Combined biologic removal of sulphate for tanning industrial wastewaters

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Abstract A biologic pretreatment technology of mixed tanneries wastewater, suitable for sulphate-rich industrial wastewaters, has been studied, in order to eliminate chemical precipitation and improve removal efficiency of the relevant pollutants. It couples an anaerobic reactor with an aerobic sulphide oxidation (ASO) step, where H_2S is partially oxidized to elemental sulphur, and includes a recirculation system. The proposed solution provided Methanogenic Archae (MA) and Sulphate Reducing Bacteria (SRB) coexistence and controlled inhibition by partial oxidation of hydrogen sulphide. The removal efficiency of the anaerobic reactor was quite dependent on temperature and hydraulic retention time (HRT). COD removal varied between 32-68 % and sulphate removal (20-60 %), referred to the mixture of the industrial effluent diluted with with 50% of recirculation, at an Organic Load (OL) ranging from 0.5 to 1.5 kg CODm^3 d^{-1} and HRT from 1 to 5 days. The entire biologic pretreatment (AHF+ASO) resulted much more efficient and COD removal increased to 64-82 %, being less dependent on temperature variations. This process removed also a significant part (85%) of Chromium (Cr^{+3}), by sorption into the biologic sludge. This two step biologic pretreatment, ensured better removal of relevant parameters than conventional chemical precipitation, avoided addition of chemical products, minimized excess sludge production, and also removed hydrogen sulphide and sulphate, resulting in a favorable alternative solution.

The effluent from this stage was submitted to a sequencing batch nitrification/denitrification step, to improve the removal of the relevant parameters. The average removal efficiency of entire process was appreciable and better than the conventional solution: COD = 88%, Sulphate = 66 % and Nitrogen (kjeldahl) = 92%, chromium (Cr^{+3}=96%). However, the presence of non degradable organic compounds delivered in the effluent from synthetic tanning, were hard to remove completely and did not allow fulfilling the severe standards for wastewater discharge in water course in terms of COD, Nitrogen (kjehldal) and color. This requires an additional polishing step.

Keywords: Tanneries Wastewater treatment; anaerobic digestion; sulphate reduction; biogas production; sulphide removal; thiobacteria.

1. Introduction

The effluents from leather tanning and finishing industry have large volume and complex and variable composition, which makes its treatment and the fulfillment of the limits fixed by the environmental law very complex (EC-IPPC, 2003). The type, quantity and variability of pollutants results in high organic load, strong salinity and high nitrogen content. It also contains additional specific contaminants such as chromium, sulphides and sulphates. The characteristics of tanneries wastewater require complex treatment sequences. Conventional solution involves specific pre-treatment processes such as homogenization, sulphide oxidation and chemical precipitation, in order to attenuate variability and reduce odors, organic load, suspended solids and chromium (Cr^{+3}). After these operations the effluent proceeds to long retention time biologic processes, for organic matter and nitrogen removal.

This conventional approach involves many operational costs and, generally, the biologic system is not capable to meet the environmental objectives, requiring improvements and oversizing, to fulfill the standard for wastewater discharge.

Application of waste reduction-elimination approach is a promissory alternative strategy for water and wastewater management, as suggested by EC-IPPC (2003). In existing facilities many of the recommended procedures are currently implemented, in order to get water and chemical savings. The conservation measures reduce water consumption and chemicals, but do not greatly reduce the pollution load or improve biodegradability. The upgrade and improvement of existing tanning Wastewater Treatment plant (WWTP) is also a current practice, in order to accommodate new and more efficient technologies.

Wastewater effluents from Tanning industry have high organic loads. Application of anaerobic biologic processes can be an attractive alternative to reduce treatment costs and increase efficiency, but this wastewater also contains sulphate rich streams. In this case, anaerobic technology can be inhibited by sulphate's reduced compounds (HS^-), and cannot be feasible.

Anaerobic digestion of high sulphate concentration industrial wastewaters can be inhibited by the out-competition of Sulphate Reducing Bacteria (SRB) over Methanogens Archae (MA), generating hydrogen sulphide at concentrations which are inhibitory for both methanogenic and sulphate reducers populations (Oude Effering, 1994).

To overcome this restriction, recent recommendations suggest separation of wastewater sources from tanning processes and apply specific pretreatment for each individual effluent (EC-IPPC, 2003). The soak liquor, rich in biodegradable organic matter, can be segregated and treated favorably by anaerobic digestion (Lefebvrea et al., 2006), without SRB interference. Then, it can be joined to the composite wastewater after physico-chemical treatments, thus reducing chemicals and oxygen supply for aeration and excess sludge. The cost of the treatment would be reduced.

In existing tanning facilities wastewater segregation can be not feasible without large investments, and anaerobic pre-treatment has be applied to the whole effluent. Thus anaerobic technology must be adapted to sulphate rich and be capable to run efficiently. On this purpose Schenk et al., (1999) proposed a solution combining the digester with a simultaneous Sulphide stripping removal column, which maintained low sulphide concentration, avoided inhibition and improved by 15 % the removal efficiency.

This solution transfers to the gas phase the removed sulphide and requires an adequate and expensive gas treatment system. For this reason, an alternative solution was proposed for overcoming of the technical hitches to apply anaerobic treatment for the sulphate rich industrial wastewaters. Instead of stripping, the sulphide control is carried-out by a biological sulphide oxidizing biologic process, in aerated reactor. Hydrogen sulphide is oxidised into molecular Sulphur S° under oxygen limited conditions, controlled by REDOX sensor. Combining the anaerobic digestion reactor with this aerated tank and a recirculation system, recycling of aerated sludge into anaerobic reactors allows sulphide concentration regulation.

Afterwards, this stage is associated to a sequencing batch reactors for COD and nitrogen removal, in order to achieve high quality and low nitrogen-based compound concentration.

In this paper, results from the biologic pre-treatment lay-out for tannery wastewater degradation was studied, capable to replace conventional chemical precipitation, to avoid chemical consumption and fulfill environmental specifications.

2. Methods

2.1. Experimental system

Figure 1 presents the experimental configuration of the laboratory-scale treatment facility, incorporating (working volume): holding tank (10 l), anaerobic hybrid filter (AHF) reactor (15 l), a first aerated reactor (25 l) for partial sulphide oxidation (PSO), a second aerated reactor (25 l) and a collecting tank. With this combination it was possible to simulate the proposed pre-treatment system and, also, the total experimental system (TES), which includes a nitrification/denitrification step. The anaerobic filter consists of 1.00 m-high PVC cylinder, with diameter of 0.15 m partially filled (25 %) with plastic media. The filling material used as biomass support was constituted by plastic rings with length of about 2-3 cm and diameter of 0.5 cm. The reactors were insulated but not provided with an external heating system.

The aerated vessels were constituted by PVC cylinder, with diameter of 0.40 m and maximum working volume of 25 liters (Fig. 1). The system worked at room temperature, monitored by temperature sensor and data logger system, in order to simulate field conditions.

Industrial wastewater was added batchwise to the stirred holding tank where it was mixed with recirculated effluent from the first aerated reactor. This prepared feedstock was pumped to the AHF with a volumetric pump, Watson Marlow, type 503 U/RL, which was regulated according to the selected loading rate and flowed down by gravity to the aerated reactors and settling tank.

The aerated tank for hydrogen sulphide oxidation into molecular Sulphur S° was kept under oxygen limitation using redox potential measurements and a timer controlling the compressor in on-off mode. Redox values were regulated to range from -140 mV to -270 mV. The same device also controlled nitrification/denitrification reactions in the second aerated reactor. In this case Redox values ranged from 0 mV to +100 mV.

The biogas flowrate was measured by a gas meter.

Sludge was periodically, manually wasted from the AHF and the aerated reactors.

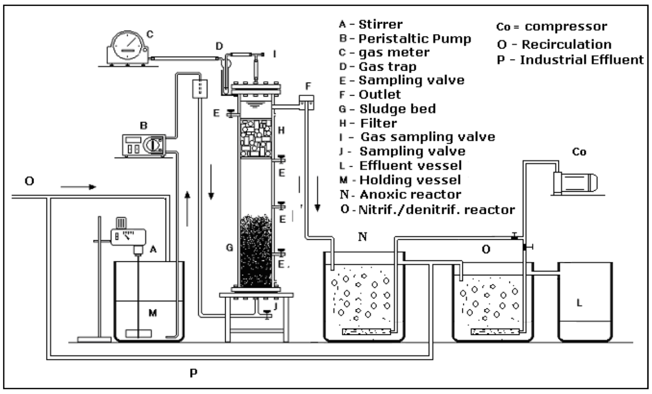

Figure 1 Experimental system

The reactors was inoculated by adding fresh anaerobic and aerobic sludge coming from a tannery wastewater treatment system up to 25% v v^{-1}.

2.2. Analytical procedures

Biogas composition was evaluated in collected samples by gas chromatography. Volatile acids were analyzed in liquid samples by extraction and gas chromatography. COD, total (TS) and volatile (VS) solids, total (TSS) and volatile (VSS) suspended solids, sulphate, total nitrogen and phosphate where analyzed according to APHA Standard Methods (1994). Sulphide concentrations in liquid samples were determined with an ion-specific sulphide electrode, according to ASTM D-4658-87. Values of pH and Redox potential were measured by potentiometry using, respectively, a glass electrode and a platinum electrode combined with an Ag|AgCl reference electrode. Sulphate and thiosulphate were measured in liquid samples by ionic chromatography. Sulphur concentrations were determined by reversed-phase liquid chromatography (Möchel, 1984).

3. Result and Discussion

3.1. Anaerobic reactor

The AHF reactor was fed during about 200 days with tannery mixed effluent diluted with 50 % effluent from the first aeration stem. Figure 2 shows the Hydraulic Retention Time (HRT) and the temperature level during the experimental period. In wintertime temperature decreased to about 15 ºC.

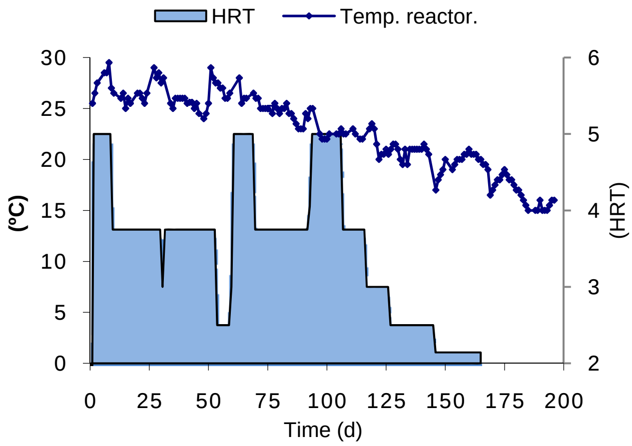

Figure 2 Temperature and HRT

Table 1 shows the industrial wastewater concentrations, revealing a heavily polluted effluent, rich in organic matter sulphate and nitrogen compounds. The industrial facility uses both synthetic and chrome tanning. Chromium spent solutions is recovered, resulting in very low Chromium (Cr^{+3}) concentration discharge.

Table 1 Wastewater characteristics

Parameter	Average	Max.	Min.
Total Solids (TS) (g/l)	6.5	12.2	3.6
Volatile Solids (VS) (g /l)	2.1	13.5	2.1
Total Suspended Solids (TSS) (mg /l)	620	1430	250
Volatile Suspended Solids (mg /l)	522	1300	230
COD (mg/l)	3843	5705	1680
Nitrogen (Kjeldahl) (mg /l)	241	434	154
Nitrogen (N_{NH4}) (mg/l)	125	302	28
Phosphate ($PO_4^{=}$) (mg/l)	42	78	8
Sulphate ($SO_4^{=}$) / (mg l)	1315	3168	275
Chromium (Cr^{3+})	22	39	7

The phosphate contained in the industrial effluent was insufficient to adequately sustain biological growth, being a limiting factor. For this reason a solution containing appropriate proportion of phosphate, Nickel, Cobalt and Iron salts was added periodically, to compensate the feedstock composition and stimulate the methanogenic biologic community.

Due to the high variability of the influent concentrations, the bioreactor was submitted to considerable changes of the operational conditions, as shown in Figure 3, which reports the organic load and the consequent evolution of biogas production. The organic load is the sum of the industrial effluent and recirculation line concentrations.

The metered methane production is low, due to SRB activity, which uses at least 0,67gr COD /gr $SO^{4=}$ reduced, to the metabolism of the bacterial communities and to the loss with effluent and recirculation. Biogas production was also affected by temperature drop in last period.

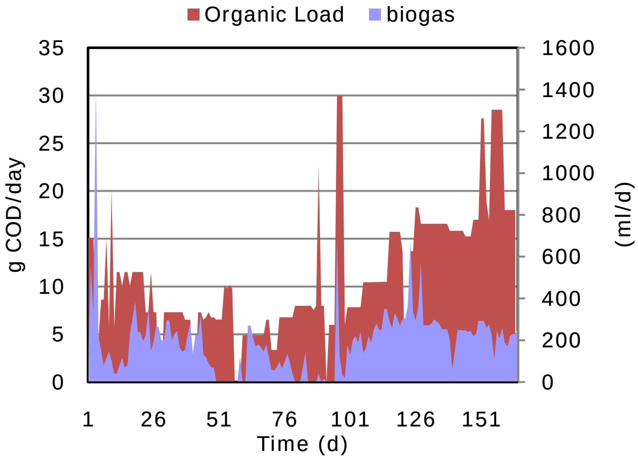

Figure 3 Organic load and biogas production

Figure 4 depicts biogas composition in terms of methane and Hydrogen sulphide composition, during the experimental period. Methane concentration was always quite high, ranging between 78% and 92%, exhibiting the transfer of carbon dioxide in liquid phase, for pH control.

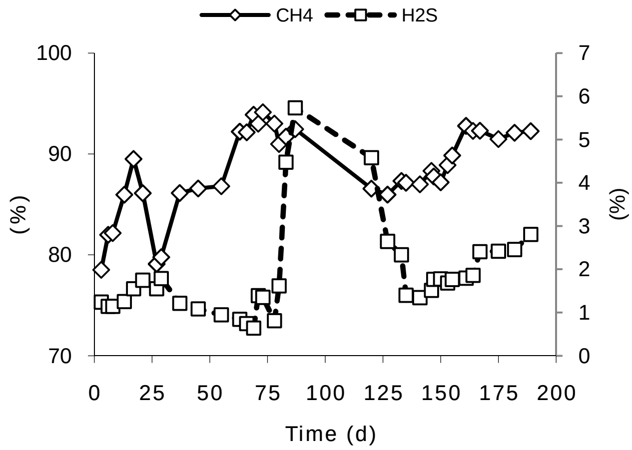

Figure 4 Biogas composition

SRB activity increased significantly after the start-up. During the days 75-120 of the experimental period the H_2S content in biogas was very high, and inhibition of methanogenic bacteria occurred. Afterwards, the system recovered. SRB activity was less affected by temperature decrease than MB.

3.2. Efficiency of removal

In figure 5 are represented the values of efficiency of removal of the anaerobic Hybrid Filter (AHF), of the anaerobic filter and first partial sulphide oxidation (PSO) (pretreatment) and of the total treatment system.

The efficiency of anaerobic reactor is evaluated in terms of the received feedstock mixture (Industrial effluent plus recirculation). The performance of this reactor was very influenced by the temperature and organic load, and the COD ranged from 62% to 22 %.

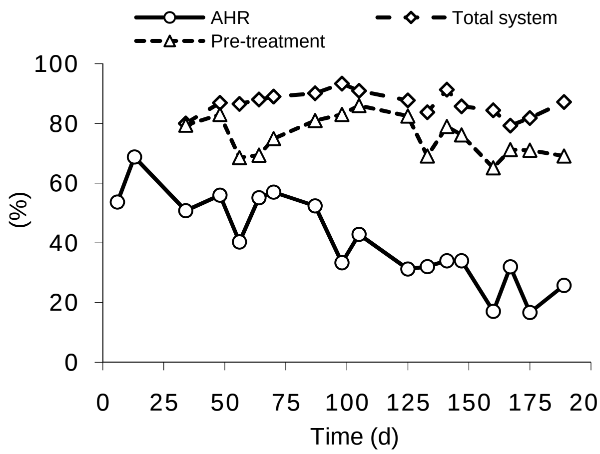

Figure 5 COD Removal

The efficiency of the pretreatment with partial sulphide oxidation (PSO) and of the total system (TES) was evaluated versus the industrial effluent concentration, showing higher values of COD removal efficiency. Efficiency of AHF and PSO varied in the range 68-82%. The TES revealed remarkable performance and its efficiency varied between 80 e 92 %. The aerobic processes were, also, less affected by temperature changes than the anaerobic step.

Figure 6 shows the efficiency of removal of Volatile Suspended Solids (VSS) and sulphate in the AHF, depicting the hydrolytic and BRS activity. Suspended solids and sulphate removals, shows a wide range of variation of efficiency (from 82 to 18 % for VSS) and from 18-to 62 % for sulphate, inherent with industrial effluent variability and temperature variation.

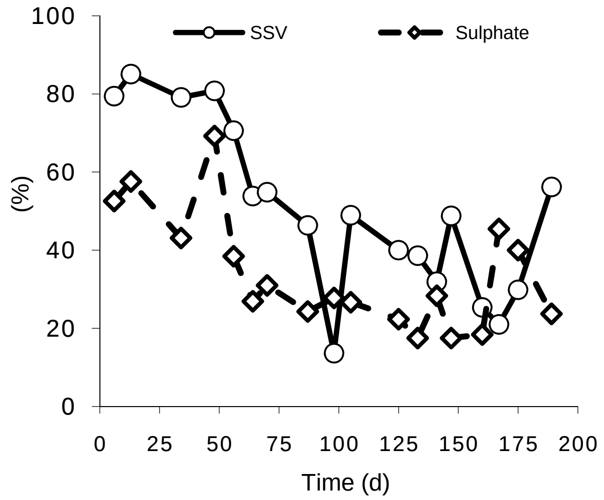

Figure 6 AHF-SSV and Sulphate Removal

Figure 7 shows the effect of nitrification/denitrification step on Nitrogen (Kjehldal and ammonia) removal, resulting in a particularly effective a efficiency rangy from 60-to 98% for the Organic Nitrogen and 80-93 % for the ammonia nitrogen.

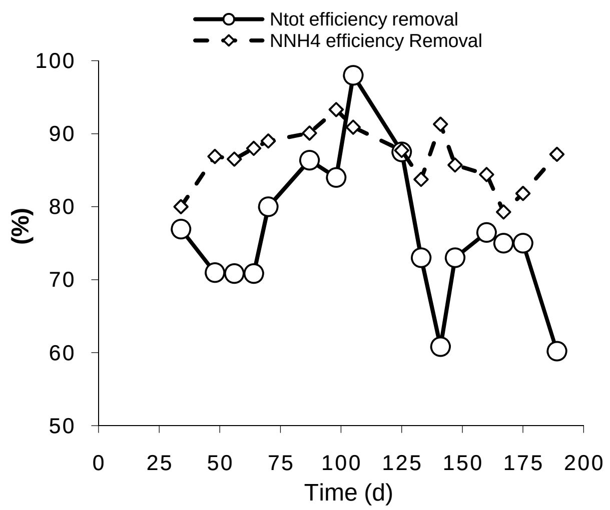

Figure 7 Nitrification/Denitrification-Nitrogen removal

3.3. Treated effluent and final considerations

The solution studied in laboratory for treatment of tanning industry effluents and to be scale-up at full-scale, showed favorable results in terms of process efficiency. Biological sulphate and methanogenic conversions performed suitably. Sulphide inhibition was adequately controlled by aeration and recirculation of *thio-bacteria* rich biomass, and the nitrification/denitrification reactor performed efficiently.

According to the laboratory experience, the expected efficiency of removal are higher than the conventional existing technology COD = 88%, Sulphate = 66 %, Nitrogen (kjeldahl) = 92%, chromium (Cr^{+3}=96%) and TSS = 68 %.

Table 2 shows the average concentration of relevant parameters in the treated effluent. Some of them are still higher than limits fixed by the environmental authorities and require an additional polishment step. Synthetic tanning discharge organic and colored compounds which are very hard to remove completely by biologic processes, requiring chemical oxidation or any other adequate process.

In any case this proposed two-step biologic treatment, based on a combination of biologic processes acting on organic compounds, (CQO), Sulphates and sulphide, discharges an effluent better than the conventional solution based on chemical precipitation e allows evaluation of important more than 50 % savings, in terms energy consumption in the biologic system, in relation to the current solution.

This technology is also easier to operate, in relation to physico-chemical processes. Avoids chemicals preparation, dosing and control, and does not produce chemical sludge, to be removed and properly disposed. The only sludge resulting from the treatment line are the not biodegradated suspended solids and the excess biologic sludge. Otherwise the system operates mainly with low growth yield anaerobic and anoxi biologic consortiums, generating low amount of biologic sludge. So the expected total excess sludge is very low, less than 10 % of the value currently obtained by the conventional system.

Table 2 Effluent Characteristics

Parameter	Proposed solution	Current solution	Limit for discharge
TSS	221	337	60
COD	587	1019	150
BOD_5	80	437	40
Nt (Kjeldahl)	64	255	15
N_{NH4}	4	187	10
$PO^{4=}_{l}$	19	8	1
Sulfatos	434	972	2000
Cr^{3+}	0.8	1	2

4. Conclusions

Conventional approach to the treatment of tanneries effluents based on chemical precipitation pre-treatment followed by aerobic/anoxic processes for carbon and nitrogen removal, has several drawbacks related with the cost of the chemicals, increase of sludge and incapacity to remove sulphates, adequately. Treatment and disposal costs are significant, due operation, transportation and charge fees, making a difficult challenge the economical exploitation of the facility. Compared with conventional physico-chemical technology, the proposed biologic system constituted by anaerobic digestion (AD) followed by partial sulphide oxidation (PSO) AD/PSO process provided the following advantages;

(i) avoided chemical consumption,
(ii) removed (70 %) sulphates and (88%) COD
(iii) Reduced energy consumption (about 60 %) in subsequent aerobic/anoxic stages.
(iv) achieved a small quantity of sulphur rich stabilised sludge, reusable in alkaline agricultural land.
(v) Allowed fulfilment of sulphate concentrations lower than 1000 mgSO4=.

The proposed alternative, based on enlarged anaerobic consortium performed stable and suitably, making further progress on the applicability of Anaerobic Digestion to sulphate rich effluents. It also reduced significantly treatment costs, by savings chemical precipitation agents, eliminating chemical sludge to be dewatered and disposed and by reducing energy consumption in the subsequent secondary treatment process.

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