Assessment and application of biological treatment of effluents from tanned sheepskins using activated sludge process

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Abstract

Due to the variety of chemicals added at different stages of processing of hides and skins, the wastewater of tannery industry has complex characteristics. The aim of this work was to evaluate of a biological treatment at laboratory-scale in aerobic reactors batch types using effluents obtained in the processes of tanning of sheepskins in order to obtain a kinetic model for the design of real-scale reactors. Settled tannery wastewater was used as influent to the aeration tank. Volatile suspended solids (VSS) and chemical oxygen demand (COD) were estimated. After adaptation of biological treatment, the treatability assay was performed to determine the kinetic parameters referred to the degradation rate of the effluent. The K (rate constant degradation) and Ks (coefficient of saturation) kinetic settings were obtained using the kinetic model of Monod, from them it was possible to calculate the residence time (50 hours) and the relation food / microorganisms (F/M = 0.47/day) for an COD initial 5000 mg/l , and SSV 3500 mg/l. Furthermore, the evolution of the system was monitored through qualitative analysis related with macroscopic sludge sedimentation and microscopic observations in which different groups of ciliates were identified.

Keywords: effluent, tannery, microorganisms, aerobic treatment, chemical oxygen demand (COD).

1. Introduction

In tanneries to control the pollution, new and appropriate corrective measures represents a cost of money that not all the companies are willing to assume. This has led to the implementation of measures to prevent pollution.

The effluents from leather industry constitute one the most complex wastes because of their high levels of pollutants, employing harmful chemical substances in their processes. Tanneries generate wastewater in the range of 30 - 35 l/Kg skin/hide processed with variable pH and high concentrations of suspended solids, BOD, COD, tannins including chromium [1]. In Argentina, the 86% of the leather manufacturing is carried out by mineral tanning methods employing chrome salts, while the remaining 14 % is performed by vegetable tannins by using natural or synthetic tannins [2]. Tanning effluents are characterized by a high concentration of organic compounds (such as proteins and lipids), inorganic (sulphides, trivalent chrome, chlorides), suspended solids (degraded hair, not dissolved lime), high salinity, anilines and other compounds that vary according to the raw hide processed. The degree of contamination of the effluent depends on the raw material processed (cow, sheep, goat), and the type of leather according to the processes and products used in the case [3].

Leather manufacturers must to follow quality water parameters as regards the generated effluents. The objective of this work was to study the feasibility of Activated Sludge Process for treatment tannery wastewater and to determinate the kinetic coefficients.

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Biodegradation of tannery wastewater using activated sludge process has been reported by many research workers [4]. Sequencing batch reactor (SBR) is a modification of activated sludge process, which has been successfully

used to treat municipal and industrial wastewater. SBR technology has gained more and more importance in wastewater treatment plants [5]. The treatment efficiency was characterized by determining physicochemical parameters and bioindicators [6]. The optimal operation of a biological treatment system depends of specific parameters and of the behavior of the biomass and microorganisms that are active in the system.

The proper functioning of a purification system can be defined by the presence or absence of certain types of organisms. Microscopic examination is a complement in the analysis of the effluent. In a stable active sludge system, there is a balance between the different trophic groups present (bacteria, protozoa, rotifers, algae and Nematodes). However, alterations to the purification process, due to a poor operation of the plant or an accidental error, can move this balance. Generally, ciliate protozoa and rotifers are altered at first by the presence of toxic, pH shocks and low levels of dissolved oxygen. Also in active sludge, during the presence of toxic or adverse product, they can assist as bioindicators [7].

2. Materials and methods

The effluent used was obtained from the pilot plant of tannery of the Center of Research and Technology on Leather employing sheep hides. The pre-treatment was performed on the beamhouse and on the tanyard line by separated to avoid toxic gas formation. Both lines were subjected to aeration, settling and precipitation through a physical-chemical process. Each effluent was sedimented and aerated to oxidize sulphides. Suspended lipids were removed in this step. In the primary treatment, coagulants and flocculants have been used to remove suspended and colloidal solids. It was left to sediment and the sediment was removed. This treatment is intended to protect downstream processes. Before the biological treatment test, the treated effluents were mixed and characterized: BOD, COD, pH, TKN, conductivity and NaCl according to standard methods [8]

The biological treatments or Secondary treatment were performed by duplicate using batch reactors aerobic type of 1 liter, with sludge from a sewage treatment plant as inoculums. pH was maintained around 7-8. In the “adaptation stage” of the biological reactor, the concentration of microorganisms present was determined: VSS (Volatile Suspended Solids), this reactor was operate for a concentrations range of 3000 and 3500 mg/l. The caudal (Q) was estimated for the industrial effluent and milk was the maintenance´s substrate. In this stage, the biological reactors were fed with a progressive increase percentage (Q) of the tannery effluent and decreased percentage of milk. In this way adaptation of the microorganisms was promoved, for 15 and 18 days, prior to the treatability test. The effluent was supplemented with phosphorus in the follow ratio: carbon: nitrogen: phosphorus 100:5:1. The following equation was used in order to calculate the Q, where the F/M (food/microorganisms ratio) relation was of 0.1:

$$Q = (\frac{F}{M}.\text{x Vr x VSS})/\text{BOD}$$

$$Vr\ (\text{reactor volume}) = 1000$$

VSS=3000-3500 mg/l

2.1 Biological treatability test

A concentration of microorganisms of 3000 mg/l and an effluent volume of 160 ml were employed for the test start. For each time, a sample was taken out from the reactor under continuous agitation and VSS and COD of the sample were determined. From these results, kinetic variables were identified, the parameters K (maximum rate of substrate removal) and Ks (average speed coefficient) were determined using the Monod and Eckenfelder kinetic models. The kinetic model that best fit was adopted for the design. With the kinetic model already defined and taking into account the allowable overturn value, the hydraulic retention times that should be considered for the degradation of the effluent was calculated [9].

2.2 Bioindicators of activated sludge

The active sludge status can be adequately characterized by observing the development of the sludge using microscopic techniques in conjunction with the physico-chemical parameters. Microscopic observation of active sludge is considered as a bioindicator of the state of operation of the treatment plant. It provides an environmental quality assessment that marks the physical-chemical characteristics. This monitoring results in high

sensitivity because any change is reflected in the composition of the species present in the sludge. Protist populations play a key role in the depredation of free bacteria and their contribution to bioflocculation. At low sludge age (< about 4 days) the simpler life forms are present. This includes amoebas and flagellates. As the sludge age increases (> about 4 days), more complex organisms such as the free swimming ciliates and stalked ciliates appear. At high sludge age multi-celled animals such as rotifers may be found [10].

For microscopic observation procedure homogeneous samples of the mixed liquor from the biological reactor were taken out in Falcon tubes, maintaining a sufficient air layer so that the oxygen would not be depleted until it was transferred to the microscopy laboratory. Samples were observed by light-field optical microscopy.

2.3 Macroscopy of the floc

Samples of the mixed liquor from the aerobic reactor were gently shaken, introduced into a 1-liter beaker and allowed to settle for 30 minutes. After that the following observations were made: color, sedimentation volume (settleable solids), turbidity and presence of suspended flocs.

3. Results and Discussion

3.1 Effluent chemical characteristics

After primary treatment both liquids, beamhouse and tanyard were mixed at 4:1 relation and they constituted the affluent for the secondary treatment. The table I shows the characteristics of this effluent mixture

Table I

Characteristics of sheep effluent	
BOD	1860 mg/l
COD	5400 mg/l
pH	4,6
Conductivity	40 mS
Cholrides	24 g/l
TKN	0,25-0,38 g/l

Rate of effluent degradation by microorganism biological oxidation was evaluated. The purpose was to obtain a kinetic model to use in a design for aerobic biological treatment systems. Aerobic system was chosen because residual sulphide in the effluent could affect the efficiency in an anaerobic treatment.

After secondary treatment, COD changed from of 5400 mgO_2/l (Table I) until 526 mgO_2/l (Table II). The VSS (volatile suspended solids) determination allowed the monitoring of the sludge, the values obtained fluctuated between 4000 - 5000 mg/l during the 24 hours of the test. However, for a specific tannery, bench scale studies to find out the optimal values of these parameters are needed prior to the design of biological unit. When VSS and COD obtained were estimated (Table II, graphic 1 and 2), the model that best adjusted was the Monod model´s which maximum substrate utilization rate (K) was 1.71/day and saturation coefficient (Ks) was 1090 mg/l. Then, these kinetic parameters were applied in the following linearized equation

$$\frac{Xt}{Sin - S} = \frac{Ks}{K} \cdot \frac{1}{S} + 1/K$$

t mean hydraulic residence time

Sin initial COD (5400 mg/l)

S final COD (250 mg/l)

X: VSS

Ks: saturation coefficient

K: maximum substrate utilization rate

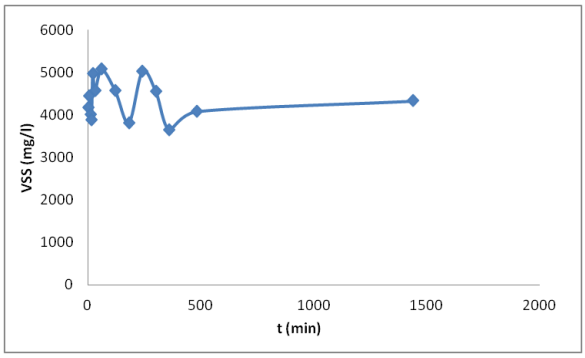
The calculated hydraulic retention time was 50 hours with a relation food / microorganisms (F / M = 0.47 / day) [11].

Table II Data of samples to calculate kinetic coefficient of Monod and Eckenfelder´s models

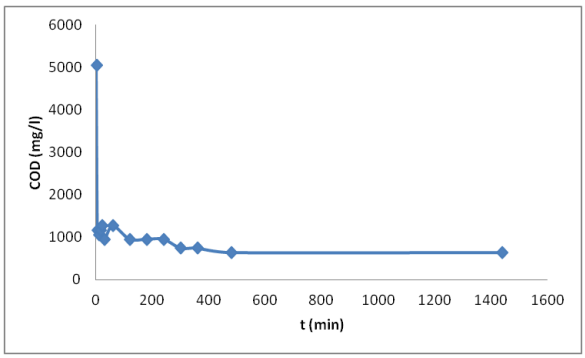
Time (min)	TSS (mg/l)	FSS (mg/l)	VSS (mg/l)	COD (mg/l)
1	7650	3470	4180	1157
5	8100	3650	4450	1052
10	7310	3290	4020	1157
15	7080	3190	3890	1262
20	8960	3980	4980	946
30	8200	3620	4580	1262
60	9280	4200	5080	946
120	8590	4020	4570	946
180	7300	3480	3820	946
240	9020	3990	5030	736
300	8430	3880	4550	736
360	6720	3070	3650	631
480	7570	3490	4080	631
1440	8170	3840	4330	526

TSS: Total Suspended Solids
FSS: Fixed Suspended Solids

Graphic 1: VSS mixed liquor at different hydraulic retention time



Graphic 2: removal of COD at different hydraulic retention time



3.2 Macro and microscopic characterization

The macroscopic test showed a brown shade of the liquor mixture for the first minutes of sedimentation. This characteristic is associated with its maturity. After 30 minutes a low turbidity was observed, the presence of suspended flocs was low and the sedimentation rate was fast.

The main microscopic characteristics of the floc were observed: irregular shape, medium size, compact structure, weak texture, medium coverage (10-50%), protozoa division 4-7sp. This simplified study allowed to determine a good sludge index, being a preliminary, quick and simple assessment of the depuration yields [12].

In the analysis of the microbiota, rotifers from Philodinidae and Lecanidae families (Fig. 1) were detected at the beginning of the test but not at the end with 100% effluent. These communities, representatives of old sludge have been observed, but this test was initiated with a sludge of high age, with flocs that had excessive time of permanence in the reactor. Further, naked amoebae of the family Amoebidae (Fig. 2) and different groups of protists alveolates have been detected. The ciliates are successive colonizing microorganisms that occupy diverse ecological niches; its presence decrease the amount of free bacteria, therefore the turbidity, improving the quality of the effluent. The greatest diversity of protist ciliates of class Oligohymenophorea was found, which can be classified in three families. Bacterivorous free-swimming ciliates of the Cyclidiidae family, Cyclidium sp. (very active, never remains at rest, only when fed) (fig 3), swimming ciliates of family Parameciidae have been identified. During the last stages sessile ciliates appears, basically peritrichous from Vorticellidae family (Vorticella sp.) (Fig. 4); in this group the formation of mobile larvae have been identified. (Fig 4') Organisms that feed bacteria, may be found alone or forming colonies, are particularly evident in activated sludge treatment systems associated with flocs. In adittion in this stage appears predator/omnivorous pleurostomates swimming of the family Litonotidae (Fig. 5) and bacterivorous spirotrichous crawling ciliates of the family Aspidiscidae (fig. 6) [13,14]. (Fig 7) The crawling ciliates use structures such as cirrus or cilia for their movement on the floc where they feed on the bacteria that are on the surface of the same.

The microscopic observation of the activated sludge constitutes a valuable contribution to determinate the evolutionary moment of the biological sludge as well as if it undergoes some alteration. One of the most efficient measures is to access to the composition and dynamics of the biological community since it indicates all time the state of operation, offering the possibility to resolve problems and improve yields.

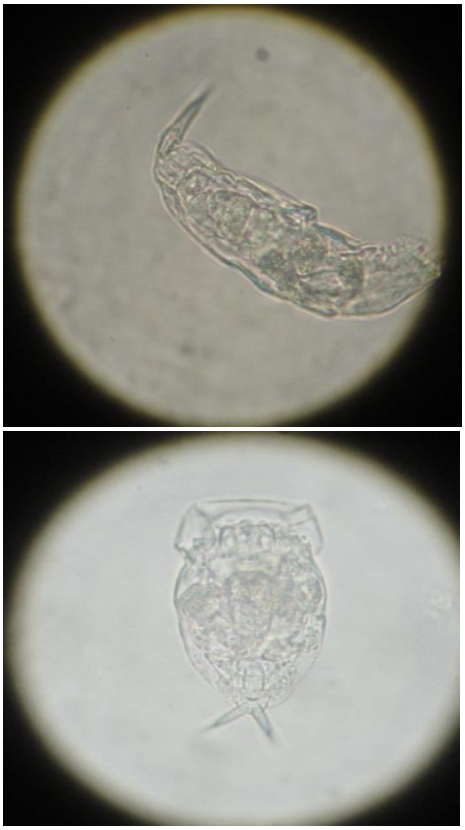


Fig. 1-Metazoa Family Lecanidae 40 x

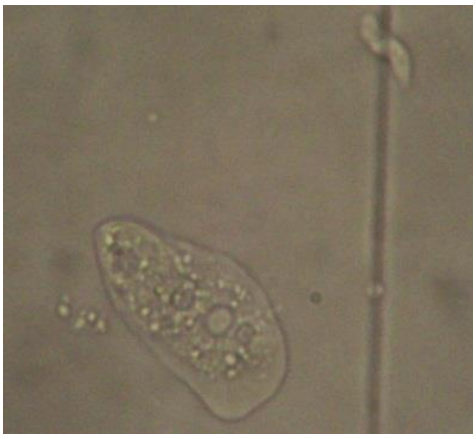


Fig. 2-naked-amoebae 40 x

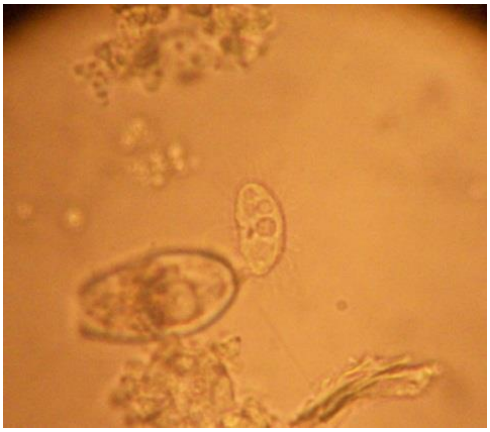


Fig. 3-Family Cyclidiidae 40x

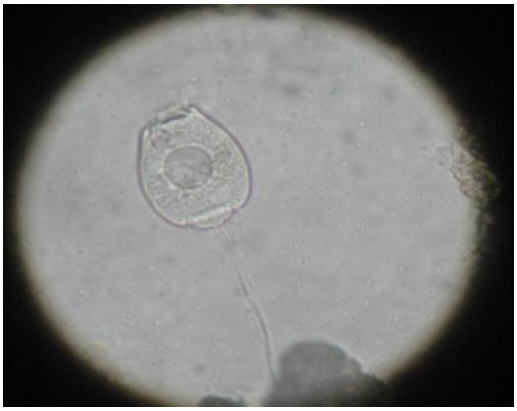


Fig. 4-Sessile ciliate Vorticella sp 40x

Fig. 4´-Stalked ciliates attached to a floc 40x

Fig. 5-Family Litonotidae 40x

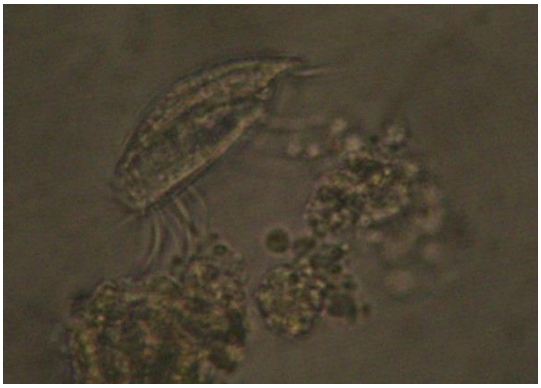


Fig. 6-Family Aspidiscidae 40x

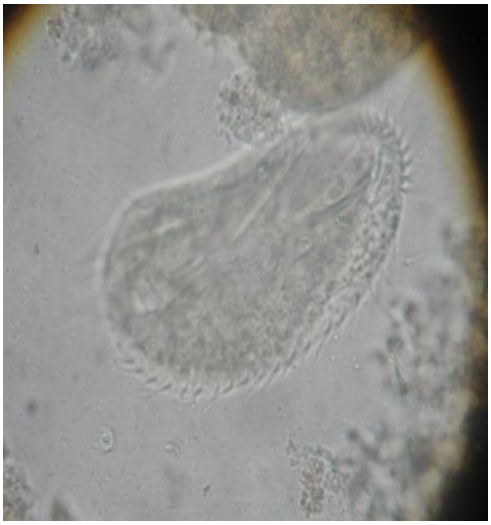


Fig. 7-Crawling ciliate-spirotrichous 40x

4. Conclusions

The problems of contamination in the tanning industry are being studied in order to establish what may be the best practical treatment of industrial waste**.** The determination of the saturation coefficient (Ks) and maximum substrate utilization rate (Ks) in an activated sludge system may be helpful in understanding the kinetics of substrate utilization by the microorganisms and to design of biological treatment facilities for tanning wastewater. It would take more than 24 hours with a similar sludge to reach the COD overturn allowed with an effluent of the same characteristics.

The characteristics of the treated effluent have affected the evolution of the microfauna that compose the activated sludge. As it has been observed, the number of live rotifers was decreasing whereas the group of litostomates was developed under all conditions. These individuals present a wide range of tolerance to the high concentration of salts in the medium precisely this type of effluent presents a high concentration of NaCl. Free bacteria have been observed to proliferate freely in the interfloc solution, thereby increasing the turbidity of the liquor mixture. Furthermore in the last stages succession the presence of telotroch swimming larvae. They were appeared when the conditions of the environment were changed to unfavourable, being able to become encyst, instead they will emit a new stalk if the environment becomes propitious. Finally it was confirmated that the characteristics of the treated effluent have affected the evolution of the microfauna that compose the activated sludge.

In this sense, the feasibility of the biological treatability test was verified and the characterization of the biological component was used as an indicator of the operation of the system.

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