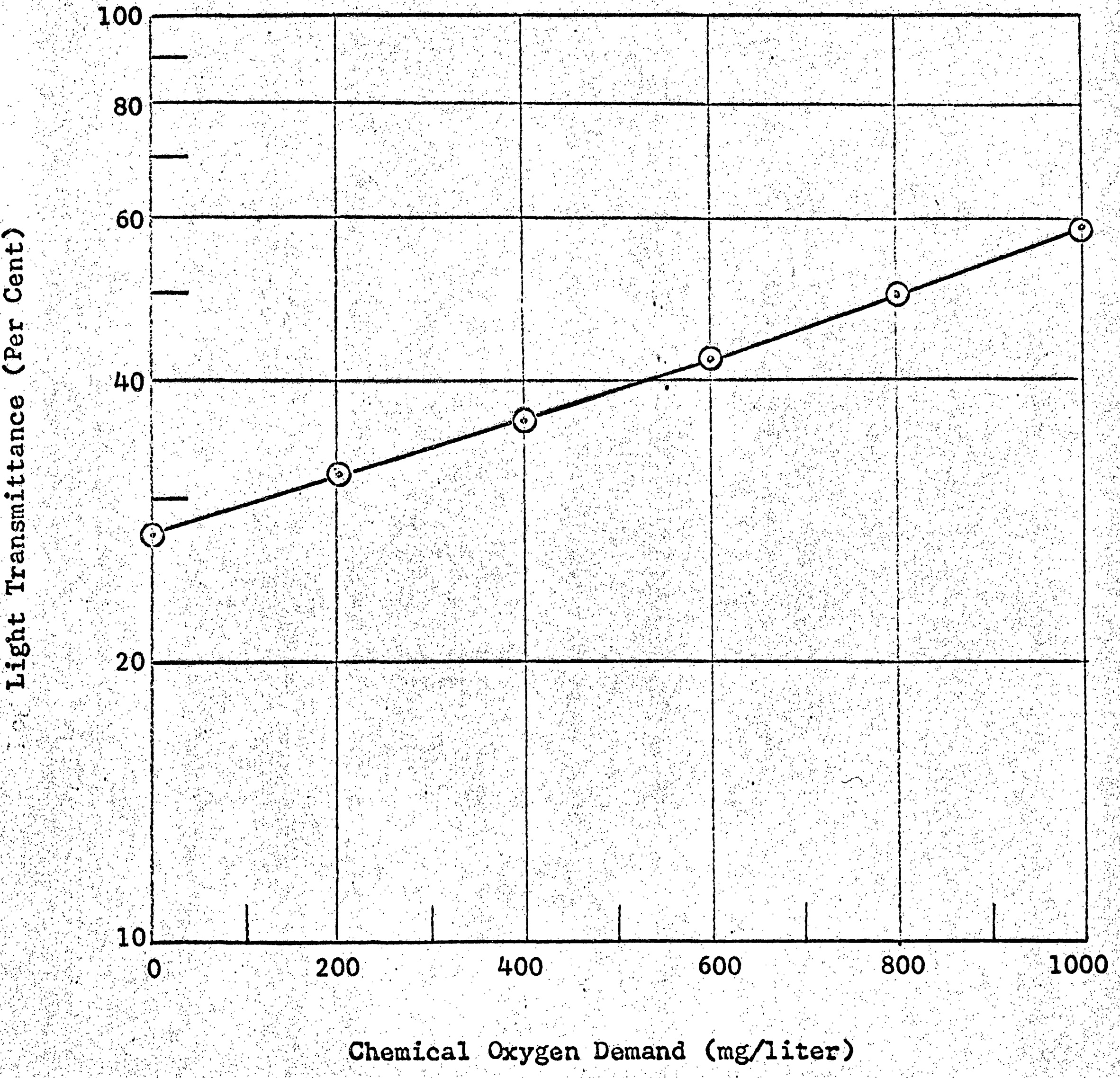

Figure 12. Standard Curve for Chemical Oxygen Demand Determinations for Coagulation with Post-Aeration

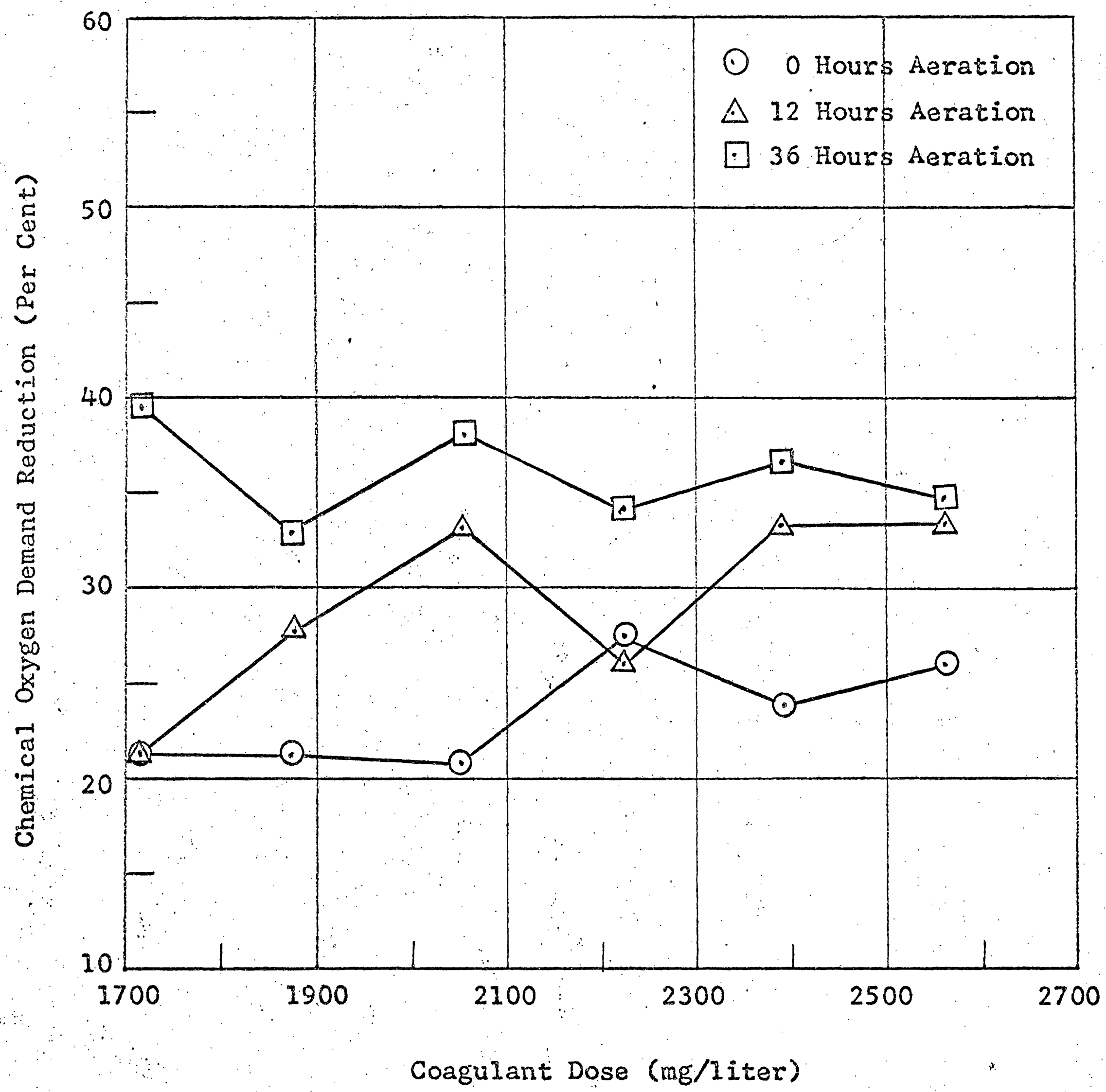

Figure 13. Chemical Oxygen Demand Reduction Determination for Chemical Coagulation and Post-Aeration with 3/4 Hour Settling

VI. DISCUSSION OF RESULTS

The primary method of treating tanning waste has been to combine all waste from the tanning process for chemical treatment. Recent work has been aimed toward separation of the wastes and effecting treatment with either chemical or biological methods. Chemical requirements or the chemical coagulant demand of the spent vegetable tannin waste are high. Biological methods used have been in general aerobic systems demanding high aeration rates and long contact times. Because of various difficulties in achieving effective treatment of this waste a combination of chemical and biological treatment was considered as a possible alternative to single process systems. The results of this investigation indicated that the combined chemical-biological treatment would afford good color removal and Chemical Oxygen Demand reduction.

There are several mechanisms by which the chemical-biological treatment may effect a Chemical Oxygen Demand reduction. The waste used in this investigation contained a large quantity of suspended matter of which a high per cent consisted of flesh and other organic particles. Coagulation and sedimentation would remove the Chemical Oxygen Demand imparted to the waste by the suspended matter. The data compiled from Chemical Oxygen Demand determinations conducted in Experiment 2A and Experiment 2B indicated that a reduction of

Chemical Oxygen Demand was accomplished through the coagulation process. This reduction was very small being in the vicinity of 20 per cent.

The second mechanism by which the reduction of Chemical Oxygen Demand may be effected is through biological stripping of the pyrogallol compounds in the dissolved solids. The mechanism was considered to be biological from a supporting study of an autoclaved and aerated sample in which throughout the aeration period no reduction of Chemical Oxygen Demand was indicated. This supported the theory that the reduction in Chemical Oxygen Demand due to aeration was not from a chemical stripping of the compounds. Aeration up to 36 hours afforded a total Chemical Oxygen Demand reduction of 40 per cent.

Data reported from previous experimentation in the field of treatment of the segregated spent tannins is reported in Biochemical Oxygen Demand reductions. These data indicate that the Chemical Oxygen Demand reductions, as correlated to these Biochemical Oxygen Demand reductions, experienced in chemical treatment systems are low. No data for aeration was available to relate to the Chemical Oxygen Demand reductions obtained from these observations.

The use of polyelectrolytes gave little increased efficiency of coagulation. The maximum dose of 5 mg/l Nalcolyte 607 was used as determined from preliminary studies. Also from preliminary studies the aluminum sulfate necessary to afford a corresponding degree of color removal was performed to illustrate the efficiency of the Nalcolyte 607 in reducing coagulant demand. Up to 30 per cent reduction in coagulant demand was indicated by the use of the polyelectrolyte in combination with aluminum sulfate. The highest degree of color removal was obtained with 12 hours aeration of either the pre-settled waste or the pre-aerated samples.

The waste characteristics determined in Experiment 1 were in general as noted in the published data of tan liquor waste characteristics. Of special significance is the high value for the five day Biochemical Oxygen Demand values obtained from the Warburg Respirometer Test. This value of 25,600 is approximately 4 to 5 times as great as all published data concerning the Biochemical Oxygen Demand of the waste and approximately three times as great as the Biochemical Oxygen Demand value obtained from the standard azide Biochemical Oxygen Demand method employed in Experiment 1. The oxygen uptake rate of the waste or k value was determined to be 0.469 with a projected ultimate Biochemical Oxygen Demand value of 27,654. These values were obtained on the raw spent vegetable tannin.

The treatment of vegetable tanning waste and especially the spent vegetable tannin is certainly as area in which forther research is needed. This investigation which dealth with the effects of chemical coagulation in combination with aeration was considered to be of value because it indicated that aeration has a defined effect on color removal and Chemical Oxygen Demand reduction. Also the results obtained from the Warburg Respirometer Test indicated that this waste has a much higher Biochemical Oxygen Demand value than previously thought. This will be of significance for any further research in which Biochemical Oxygen Demand reduction will be used as an efficiency of treatment parameter. Significant reduction in Chemical Oxygen Demand were not produced by the combination of methods. It was demonstrated that biological processes would effect greater reductions in Chemical Oxygen Demand than a chemical process. It could not therefore be determined whether or not this process was economically feasible as a treatment process for Chemical Oxygen Demand or Biochemical Oxygen Demand removal.

VII. CONCLUSIONS

The results of this investigation led to the following conclusions:

1. Biological treatment using aeration prior to chemical coagulation significantly lowered the coagulant demand necessary to achieve high color removal, suspended solids removal, and Chemical Oxygen Demand reduction. Further preaeration of the waste is of questionable value since a decrease in suspended solids and color reductions are noted along with a substantial increase in Chemical Oxygen Demand removal.
2. Biological treatment using aeration of the supernatant from the chemical coagulation process yielded increased color removal, suspended solids removal, and Chemical Oxygen Demand removal for up to 12 hours of aeration. Suspended solids concentration increased from this time throughout the extent of the aeration period yielding an apparent decreased color removal. Chemical Oxygen Demand reductions increased throughout the aeration process.
3. Biochemical Oxygen Demand values for the waste using standard azide or manometric methods are of little

significance and exhibit a gross error as compared to values obtained by the Warburg method. The Warburg five day Biochemical Oxygen Demand value is 25,600 mg/l compared to 8,000 from the standard azide or manometric method.

4. If treatment is to be accomplished by aeration in combination with chemical coagulation and settling, the order in which these processes are performed has little affect upon the results obtained.

VIII. SUMMARY

The object of this investigation was to determine the effect of aeration in combination with chemical coagulation on the treatment of spent vegetable tannin liquor. Chemical coagulation was desirable because it effectively reduced the color and suspended solids of the tanning waste. Aeration was thought to be a possible means of reducing the Chemical Oxygen Demand of the waste by biological stripping of the pyrogallol compound in the spent waste.

The processes used for the combination aeration-coagulation system consisted of pre-aeration of the raw waste prior to chemical coagulation and a second system in which the chemically coagulated raw waste supernatant liquor was aerated for various periods of time. Nalcolyte 607 cationic polyelectrolyte in various combinations with aluminum sulfate was used as the coagulants in the coagulation tests. Preliminary studies using other Nalco Company polyelectrolytes produced negligible results. Coagulation of the waste using ferric chloride and lime produced questionable results resulting in their omittance from this investigation. For the Nalcolyte 607 and aluminum sulfate coagulation tests, coagulant dosage, color removal, volume of sludge, pH, suspended solids, and Chemical Oxygen Demand were measured for each sample after specified settling periods.

Color reduction was substantial with aeration of the waste up to 12 hours for the pre-aeration or post-aeration systems. Color reductions up to 94 per cent were obtained at this aeration time with a suspended solids reduction of 96 per cent. Chemical Oxygen Demand reductions of the waste were increased throughout the period of aeration with a maximum reduction of Chemical Oxygen Demand of 40 per cent at 36 hours of aeration.

Of significance from this investigation was the Biochemical Oxygen Demand value and oxygen uptake rate obtained from the Warburg Respirometer Test. The Biochemical Oxygen $Demand_5$ value of 25,600 mg/l obtained for the spent tan liquor indicated an increase of 4 to 5 times of all reported values in the literature. The oxygen uptake rate of the waste, K, was found to be 0.469.

IX. ACKNOWLEDGMENTS

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He also wishes to thank the Leas and McVitty Corporation, Pearisburg, Virginia, for their continual supply of fresh waste and for presenting him with the necessary information concerning the constituent materials of the waste. The author further expresses appreciation to the Nalco Chemical Company for making available the samples of Nalcolyte polyelectrolytes used in this investigation.

The author also wishes to give special acknowledgment to the entire membership of the Water Quality and Waste Treatment class of Virginia Polytechnic Institute for furnishing him with the results of the Warburg Biochemical Oxygen Demand analysis of the waste.

The author also acknowledges for her able assistance and excellent typing of this thesis.

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APPENDIX A

Illustrated Example of the Color Removal Analysis

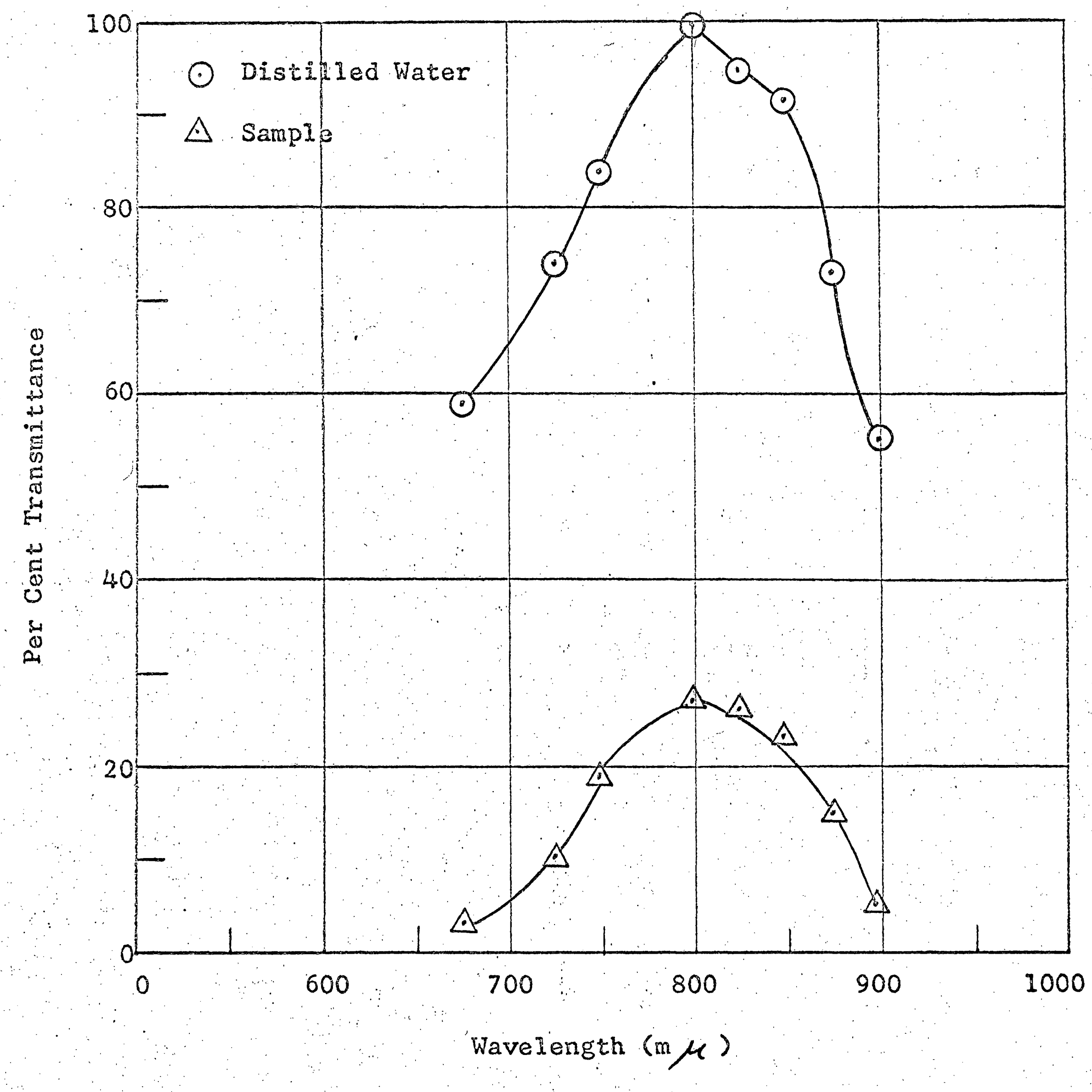

Figure 14. Spectrum Curve For Color Removal Analysis

<u>Example:</u> <u>Method for Color Removal Analysis</u>

1. This example was performed using a sample of supernatant from the preaeration with chemical coagulation treatment of the spent vegetable tan liquor. The spectrum curves for the distilled water and the sample are shown in Figure 14.

2. The median wavelength for maximum absorbtion of light, 800 mμ, was used to measure the maximum light absorbtion. The maximum light absorbtion was found for the sample by measuring the vertical distance between the sample spectrum curve and the distilled water curve. This example is illustrated in Figure 14.

   Vertical Distance Between Curves = 73.0

   Total Distance Under Distilled Water Curve = 100.0

   Maximum Light Absorbtion = .730

3. The maximum light absorbtion value was then entered into the standard curve shown in Figure 15. This standard curve was obtained by the same procedure as described in the Methods and Materials chapter. A per cent dilution was obtained for the maximum light absorbtion value above which also was used as the per cent color removal.

   Per Cent Color Removal = 94.5

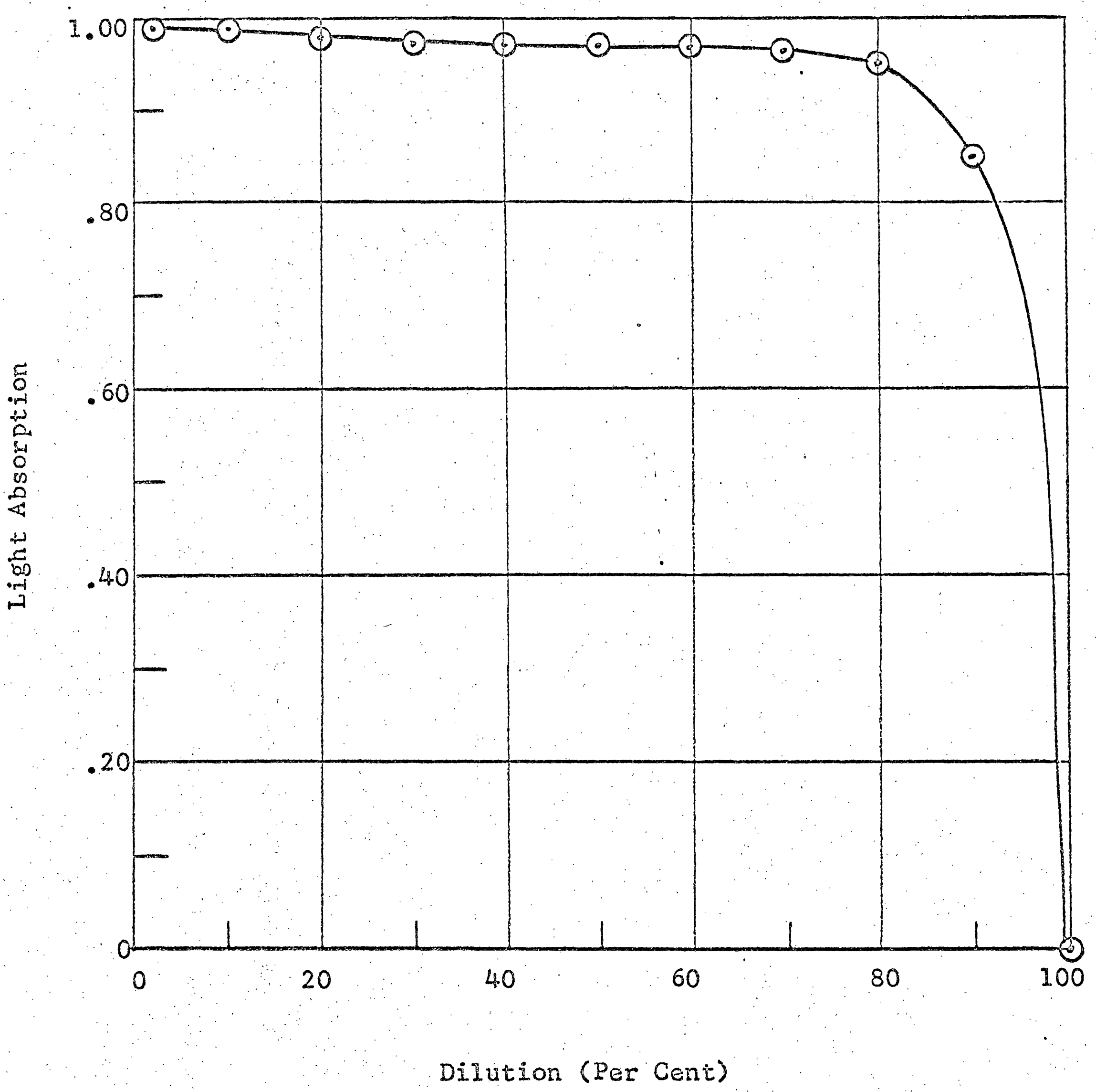

Figure 15. Standard Curve For Color Removal Analysis

APPENDIX B

Tables for the Effect of Aeration and Chemical Treatment on Spent Vegetable Tan Waste

TABLE 1

Sample Aeration Time (Hours)	Dosage (P.P.M.) Nalcolyte 607	Dosage (P.P.M.) $Al_2(SO_4)_3 \cdot 14H_2O$	Settling Time	Initial pH Sample	pH of Sample Supernatant	Per Cent Color Removal	Per Cent Sludge Vol.	Per Cent C.O.D. Reduction	Per Cent S.S. Removal
12	5	1027	3/4	5.20	4.90	76.1	78	*	*
12	5	1198	3/4	5.20	4.90	90.3	80	*	*
12	5	1370	3/4	5.20	4.82	89.5	84	*	*
12	5	1541	3/4	5.20	4.74	87.6	80	*	*
12	5	1712	3/4	5.20	4.63	86.4	82	*	*
12	5	1027	24	4.90	5.01	92.1	30	21.1	90.8
12	5	1198	24	4.90	5.15	93.5	40	23.8	94.6
12	5	1370	24	4.82	5.15	91.5	35	27.6	96.2
12	5	1541	24	4.74	5.02	92.3	40	27.6	84.2
12	5	1712	24	4.63	5.03	92.5	40	34.2	77.9
24	5	514	3/4	5.70	5.21	77.2	66	*	*
24	5	645	3/4	5.70	5.10	64.5	70	*	*
24	5	856	3/4	5.70	5.13	74.3	84	*	*
24	5	1027	3/4	5.70	4.90	82.7	80	*	*
24	5	1198	3/4	5.70	4.80	50.0	90	*	*
24	5	514	24	5.21	5.60	86.3	30	4.7	62.5
24	5	645	24	5.10	5.52	84.0	30	10.1	62.8
24	5	856	24	5.13	5.46	84.0	40	10.3	62.0
24	5	1027	24	4.90	5.35	88.0	35	10.3	69.7
24	5	1198	24	4.80	5.25	92.0	38	20.8	68.4

Effects of Pre-Aeration and Aluminum Sulfate with Nalcolyte 607 Polyelectrolyte Coagulation

* Data not applicable for presentation

TABLE 1 (Continued)

Sample Aeration Time (Hours)	Dosage (P.P.M.) Nalcolyte 607	$Al_2(SO_4)_3 \cdot 14H_2O$	Settling Time	Initial pH Sample	pH of Sample Supernatant	Per Cent Color Removal	Per Cent Sludge Vol.	Per Cent C.O.D. Reduction	Per Cent S.S. Removal
36	5	2054	3/4	6.60	4.71	2.5	70	*	*
36	5	2226	3/4	6.60	4.60	20.0	75	*	*
36	5	2397	3/4	6.60	4.55	50.0	80	*	*
36	5	2568	3/4	6.60	4.53	20.0	90	*	*
36	5	2739	3/4	6.60	4.50	71.8	90	*	*
36	5	2054	24	4.71	4.92	73.8	40	28.9	47.6
36	5	2226	24	4.60	4.80	80.0	44	28.9	39.5
36	5	2397	24	4.55	4.83	82.1	45	30.2	54.1
36	5	2568	24	4.53	4.85	8.70	50	30.9	60.1
36	5	2739	24	4.50	4.73	85.3	45	34.2	63.5

* Data not applicable for presentation

TABLE 2

Sample Aeration Time (Hours)	Dosage (P.P.M.) Nalcolyte 607	$Al_2SO_4 \cdot 14H_2O$	Settling Time (Hours)	Initial pH of Waste	pH of Waste Supernatant	Per Cent Color Removal	Per Cent Sludge Volume	C.O.D. P.P.M.	Per Cent C.O.D. Removal	S.S.	Per Cent S.S. Removal
0	5	1712	3/4	5.20	4.60	40	82	*	*	*	*
0	5	1882	3/4	5.20	4.55	40	85	*	*	*	*
0	5	2054	3/4	5.20	4.50	77	85	*	*	*	*
0	5	2226	3/4	5.20	4.50	74	94	*	*	*	*
0	5	2397	3/4	5.20	4.45	40	96	*	*	*	*
0	5	2568	3/4	5.20	4.40	40	96	*	*	*	*
0	5	1712	24	5.20	4.60	83.0	28	30,000	21.1	820	69.0
0	5	1882	24	5.20	4.55	83.0	29	30,000	21.1	1210	54.2
0	5	2054	24	5.20	4.50	90.0	34	29,250	20.9	1240	53.1
0	5	2226	24	5.20	4.50	90.0	37	27,500	27.6	840	68.2
0	5	2397	24	5.20	4.45	92.0	38	29,000	24.0	840	68.2
0	5	2568	24	5.20	4.40	89.5	38	28,000	26.2	830	68.6
12	5	1712	3/4	4.60	4.60	78	*	29,500	20.8	1105	58.2
12	5	1882	3/4	4.55	4.50	80	*	27,500	27.6	1240	53.1
12	5	2054	3/4	4.50	4.40	76	*	26,000	33.5	1060	59.9
12	5	2226	3/4	4.50	4.40	84	*	28,000	26.2	890	66.3
12	5	2397	3/4	4.45	4.30	83	*	26,000	33.5	850	67.9
12	5	2568	3/4	4.40	4.30	86	*	26,000	33.5	845	68.2
36	5	1712	3/4	4.60	5.60	60	*	23,000	39.5	1885	28.7
36	5	1882	3/4	4.50	5.65	52	*	25,500	32.9	1885	28.7
36	5	2054	3/4	4.40	6.30	20	*	23,500	38.2	2270	14.2
36	5	2226	3/4	4.40	4.50	84	*	25,000	34.2	950	64.1
36	5	2397	3/4	4.30	4.50	86	*	24,000	36.8	1030	61.0
36	5	2568	3/4	4.30	4.55	80	*	25,000	34.2	1070	59.5

The Effects of Chemical Coagulation and Post-Aeration on Treatment of Tannery Waste

* Data not applicable for presentation

APPENDIX C

Illustrated Example of the Warburg $B.O.D._5$ and Oxygen Uptake Rate, k, Determination

The procedure in determining the Biochemical Oxygen Demand constants using the Thomas Graphical Method consisted of the following steps:

1. From the experimental results y and t, the value of $(t/y)^{1/3}$ was calculated for each day. y is the Biochemical Oxygen Demand reading for the time t.
2. Plotted $(t/y)^{1/3}$ versus t on arithmetic graph paper and by eye drew in the best straight line fit
3. From the plot measured the intercept A and the slope B.
4. Finally, calculated K and L from the equations

$$K = (2.61B)/A$$

and

$$L = 1/(2.3KA^3)$$

Figure 16 illustrates an example using this method of determination.

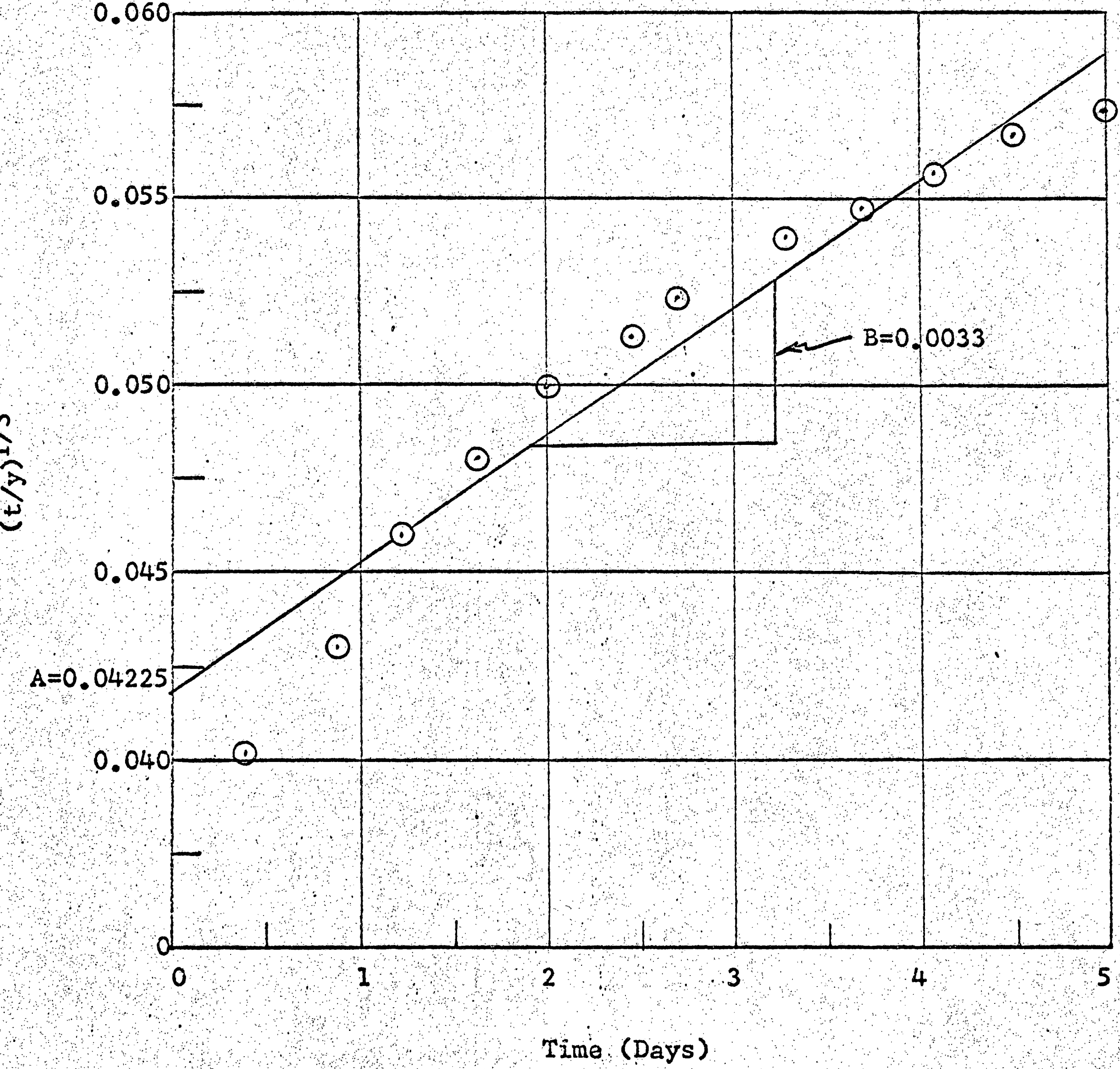

Figure 16. Determination of Oxygen Uptake Rate and $B.O.D._5$ for Spent Tan Liquor

TABLE 3

Day	Time	O_2 Uptake mg/1 13	O_2 Uptake mg/1 14	Average Uptake mg/1	Dilution Factor	B.O.D. mg/1	B.O.D. Control mg/1	B.O.D. Spent Tan mg/1
0	1730							
	1930	43	43	43	40	1720	54	1666
	2030	55	57	56	40	2240	72	2168
	2130	73	78	75	40	3000	106	2894
	2330	98	100	99	40	3960	124	3836
	0130	122	123	122	40	4880	154	4726
	0330	151	157	154	40	6160	186	5974
	0530	175	184	179	40	7160	214	6946
	0730	211	222	216	40	8640	268	8372
	0930	227	237	232	40	9280	290	8990
	1130	242	256	249	40	9960	310	9650
	1330	254	266	260	40	10400	344	10056
	1545	270	281	275	40	11000	372	10628
1	1930	292	303	297	40	11880	406	11474
	2330	313	325	319	40	12760	452	12308
	0730	355	368	361	40	14440	526	14114
	0830	365	377	371	40	14840	550	14290
	1130	374	387	380	40	15200	564	14636
	1630	396	410	403	40	16120	608	15512
2	1930	410	424	417	40	16680	634	16046
	2130	417	431	424	40	16960	650	16310
	2330	425	439	432	40	17280	666	16614
	0730	461	477	469	40	18760	730	18030
	1130	491	490	490	40	19600	744	18856
	1330	497	496	496	40	19840	756	19084
	1530	504	504	504	40	20160	774	19386
3	1930	518	519	518	40	20720	806	19914
	2330	529	530	529	40	21160	836	20324
	0730	553	554	553	40	22120	896	21224
	1130	564	564	564	40	22560	920	21640
4	0930	622	624	623	40	24920	1084	23836
5	1430	723	724	723	40	28920	1266	27654
6	2330	743	737	740	40	29600	1336	28264
	0815	769	761	765	40	30600	1400	29200
	1400	787	777	782	40	31280	1438	29842

Spent Tan Liquor - 10 ml Activated Sludge, 0.5 ml Spent Tan Liquor, 9.5 ml D.W.

APPENDIX D

Effect of Aeration on Autoclaved Waste

Aeration of autoclaved waste has no effect on the reduction of Chemical Oxygen Demand value for spent tan liquor as illustrated in Figure 17. The autoclaving of the waste produced a decrease in the Chemical Oxygen Demand.

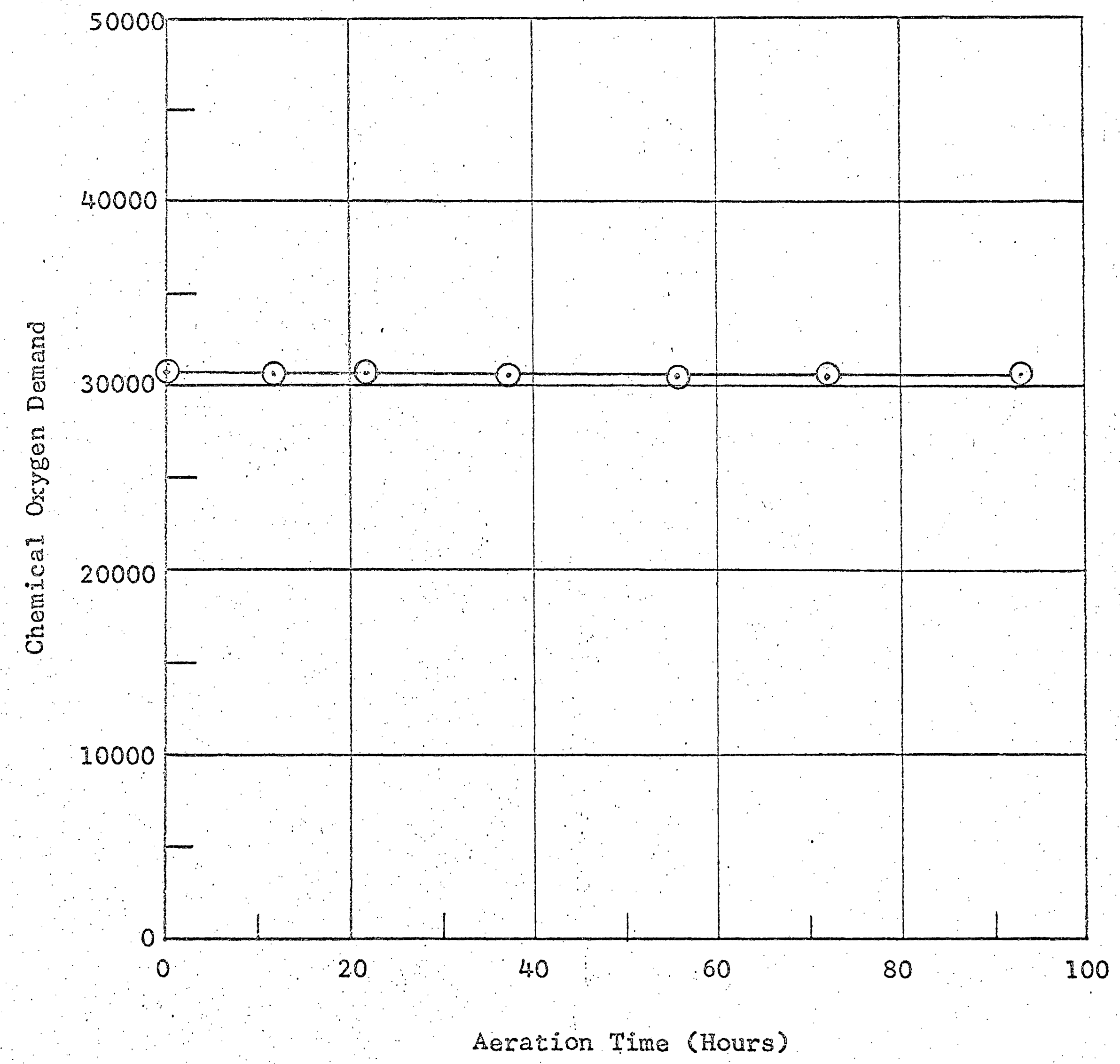

Figure 17. Effect of Aeration on Chemical Oxygen Demand of Autoclaved Spent Tan Liquor

ABSTRACT

CHARACTERIZATION AND TREATMENT OF
SPENT VEGETABLE TAN LIQUORS

by

William Howard Edwards

The objective of this investigation was to determine the effect of aeration in combination with chemical coagulation on the treatment of spent vegetable tan liquor. Chemical coagulation was desirable because it effectively reduced the color and suspended solids of the tanning waste. Aeration was thought to be a possible means of reducing the Chemical Oxygen Demand of the waste by biological stripping of the pyrogallol compound in the spent waste.

Samples collected from the aeration-coagulation system were periodically analyzed for Chemical Oxygen Demand, pH, suspended solids, color removal, volume of sludge produced, and coagulant demand. These values were correlated with those values obtained for the characteristics of the raw spent waste. Color reductions up to 94 per cent were obtained up to an aeration period of 12 hours with a suspended solids reduction of 96 per cent. Chemical Oxygen Demand reductions of the waste were increased throughout the period of aeration with a maximum reduction of 40 per cent at 36 hours of aeration.

Significance of the five day Biochemical Oxygen Demand value of 25,600 mg/liter for the raw spent waste indicated a 4 to 5 increase over all reported values from the literature.