Performance evaluation of aerobic reactor and *Sarcocornia perennis* to reduce the COD and chloride of effluents from tanning sheepskins

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Abstract: Tannery is an industry that generates wastewater characterised by high levels of organic matter, chrome, dissolved solids, sulphides and high salinity. The aim of this work was to evaluate at laboratory scale, the decrease of chemical oxygen demand (COD) and salinity from effluents from tanning sheepskins, using physical chemical methods in primary treatment, and bioreactor and wetlands for secondary and tertiary treatment, respectively. Effluents were collected from tanning processes of sheepskins carried out on the Center of Research and Technology on leather tannery plant, La Plata, Argentina. Conventional primary treatments selecting coagulants and flocculants were employed. For secondary treatment, batch bioreactors were designed, and the maximum COD removal was 60–70%. For the tertiary treatment, wetlands at laboratory scale were employed. In this test wetlands were filled with granite stone, with and without the plant *Sarcocornia perennis*, and COD decreased on average by 64% additional and chlorides concentration decreased by around 15%.

Keywords: effluent; tannery; activated sludge; wetlands; *Sarcocornia perennis*.

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1 Introduction

Among all the industrial wastes tannery effluents are ranked as the highest pollutants (Shen, 1999). The wastewaters generated in the course of the production process are highly complex and considered one of the most hazardous pollutants of industry, and need proper treatment by physical/chemical and/or biological means before discharge (Calheiros et al., 2014). The tanneries generate wastewater in the range of 30–35 l/kg skin/hide processed with variable pH and high concentrations of suspended solids, BOD, chemical oxygen demand (COD), tannins including chromium (Nandy et al., 1999). 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 (Cantera and Angetinetti, 1987).

The tannery effluent is generally treated by physicochemical and biological methods such as activated sludge process (Ilyas et al., 2013). The basis of this treatment is the assimilation of the organic material by microorganisms in the presence of oxygen. The studies performed showed that it is possible by this method to remove a high percentage of COD, what means that it is useful and of high efficiency (Haydar et al., 2007). Moreover, constructed wetlands (CWs) are systems considered to treat wastewaters by biological means to a secondary or tertiary level as a developing cost-effective and environmentally friendly phytoremediation technology (Calheiros et al., 2007; Dotro et al., 2010). The presence of salts in high amounts in wastewaters may adversely affect the biological processes in the wastewater treatment systems since hypersaline effluents are often recalcitrant (Lefebvre and Moletta, 2006). CW systems with salt tolerant plant species are a promising solution for polishing saline effluent from the tannery industry to levels fulfilling the discharge standards (Calheiros et al., 2012). Thus, *Sarcocornia perennis* (Miller) Scott, a perennial halophytes growing in San Antonio marsh (Patagonia, Argentina) was selected for carrying out the phytoremediation assays.

In Argentine (Res. ACUMAR 366/2010), contaminant agents are declared those industrial establishments whose discharges are outside the normed parameters: COD = 250 mg O_2/l; BOD = 50 mg O_2/l; total nitrogen = 35 mg/l; total chrome = 2 mg/l; chlorides = 0.5 mg/l (Bergagna, 2010). In this context, the little tanneries (production of <200 skins) are those that are more vulnerable as they have not enough means to reduce the generation of discharges or optimise its treatment. The aim of the research presented in this work was to evaluate at laboratory scale, the decrease of COD and salinity from effluents from tanning sheepskins using physical and chemical methods in primary treatment, bioreactor and wetlands in secondary and tertiary treatment, respectively.

2 Materials and methods

2.1 Primary treatment

The effluent used was obtained from the pilot plant of tannery of the Center of Research and Technology on Leather (CITEC), La Plata, Argentina, employing sheep hides. The primary treatment was performed on the tanning and beamhouse lines sequentially to avoid toxic gas formation and because different amounts of coagulant were employed in each case. The beamhouse effluent (COD initial: 35,000 mg O_2/l) was left to sediment and the supernatant was aired for 72 h to oxidise the sulphides. Suspended lipids were also removed at this step. After that, it was coagulated with ferrous alum (1,5% p/v) stirring at 150 rpm during 3 min, the pH was shifted to 7.0 and then Polifloc 53/90 (Cahesa) 4%v/v was added as flocculant, with stirring at 25 rpm during 15 min. It was left to sediment for 30 min and the sediment was removed. Tannery effluent (COD initial: 48,000 mg O_2/l) was treated in the same way but in this case it was optimised by employing a ferrous alum concentration of 2% p/v. Supernatants of both treatments were mixed and they constituted the affluent for the secondary treatment.

2.2 Secondary treatment

The secondary treatment tests were performed using batch reactors with decanting tanks of 1 l of capacity. Effluents obtained after primary treatment were set frozen (–20°C) up to they were discharged into the reactors. The inoculum, organic material composed of microorganisms, was provided by a bovine tannery. The active sludge system consists of a biomass of microorganisms in homogeneous suspension in a reactor with air supply and inflow of the primary effluent. The reactor was operated for a volatile suspended solids (VSS) concentrations range of 3000–3500 mg/l (Haydar et al., 2007). The feed (Q) was calculated according to the following equation:

$$Q = (F/M \times V_r \times \text{VSS})/\text{BOD},$$

where *F/M* (food/microorganisms ratio) = 0.025 – 0.1; V_r (reactor volume) = 500–1000 ml; VSS = 3000–3500 mg/l; BOD = COD (mg O_2/l) x 0.28 (Eckenfelder, 2000).

Each 48–72 h the reactors were fed (Q) with the effluent obtained in a total of 22 reaction cycles. At each stage, the aeration was stopped, samples were analysed (COD, pH and VSS) and the supernatant was replaced by fresh effluent mixture. COD was determinate according to Cantera (1994), pH and VSS (Standard Methods Method 2540, 1992).

2.3 Tertiary treatment

Effluents obtained after the secondary treatment were employed as affluent. Wetlands were built at laboratory scale, filled with granite stone, with and without the *Sarcocornia perennis* vegetal species. *Sarcocornia perennis* plants were collected in the San Antonio marsh (Patagonia, Argentina) and then sent to the CITEC laboratory. Every week, reactors are emptied and fed again with the secondary effluent (as batch). It worked with a total of six wetlands, three of them with plants (CP) and the other three without plants (SP). In each cycle, during 10 weeks, input and output samples were taken and analysed as regards their concentration of chlorides, COD, pH and conductivity. Chlorides were determinate by Standard Methods (Standard Methods Method 4500, 1992). The conductivity was measured with the 4150 JENWAY conductimetre in millisiemens (mS) at 25°C.

3 Results and discussion

3.1 Primary treatment

The primary treatment of sedimentation, aeration, coagulation and flocculation was optimised according to Imran et al. (2012) and applied to the beamhouse effluent (COD initial: 35,000 mg O_2/l) and to the tanning effluent (COD initial: 48,000 mg O_2/l). After primary treatment both liquids, beamhouse/tanning, were mixed at 4 : 1 relation. Table 1 shows the characteristics of the effluent mixture.

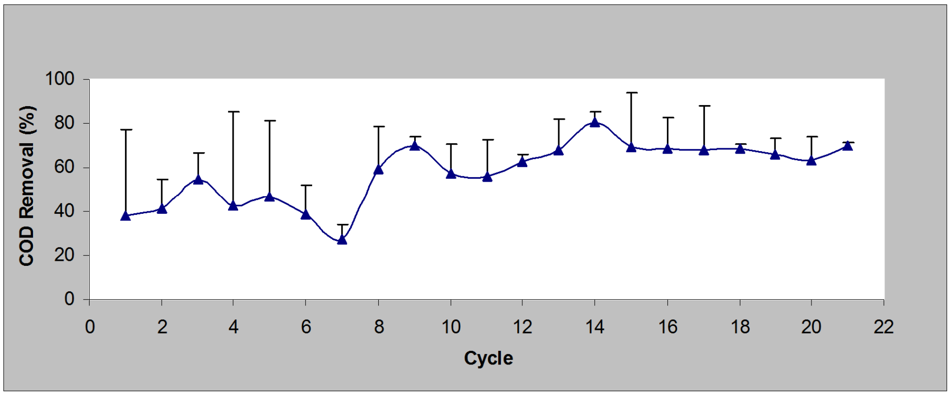
Table 1 Characterisation of the effluent (primary treatment)

Effluent beamhouse/tanning (*4 : 1*)	
COD	11000 mg O_2/l
pH	6.5
NKT	0.25 g/l
Conductivity	40 mS
Chloride	22 g/l
TS	36.5 g/l
TSS	1.16 g/l
VSS	0.78 g/l

3.2 Secondary treatment

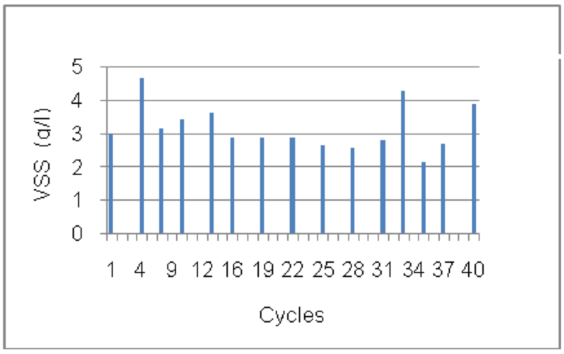
The effectiveness of this process not only relates to the degradation of pollutants, but also influences the separation of the solid–liquid phases. In the first section of experiments, the COD removal values were very variable but in the last 10 cycles a process optimisation was achieved with COD removal% values from 54% to 87% (Figure 1). At this step, the COD input was in the range of 2000–5000 mg O_2/l and the COD output in the range of 1400–2000 mg O_2/l. These values are in agreement with the values (61–84%) reported by Haydar et al. (2007) although effluents with initial COD values (1221–1662 mg O_2/l) were used; while Durai et al. (2011) using a sequential batch bioreactor system for the treatment of effluents from the leather industry with initial COD of 1560–6240 mg O_2/l achieved a COD removal of 79%. The VSS determination allowed the monitoring of the sludge, the values obtained fluctuated between 2.5 g/l and 4.7 g/l, but in most of cycles the value was ~3 g/l (Figure 2).

Figure 1 Chemical oxygen demand (COD) removal (see online version for colours)



Data are means of duplicates, the bars represent standard error.

Figure 2 Volatile suspended solids (VSS) of secondary treatment (see online version for colours)

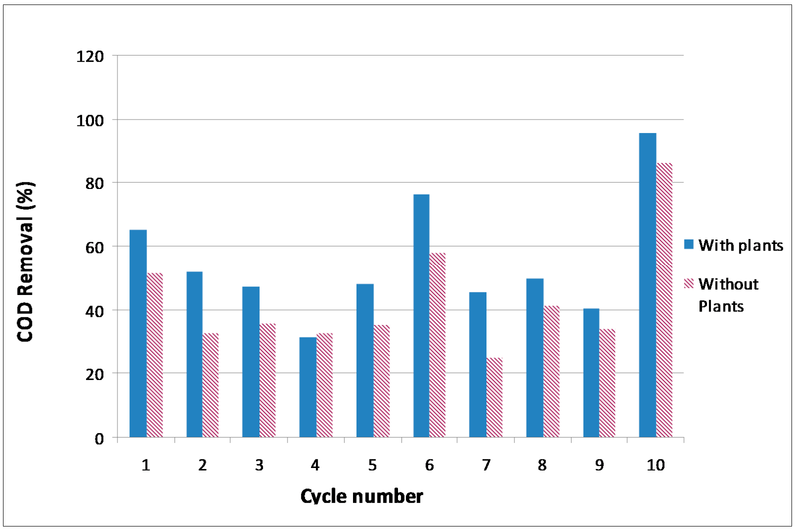


Data are means of duplicates, errors were less than 5%.

3.3 Tertiary treatment

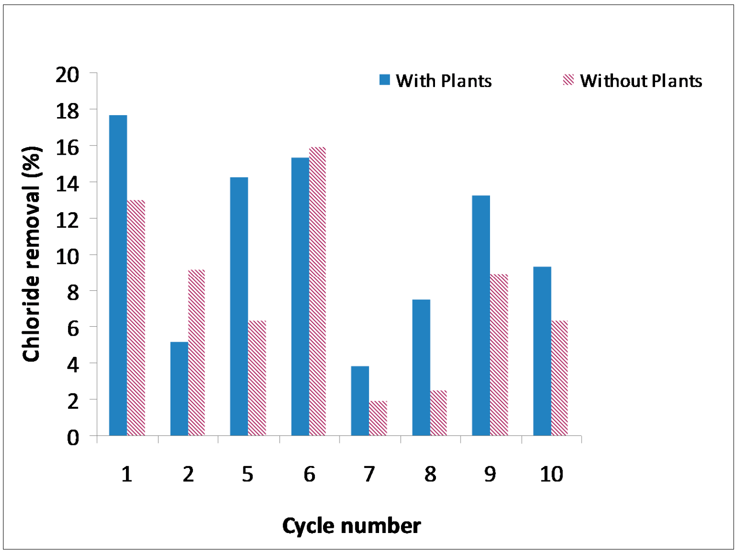
The results obtained in the tests carried out with wetlands regarding to COD and chloride removal (with and without the halophyte *S. perennis* species) are shown in Figures 3 and 4, respectively. The COD removal percentages were within the range of 25–87%, but for the reactors with *S. perennis*, removal data became slightly greater. According to these results the plants would be improving the COD removal.

Figure 3 Chemical oxygen demand (COD) removal (tertiary treatment) (see online version for colours)



Data are means of duplicates. Errors were less than 5%.

Figure 4 Chloride removal (tertiary treatment) (see online version for colours)



Data are means of duplicates. Errors were less than 5%.

Figure 4 shows the average percentage values for chloride removal. The figure shows a wide variability in the results obtained, with maximum removal percentages near to 15%. These results are similar to those reported for the treatment of high salinity tannery effluents using wetlands constructed with Arundo donax and Sarcocornia fruticosa (Calheiros et al., 2012). It must be taken into account that the chloride concentration of the original effluent is a high one, then, the 15% removal of chlorides in this step leads to the final concentration around 4.6 g/l still far from the download values allowed. The characterisation of the effluents after tertiary treatments is shown in Table 2.

Table 2 Characterisation of effluents after tertiary treatments for the triplicates (1, 2, 3) of mesocosms with plants (CP) and without plants (SP)

Test	*Volume* (ml)	*pH*	*Conductivity* (mS)	*Chloride* (g/l)	*COD* (mg O_2/l)
CP1	265.5	8.03	13.7	4.7	446
CP2	265.5	7.92	13.6	4.6	353
CP3	260	8.12	13.8	4.6	444
SP1	272	8.15	13.2	4.5	545
SP2	272	8.12	13.2	4.5	537
SP3	273	8.16	13.4	4.6	569

Values shown represent the average of the 10 cycles checked.

4 Conclusions

The preservation of tannery industry is very important, especially to Argentina, owing to its historical and economic values. The problems of contamination by the tanning industry are being studied in order to establish what may be the best practical treatment of the wastes generated. In this study, the effluent initially obtained after the beamhouse process and the tanning of sheepskins was treated sequentially employing primary, secondary and tertiary treatments. At the end of the process, it was reached a decrease of two orders of magnitude of the initial COD that was exceptionally high for the original effluents of tannery (48,000 mg O_2/l) and those of beamhouse (35,000 mg O_2/l). With the primary treatment values of COD were around 11,000 mg O_2/l, after secondary treatment (activated sludge) the COD values were around 1400–2000 mg O_2/l. After tertiary treatment an effluent was obtained with a pH near 8.0 with a chloride average concentration of 4.6 g/l, 13 mS conductivity and an average COD of 414 mg O_2/l when mesocosms with *S. perennis* were employed. These preliminary results are promising and they must be proved by more experimental data.

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