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Evaluation of the aerobic and anaerobic degradation of an industrial effluent from vegetable tannery processing of leather on batch reactors

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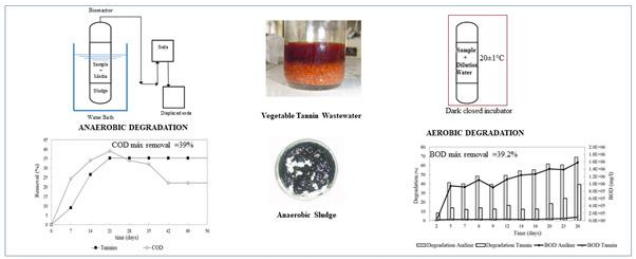
Graphical abstract



Abstract

In this study, the aerobic and anaerobic biodegradability of the industrial wastewater from the vegetable tanning process were evaluated. Water from a food wastewater treatment system was used as seed inoculum for the aerobic process and mature granular methanogenic sludge from a brewery industrial wastewater plant was used for the anaerobic process. The water from the tanning industry had a biological to chemical oxygen demand ratio of 33% with values of total chemical oxygen demand (COD) in the range of 342000 mg O_2/L and total dissolved solids of 506595 mg/L. The assay of the tannery effluent under aerobic conditions resulted in a degradation of tannins of 39.2% after 26 days, while the anaerobic degradation had an average of 65% with a 35% attributed mainly to degradation of tannins. The production of methane and Volatile Fatty Acids, during the anaerobic treatment, suggests a potential adaptation of biological organisms present in the mature anaerobic granular methanogenic sludge.

Keywords: Tannery wastewater, tannins, anaerobic degradation, aerobic degradation, industrial effluent.

1. Introduction

The tannery industry represents an important portion of the worldwide economy. The Food and Agriculture Organization has estimated that in 2006 the total production of hides and skins was 18.7 billion square feet with a total revenue of 2.9 billion dollars, with China, Italy, Brazil, Russia and India being the major producers of leather (UNIDO, 2010). The process of turning animal skin into leather involves a series of steps such as removal of hair, tanning and dying. All these steps require the use and disposal of water, with an estimated water consumption of 25-80 m^3 per ton of skin or hides during the tanning processes alone (Romero-Dondiz *et al.*, 2015). As a result of the large requirement of water in the process and the significant generation of wastewater, tanneries are often built close to rivers or 'within pipeline distance to the sea' (UNIDO, 2010), where industrial discharges occur. This therefore has a detrimental on the environment, especially in countries where there is weak environmental legislation and control.

Although there are different types of tanning methods, the majority of techniques include similar steps for the preparation of the skin and the stabilization of the leather. For example, in the area of San Benito in Bogotá (Colombia), where the industrial water samples were collected, small- and medium-sized companies use a process in which the raw animal skin is initially preserved with salts such as NaCl and $NaHCO_3$ at the slaughterhouses. Once in the industrial facilities, a cleaning process takes place wherein the skin is rinsed thoroughly with water in order to remove external agents such as faeces, blood, mud and salt. Skin that is exposed to salt preservation is immersed in water for 180 hours to hydrate the skin and induce a swelling process. The next step involves removing the hair and epidermis of the skin. For that, the skin is exposed to alkaline solutions such as sodium sulphide or sodium carbonate, which affect the collagen tissue through a saponification reaction of the natural fat contained in the skin. The saponification favours the extraction and elimination of proteins from the skin by biodegrading the proteins and fibres due to the alkalinity and by making the proteins soluble in water. The skin is then exposed to mechanical removal of the hair and remaining muscle and

fat. Before the tanning process, the excess of carbonates is removed in a process called 'deliming'. Some processes also include the use of enzymes, bacteria or fungi to remove the remaining fibres of collagen followed by an acidification of the raw skin (Dixit *et al.*, 2015).

During the tanning process, the skin is treated in order to preserve the material against any biological degradation. Different chemical products are used in this stage, which determine the final texture of the leather. One of the most common methods for preserving the leather is the chrome method in which salts of trivalent chromium (Cr^{3+}) are used (Fathima *et al.*, 2015). Tanning with chromium salts leads to the production of light and flexible leather, ideal for the manufacture of dresses and accessories. Another tanning method is the 'vegetable' method (Kanagaraj *et al.*, 2015) in which tannins from plants (for example from the tree *Schinopsis sp*.) are used to obtain thick and rigid leather such as those used in footwear and saddlery industry. Tannins are compounds with high molecular weight and high content of phenol-hydroxyl groups. The hydroxyl group allows tannins to bond with proteins and other macromolecules of the animal skin due to their affinity to form protein-tannin complexes (Makkar et al, 2007), making the leather more stable and minimizing its natural degradation. Furthermore, the antiseptic capacity of tannins, protects the leather against fungus, bacteria and yeast.

Additionally to Cr^{3+} salts and vegetable tannins, a variety of compounds can be used during the preservation of the leather, such as aluminium salts, alums, formaldehyde, melanin-urea, styrene, and maleic anhydride (Lofrano *et al.*, 2013). After the tanning process and before drying the leather, the material is exposed to other treatments such as dying and greasing, which are optional depending on the desired quality of the final product. The different alternatives of leather manufacture result in a generation of wastewater with very different physicochemical properties. As a result, the selection of the most appropriate wastewater treatment for a specific type of effluent that results is a challenging task (Ayoub *et al.*, 2013).

Different technologies have been studied for the treatment of tannery wastewater, including filtration (Romero-Dondiz *et al.*, 2015), adsorption (Gomes *et al.*, 2016), ion exchange (Gutterres and Mella 2014), chemical coagulation and flocculation (Mella *et al.*, 2017), electrochemical methods (Keerthi, *et al.*, 2013; Isarain-Chávez *et al.*, 2014), ozonation (Mella *et al.*, 2017), advanced oxidation processes (Charumol and Keerthinarayana 2017; Cruz-Rizo *et al.*, 2017; Sekaran *et al.*, 2013) and membranes (Keerthi *et al.*, 2013). However, these methods require specialized infrastructure, making them expensive, especially for small- and medium-sized tanning industrial companies.

On the other hand, biological processes are an inexpensive alternative for treating effluents. However, the physicochemical properties of the tanning wastewater make it difficult to treat the water biologically (Goswami and Mazumder, 2014) as the tannins affect the natural development of the microorganisms responsible for the degradation of organic matter. Tannins inhibit enzymatic processes, alter the membranes and limit the transfer of metallic ions across them (Scalbert, 1991). Despite the toxicity of tannins, some organisms such as bacteria (*Achromobacter* sp., *Klebsiella pneumoniae*, and *Streptococcus caprinus*), fungi (*Aspergillus* sp., *Fusarium* sp) and yeast (*Candida nitrativorans*, *Debaromyces hansenii, Pichia adzetti*) have shown capacity to grow in this type of wastewater and even degrade tannins under specific conditions (Kanagaraj and Mandal, 2012; Mingshu *et al.*, 2006). Some of the defensive mechanisms that these species use are the production of polymers biocompatible with tannins, synthesis of enzymes resistant to tannin toxicity and production of siderophores capable to oxidising and degrading tannins (Bhat *et al.*, 1998). This microbial degradation makes viable the use of biological methods in the treatment of this type of industrial effluents. Yet studies are required to identify potential sources of organisms capable of adapting to the toxicity of tannins. In this study, the aerobic and anaerobic biodegradability of the industrial wastewater from the vegetable tanning process was evaluated using water from a food wastewater treatment system as the seed inoculum for the aerobic process and mature anaerobic granular methanogenic (MAGM) sludge from a brewery industrial wastewater plant.

2. Methods

The biodegradability of wastewater from the vegetable tanning process of leather (industrial effluent) using Quebracho (*Schinopsis sp*.) was evaluated under aerobic and anaerobic conditions. Samples of the wastewater were collected from the discharge of the tanning batch reactor (i.e. rotating drum) and preserved following the Standard Methods (APHA, 2005). The aerobic degradation was studied using the method of closed bottle test. The dilution water was prepared according to the Standard Methods (5210-B) (APHA, 2005), using a phosphate buffer solution, containing $MgSO_4$, $CaCl_2$ and $FeCl_3$ at the concentrations suggested in the standard method. The dilution water was then saturated with oxygen by injecting a continuous air-flow for 24 hours. Water from a food wastewater treatment system (BOD_5=480 mg/L and COD=800 mg/L) was used as the seed inoculum. The controls used in the aerobic degradation experiments are shown in Table 1 in which aniline was used as a control compound. A total of 60 bioreactors (300 mL Winkler bottles) were used for the tests, controls and replicates. The bioreactors were incubated at 20±1°C, in darkness for 26 days. The measurements of oxygen were performed every two days using an oximeter (WTW InoLab OxiLevel 2).

The anaerobic degradation was performed by measuring the methane production over a period of 48 days. Mature anaerobic granular methanogenic (MAGM) sludge, from a brewery wastewater treatment plant, was used for all the anaerobic experiments. In order to provide the optimal conditions for the anaerobic organisms, the pH of the wastewater was adjusted to the range of 7 and 7.2. Likewise, the media was enriched with mineral, reductive and vitamin solutions. The mineral solution contained

KH_2PO_4, $Na_2HPO_4 \bullet 2H_2O$, NH_4Cl, NaCl, $MgCl_2 \bullet 6H_2O$, HCl, H_3BO_3, $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, NaOH, Na_2SeO_3, Na_2WO_4, Na_2MoO_4, and Resarzurin at the concentrations suggested in the standard method. For the reductive solution, $NaHCO_3$ and $Na_2S \bullet 9H_2O$ in the proportion of 4:2.4 w/w was used. The vitamin solution was prepared using $CaCl_2 \bullet 2H_2O$, Biotin, Nicotinamide, p-aminobenzoic acid, Tiamine, Pantotenic Acid, Piroxidamine, Cianocobalamine; Riboflavine. All these solutions were sterilised in an autoclave at 120°C and 15 psi and deaerated with nitrogen gas to eliminate the dissolved oxygen before being used.

Table 1. Experimental bottles and controls used in the aerobic analysis of biodegradability

	Industrial waste water	Aniline	Seed inoculum	Dilution water
Experiment	8 mL	-	1mL	Yes
Control 1	-	-	1mL	Yes
Control 2	-	1mL	1mL	Yes
Control 3	-	1mL	-	Yes

Table 2. Standard methods used in the physicochemical characterization of the industrial and treated wastewater

Property	Standard method/technique
Total solids (TS)	APHA 2540 B. Gravimetric method
Total, fixed and volatile suspended solids (TSS, FSS, VSS)	APHA 2540 D. Gravimetric method
pH	APHA 4500-H+ B. Electrometric method
Alkalinity	APHA 2320 B. Titration method
Total and soluble COD	APHA 5220 C Closed reflux - Titrimetric method
BOD_5	APHA 5210 B. 5 days test at 20 C
Total nitrogen	APHA 4500-Norg B. Macro-Kjeldahl method
Ammonium nitrogen	APHA 4500-NH3 B and 4500-NH3 E. Distillation and titration
Phenols	APHA 5530- C. Extraction with chlorophorm

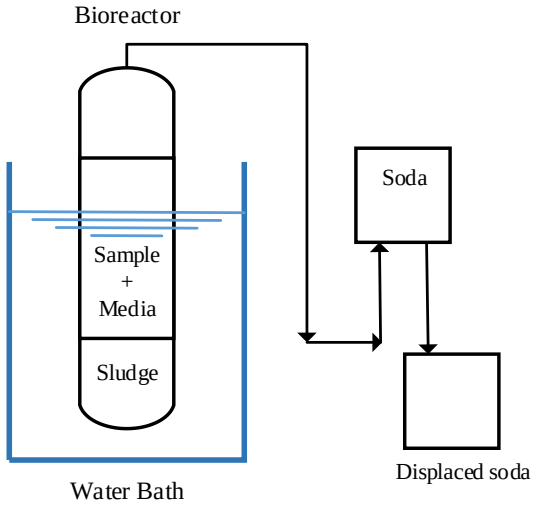


Figure 1. Scheme of adiabatic setup

The anaerobic bioreactors were filled with the industrial effluent and the MAGM sludge maintaining a mass relation chemical oxygen demand and volatile suspended solids (COD/VSS) of 5:1 and 1:1. (i.e. 5g of COD of wastewater per 1g of VSS of the sludge or 1g of COD of wastewater per 1g of VSS of the sludge). The mineral, reductive and vitamin solutions were then added in a proportion of 1%, 5% and 1% v/v respectively. The temperature of the bioreactors was controlled using a thermostatic water bath set up at 30°C. The bioreactors were sealed and a plastic tubing was used to connect the top of each reactor with inversed face-down water traps containing soda (Figure 1). This method enables the study of the biodegradability by measuring the volumetric production of methane and therefore establishing the activity of the anaerobic bacteria (Field, 1987).

The physicochemical characterization of the industrial effluent and the treated wastewater was performed using the Standard Methods as shown in Table 2. The volatile fatty acids (VFA) were measured through spectrophotometry using the ferric hydroxamate reaction (Siedlecka *et al.*, 2008). The condensed tannins were measured using the Butanol-HCl method (Porter *et al.*, 1986).

A second set of anaerobic experiments were performed, in order to study the toxicity of the industrial water on the anaerobic organisms after being treated anaerobically. After 48 days of treatment, the industrial wastewater was exposed to another anaerobic treatment performed under similar conditions as the previous experiments. The production of methane, oxygen and nitrogen was determined using TCD-chromatography (Varian 3400) with a column MolSieve 5A45/60 de 2mx1/8", at 50°C with a flowrate of helium of 30 mL/min.

3. Results and discussion

An initial characterization of the sludge (Table 3) showed that the sample contains equal portions (50/50) of fixed and volatile suspended solids.

Table 3. Initial characterization of MAGM sludge

TSS (mg/L)	FSS (mg/L)	VSS (mg/L)
82675	40950	41725

As shown in Table 4, the initial characterization of the wastewater from the vegetable tanning process showed low values of pH and high values of total COD. Almost 33% of the total COD corresponded to soluble COD. The ratio BOD/COD of the wastewater was 0.33, indicating a

potential biodegradation of only 33%. Although the result obtained was low compared to the recommended BOD/COD ratio of 0.5 for biological degradation (Samudro and Mangkoedihardjo, 2010), other studies have reported initial BOD/COD ratios lower than 0.5 with final degradation higher than 50% (Borglin *et al.*, 2004; Ghasimi *et al.*, 2009) due to the adaptation of the microorganisms to the adverse environment. In terms of solids, 98% of the total solids were dissolved solids in which 87.2% were fixed dissolved solids. For this type of effluent, dissolved solids have been related mainly to the presence of tannins (He *et al.*, 2007). On the other hand, suspended solids are related mainly to remains of animal skin such as proteins (Dixit *et al.*, 2015). The presence of sulphides and ammoniacal nitrogen in the tanning wastewater are due to the use of ammonia and salts such as sodium sulphide during the unhairing and deliming processes.

Table 4. Initial characterization of the Industrial effluent (wastewater from the vegetable tanning process)

Physicochemical property	Units	Value
pH	-	4.3
Alkalinity	mg/L $CaCO_3$	0
Soluble COD	mg/L O_2	112000
Total COD	mg/L O_2	342400
BOD_5	mg/L O_2	114667
Phenols	mg/L	<0.01
Ammoniacal Nitrogen	mg/L $N\text{-}NH4^+$	280
Total Kjeldahl Nitrogen	mg/L N	448
Total Solids	mg/L	515675
Total Fixed Solids	mg/L	459170
Total volatile Solids	mg/L	56505
Total Suspended Solids	mg/L	9380
Total Dissolved Solids	mg/L	506595

3.1. Aerobic biodegradation

Aerobic degradation of tannins are usually not effective due to the high toxicity of tannins to aerobic microorganism (Bhat *et al.*, 1998). Furthermore, tannins can be degraded resulting in other toxic by-products such as resorcinol, pyrogallol and phloroglucinol (Patra, 2012). In this study, aerobic degradation was carried out as a baseline to be compared to anaerobic conditions using aniline as control. Under the experimental conditions, the BOD of the aniline was far higher than the BOD for the degradation of the industrial effluent (Figure 2). Since the BOD for the degradation of tannins was very low at the beginning, the consumption of oxygen was mainly attributed to microorganism's metabolism rather than potential chemical oxidation of tannins (which would have occurred from the first day). Likewise, the increment of oxygen demand after 12 days suggested a potential adaptation of the microorganism to the environmental conditions. The BOD of the control compound (aniline) reached 69% of degradation after 26 days, while the industrial effluent with tannins reached only 39.2% of degradation. Similar results were found by Balakrishnan et al.(2018) during a 72 hours aerobic treatment of a similar industrial effluent where the maximum removal of tannins was 24%.

3.2. Anaerobic biodegradation

In order to guarantee a proper supply of nutrients to the system, the relation between COD, nitrogen and phosphorous (COD:N:P) was checked. Results showed a COD:N:P relation of 350:5:1 which are optimum for the anaerobic digestion (Namour and Müller, 1998). The biodegradability of the effluent was evaluated through the production of methane and changes in the dissolved COD, using samples without tannins as controls. As shown in Figure 3, experiments carried out with a mass of COD/VSS ratio of 1:1 displayed minimal generation of methane and degradation of COD with values similar to the controls; therefore, the analysis of these experiments are not included herein. On the other hand, experiments with a COD/VSS ratio of 5:1 displayed a rapid initial production of methane observed during the first seven days, followed by a decrease on the methane production rate. The plateau on the methane production and in the production of volatile fatty acids (VFAs) (Figure 4) are related to the potential inhibition of the anaerobic organisms due to the toxicity of tannins. The biodegradation of the industrial effluent, calculated from the production of methane, was an average of 65% expressed as reduction of *COD*.

3.3. Variation of pH, alkalinity, soluble COD and volatile fat acids

Values of pH were adjusted during the addition of the mineral media obtaining an initial pH of 7.2 ± 0.05. During the anaerobic biodegradation of the industrial effluent for a COD/VSS 5:1, the pH was in the range of 7.17 to 7.44. In terms of alkalinity, an initial drop occurred during the first 14 days with a decrease in concentration of $CaCO_3$ of 30% as shown in Figure 4. Between days 14 and 35 values of alkalinity were similar to the initial value. After day 35 an increase of 42% in the alkalinity occurred. In contrast, the concentration of VFAs increased during the first 7 days of the anaerobic biological treatment, followed by an irregular decrease of the concentration in the following 42 days, with a final value of 3620 mg/L. VFAs are produced during the anaerobic digestion, indicating an adaptation of the anaerobic organisms to the environmental conditions.

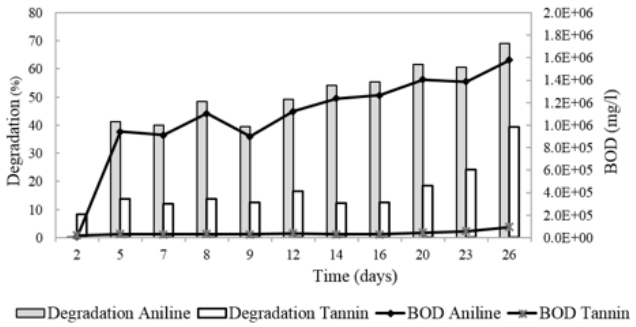


Figure 2. BOD and degradation of industrial effluents with tannins and control compound

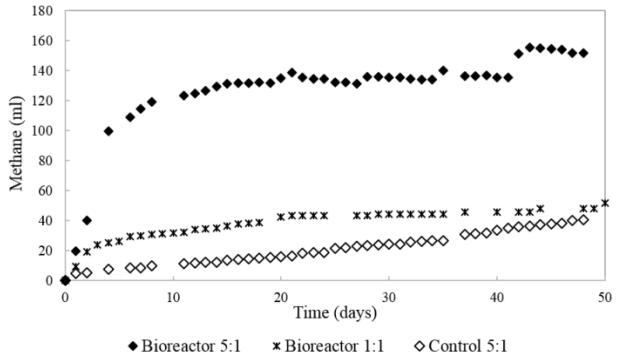


Figure 3. Production of methane under anaerobic condition with different COD/VSS ratio

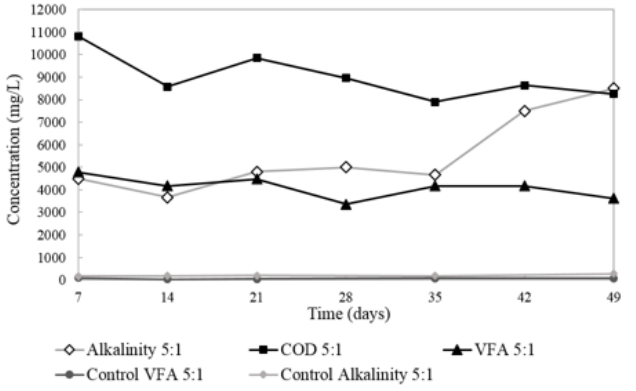


Figure 4. Variation of COD, alkalinity and Volatile Fatty Acid (VFAs) during the anaerobic degradation

3.4. Removal of COD and tannins

Although the anaerobic biodegradation of the effluent accounted for 65% of total COD, the maximum removal of soluble COD was only 35% which is attributed mainly to the degradation of tannins as shown in Figure 5 for a COD/VSS ratio 1:1. Consequently, the remaining percentage of degradation under anaerobic conditions can be related to degradation of biodegradable macromolecules such as protein and fats and a potential adsorption of tannins to the biomass (He *et al.*, 2007), which is evidenced by the formation of VFAs during the first stage of the process and the production of methane previously discussed. Based on these results, the COD removal rate was calculated in 0.121 g COD/gVSS·day and the maximun biodegradation rate was estimated to be 0.018 mg COD-CH_4/mg VSS·day.

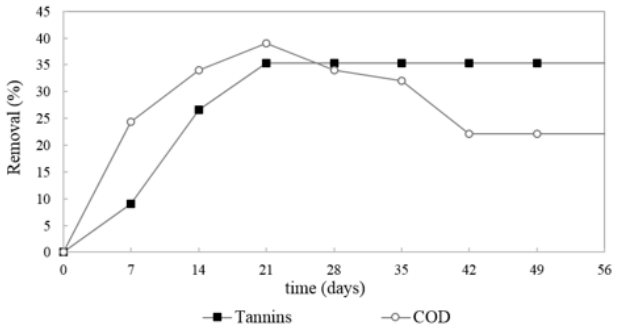


Figure 5. Removal of COD, and tannins during the anaerobic degradation

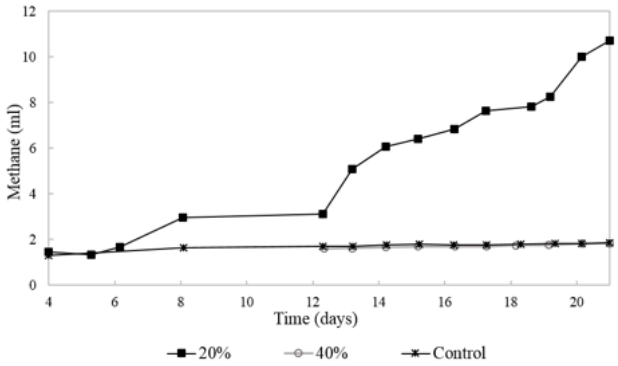


Figure 6. Methane production during second anaerobic treatment

3.5. Second anaerobic process of the industrial effluent

Treated water from the anaerobic experiments was exposed to a second anaerobic treatment with the same MAGM sludge, with constant agitation and methane production was measured using high-performance liquid chromatography. Different proportions of treated wastewater were used for the experiments; but only bioreactors with proportions of wastewater lower than 40% V/V displayed production of methane. The generation of methane started after day 8 as shown in Figure 6. In contrast to the first anaerobic treatment, minimal methane was produced during the first 12 days. After day 12, there was an increase in the rate of methane production, suggesting that the microorganisms present in the sludge required a period of adaptation. Nevertheless, the production of methane after 20 days was considerably lower than the production of methane during the first anaerobic treatment in the same period of time. These results suggest one more time that a large portion of degradation in the first anaerobic treatment was due to removal of suspended COD. In other words, the low production of methane in the second treatment was caused by the limited carbonaceous substrates available for the microorganisms. Consequently, results show that although there was a reduction in the tannin concentration during the first treatment, the remaining fraction of tannins and its degradation by-products are not preferred for the metabolism by anaerobic microorganisms.

4. Conclusions

Industrial effluent from the vegetable tanning process was characterised and exposed to anaerobic biodegradation using MAGM sludge. The raw effluent displayed low pH with COD and BOD_5 values in the order of 342000 and 114000 mg/L respectively. The biodegradation of the effluent resulted in a removal of 37% and 65% of total COD under aerobic and anaerobic conditions respectively. The degradation of tannins under aerobic and anaerobic conditions were 35% and 39.2% respectively, suggesting a resistance of the microorganisms to the antiseptic properties of the tannins present in the wastewater. These low values in tannin degradation were attributed to the hard adaptability of the organisms present in the seed inoculum and in the MAGM sludge, and the toxicity of tannin oxidation by-products.

During the first 7 days, a rapid production of methane and VFAs suggested an adequate degradation of the vegetable tannery effluent by the anaerobic organisms. The total degradation (65%) under anaerobic conditions were attributed to tannins degradation (39%), organic matter degradation by microorganisms and to the adsorption to the proteins of the biomass present at the MAGM sludge (26%). A second anaerobic treatment showed the requirement of a period of stabilization of the mature sludge and lower production of methane compare with the initial anaerobic treatment, due to removal of soluble COD. The preliminary results presented herein, show a great potential for promoting the design and realization of complimentary studies aimed at finding a combination of different aerobic/anaerobic treatments for different loadings of vegetable tanning effluent. Further studies will provide sustainable effluent treatment solutions to leather producers, lowering the environmental impact of the use of chemical wastewater treatment products, and generating methane that can be reincorporate in Another process.

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