Assessment of Biodegradability of Synthetic Tanning Agents Used in Leather Tanning Process

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***Abstract*----The goal of this research was to assess the biodegradability of two synthetic tanning agents (syntans), Phenol condensation product and Nitrogen containing resin using Respirometry. The evaluation involved the analysis of oxygen uptake rate (OUR), profiles by respirometry. The study was conducted with different syntan concentrations of 50mg/L, 100mg/L, 150mg/L and 200mg/L. The oxygen uptake rate (OUR) of mixed liquid is 60 mg/L h with 50mg/L phenol condensation product and is found to be higher than with the concentrations 100, 150 and 200 mg/L h. The percent chemical oxygen demand (%COD) removal was decreased with increased syntan concentration indicating high rates of biodegradation at low concentration and toxicity impacts or low rates of biodegradation at higher concentrations. Whereas the Nitrogen Containing Resin showed complete inhibition on oxygen uptake rate of mixed liquor at all concentrations and very low % COD removals as well showing less biodegradability or potential toxic impact on the activated sludge.**

Keywords: Respirometry, Syntan, Oxygen uptake rate, Sludge Stabilization, Biodegradation

I. INTRODUCTION

Tanning is a process by which animal hides and skin is converted into a stable material which is resistant to microbial attack and has enhanced resistance to wet and dry heat. During leather processing the hides and skin undergoes a series of pre-tanning, tanning, and post tanning operations (Cokgor et al., 2008). The collagen of the skin reacts with plant materials containing polyphenols (vegetable tanning) or chromium (chrome tanning). In addition about 130 different chemicals including surfactants, acid and metal organic dyes, natural or synthetic tanning agents, sulfonated oils, salts, etc are employed in leather making process (Ganesh et al., 2006). Synthetic tanning agents are high molecular organic compounds which are used to make hides and skin into an imputrescible material called leather (Rema et al., 2010). Most of the syntans are manufactured by the condensation of aromatic compounds like phenol, phenol sulphonic acid or naphthalene sulphonic acid with formaldehyde (Kleban, 2002).

Tanneries generate waste water in the range of 30- 35L/Kg skin/hide processed with variable pH and high concentrations of suspended solids, BOD, COD, tannins and chromium (Vijayaraghavan and Murthy, 1997; Iqbal et al., 1998; Szpyrkowicz et al., 2001). The tannery effluents cause severe environmental problems and have toxic effect on aquatic organisms. Since all the physico-chemical treatment processes of tannery wastewater are associated with the operational problems and maintenance cost, new methods have been developed mostly the biological methods. The biological treatment systems used for the treatment of tannery effluents are inadequate or less cost effective.

In this context, respirometric techniques are used to evaluate the biodegradability of two synthetic tanning agents, Phenol Condensation Product and Nitrogen Containing Resin. Respirometry has been a well established technique used to measure the amount of oxygen consumed by the microorganisms in activated sludge with respect to time. Respirometry is based on the fact that oxygen uptake rate is directly related to the biomass activity and substrate consumption (Spangers et al., 1996; Fall et al., 2006). OUR measurements can provide much information concerning treatment plant performance, degradability of organic materials, in order to predict possible optimizations of treatment plant (Hagman et al., 2007). According to Oliveira et al. (2007),

oxygen uptake by microorganism is closely related to substrate removal because it stimulates the degradation process. These techniques have been widely used for assessing the biodegradability, toxicity, and biokinetic parameters of toxic and nontoxic wastewaters (Vanrollegham et al., 1999; Chu et al., 2003). Biodegradability studies have been reported for a synthetic tanning agent CNSF (a condensation product of 2-naphthalene sulphonic acid (2-NSA) and formaldehyde) using activated sludges and the fungus (Song et al., 2005).

The objectives of this study are to investigate the aerobic stabilisation of sludge and the applicability of stabilised sludge for biodegradability assessment of synthetic tanning agents by respirometry. Since the aerobic stabilization had a more pronounced positive effect on the toxicities of sludges and no toxicity after aerobic stabilization (Mantas et al., 2007), the current study focused on the stabilization of sludge also. Since the present study focused only to assess the biodegradability with the use of respirometry, the respirograms obtained were not subjected to modeling.

II. MATERIALS AND METHODS

A. Sludge Stabilization:

A bench scale Fill and Draw Reactor made of Plexiglas, with a total working volume 6 L was used for the study. At the base of the reactor two aerator stones were placed at opposite ends to maintain an aerobic growth of activated sludge. The inoculum was made by mixing both sludges collected from a secondary settling tank of common effluent treatment plant of Tannery wastewater. The continual aerated fill and draw reactor was operated with manual feeding and manual sludge and effluent withdrawal. Sucrose was used as a sole carbon source during stabilisation. The Reactor was operated with sludge age between 6-10 days and a hydraulic retention time (HRT) of one day for a period of 50 days. The Respirometric tests were then conducted with the stabilised sludge from the fill and draw reactor.

B. Respirometer System:

Respirometry tests were conducted by using a challenge AER-200 (challenge environmental systems, Inc., Faytteville, AR) aerobic respirometer system. Mohan et al. (2006) had also used the same respirometer to study the biodegradability of surfactants, Triton X-100 and Rhamnolipid. The set-up consists of four reaction vessels or reactors of 500 ml volume, a stirring base for mixing the samples, a pressurised oxygen cylinder for supplying oxygen, a cell base containing flow measuring cells, an interface module for data acquisition, and a computer. Teflon coated magnetic stirring bars with spinning rings were used for mixing the sample. Carbon dioxide absorption tubes were inserted into each reaction vessel. These tubes were usually filled with 5 ml of 30% KOH to trap CO_2 released from the reaction and care should be taken to prevent overflow from each absorption tube, which could potentially affect the pH in the reactor. The reaction vessels were then sealed with a screw cap having a butyl rubber septum. As the oxygen flows through each cell under the influence of vacuum caused by oxygen uptake, oxygen bubbles are formed in the flow measuring cells and these bubbles are detected by the detector unit. The bubbles are registered by the computer to produce a cumulative measure of oxygen uptake and oxygen uptake rate.

C. Analytical Parameters:

Measurement of pH, mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were measured according to standard methods (American Public Health Association et al, 1998). Initial and Final COD for the filtered samples were measured according to closed reflux-colorimetric method. Dissolved Oxygen (DO) was measured by using DO probe Thermo ORION.

III. RESULTS AND DISCUSSION

A. Stabilization Profiles of Activated Sludge:

The performance of the fill and draw reactor during the Aerobic sludge stabilization is given in figure 2. The pH of the reactor is maintained in the range of 7-8, to favour the active growth of the heterotrophic microorganisms. The variation of biomass is represented in fig. 2a. The Biomass concentration (MLSS and MLVSS) is increasing during each sludge retention time. At the end of each operation period some amount of sludge is wasted to remove the dead biomass which can also contribute to MLVSS. The MLVSS/MLSS ratio (fig.2b) is maintained in the range of 0.4-0.7 and the Sludge volume index; SVI is maintained in the range of 50 to 80 indicating the reactor is operated efficiently during stabilisation without any bulking activity. Fig.2c depicts the variation of Initial and final COD. The percentage COD removal (Fig.2d) is increasing with increase in biomass concentration and is mainly due to the formation of compact aerobic granules during stabilization.

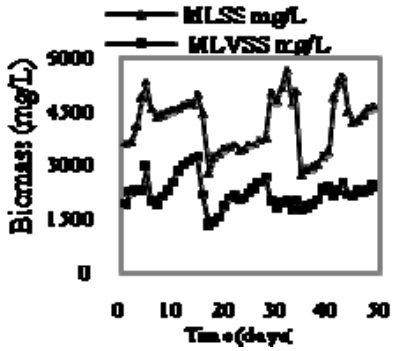

Fig. 2a. Variation of biomass

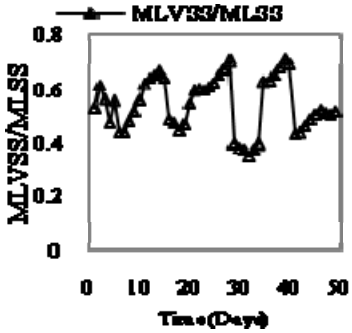

Fig. 2b. MLVSS/MLSS

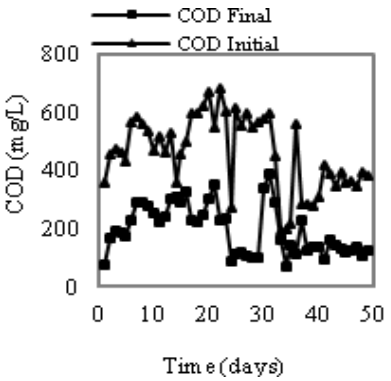

Fig. 2c. Initial and final COD

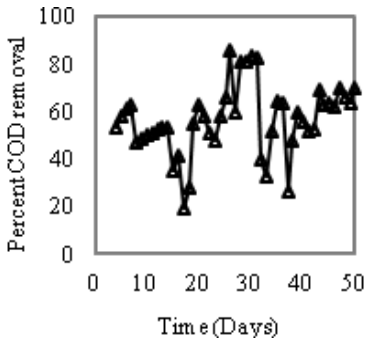

Fig. 2d. COD Removal efficiency

Figure 2: The performance of the Fill and Draw Reactor during aerobic sludge stabilization

B. Respirometer Response with the Phenol Condensation Product:

Figure 3 shows Respirograms for both the oxygen uptake profile (fig. 3a) and oxygen uptake rate profile (fig.3b) during the aerobic biodegradation of phenol condensation product with the 50, 100, 150 and 200mg/L concentrations. From the figure 3a it can be observed that oxygen uptake curves shows lag phase of 4hrs representing the acclimatization time. Increase in oxygen uptake at 50 mg/L concentration is above that for the control indicates lack of inhibition on respiration activity, whereas a decrease in oxygen uptake relative to control was observed at 100 mg/L concentration indicating potential toxic effect on respiration.

The oxygen uptake rate curve at 50 mg/L syntan concentration is above that for the control and that for 100mg/l is below that for the control as shown in figure 3b. The oxygen uptake rate is 60 mg/L h with the 50 mg/L syntan 1 concentration and 12 mg/L h with the 100 mg/L concentration.

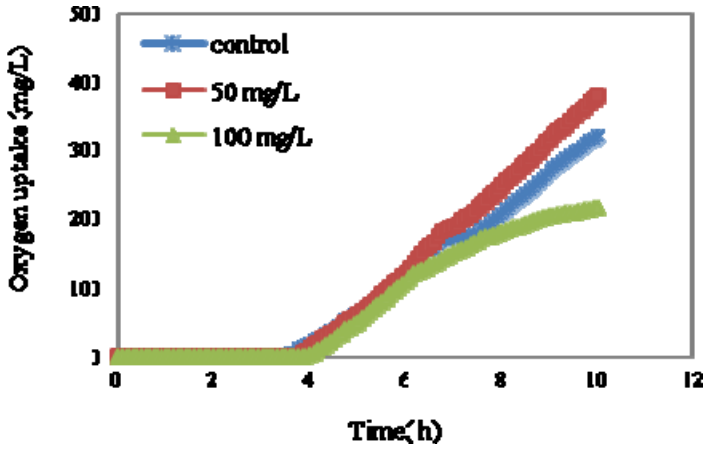

Fig. 3a. Oxygen uptake profile

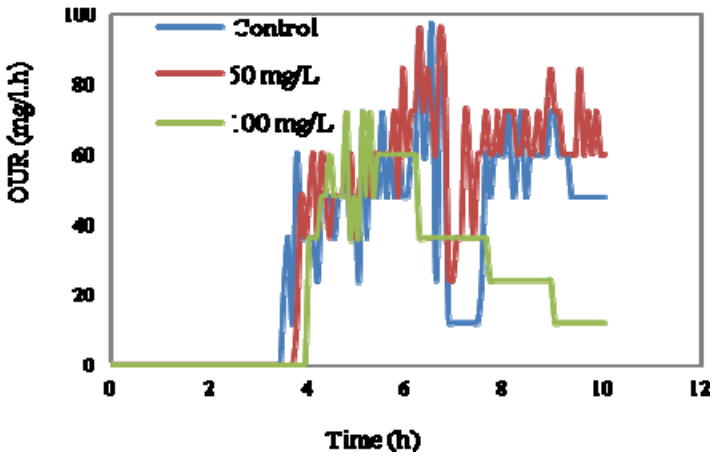

Fig. 3b. OUR profile

Figure 3: Respirograms of mixed liquor with phenol condensed product concentrations 50 and 100m g/L

Respirograms of mixed liquor with concentrations 150 and 200mg/L were depicted in figure 4. A further decrease in oxygen uptake (fig.4a) and OUR (fig.4b) were also observed with an increase in syntan concentration from 150 to 200mg/L is mainly due to the potential inhibition effect on respiration which in turn is related to the low rates of biodegradability.

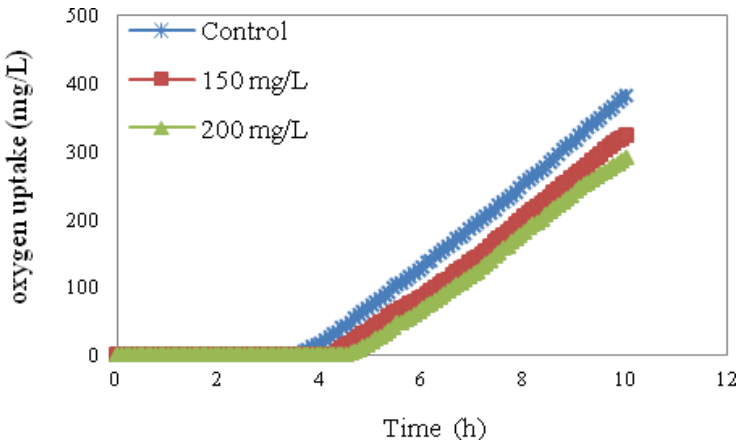

Fig. 4a. Oxygen uptake profile

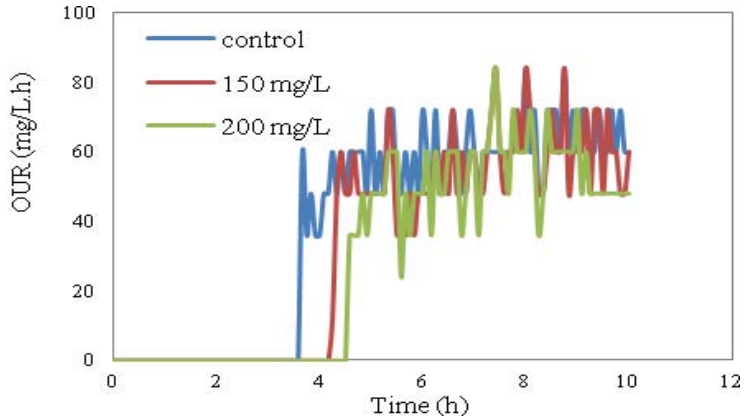

Fig. 4b. OUR profile

Figure 4: Respirograms of mixed liquor with phenol condensed product concentrations 150 and 200 mg/L

A decrease in COD removal with an increase in syntan concentration from 50 to 200 mg/L was observed in Table 1. A 10 hrs respirometry results in 17.6 % COD removal with the 50 mg/L syntan 1 concentration and 6.25, 2.5, 2 % with the concentrations 100, 150, 200mg/L respectively. This can be

hypothesised that lack of toxicity or high rates of biodegradability with the 50mg/L phenol condensation product dose and low rates of biodegradability or toxic impact with the increased doses.

TABLE 1. MEASURED CHARACTERISTICS OF COD REMOVAL WITH THE PHENOL CONDENSATION PRODUCT

Concentration	Initial COD(mg/L)	Final COD(mg/L)	% COD removal
50 mg/L	170	140	17.6
100 mg/L	320	300	6.25
150 mg/L	400	390	2.5
200 mg/L	510	500	2

C. Respirometer Response with the Nitrogen Containing Resin:

The Respirograms of mixed liquor with the nitrogen containing resin concentrations 50 and 100mg/L was illustrated in figure 5. The oxygen uptake profile (fig.5a) and OUR profile (fig.5b) showed a long lag phase of 5 hrs representing the increased acclimatisation time. The oxygen uptake at concentrations 50 and 100 mg/L is below that for the control indicate the toxicity of the test compound on the oxygen uptake by the biomass. At the end of 10 hrs the oxygen uptake rate is 36 mg/L h with 50mg/L syntan concentration and 24 mg/L h with the 100 mg/L concentration.

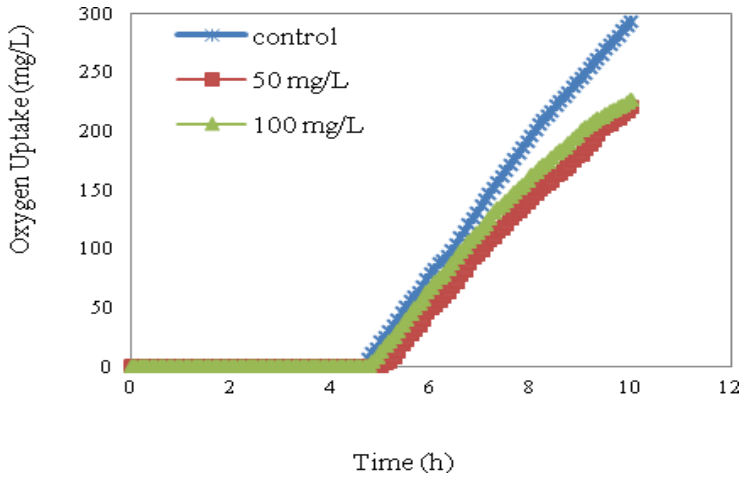

Fig. 5a. Oxygen uptake profile

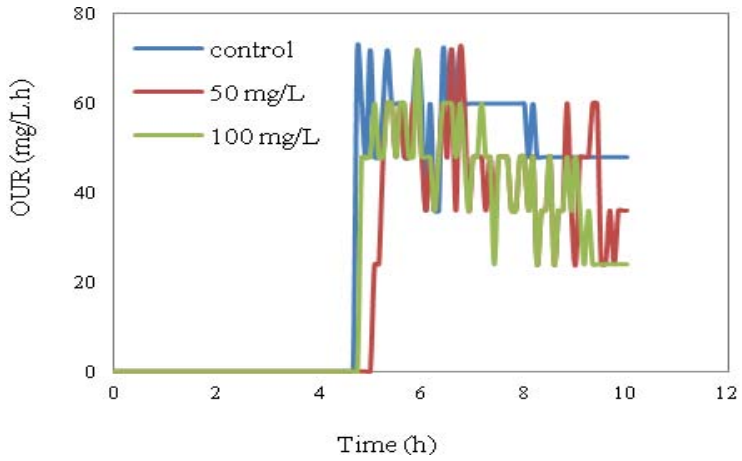

Fig. 5b. OUR profile

Figure 5: Respirograms of mixed liquor with nitrogen containing resin concentrations 50 and 100m g/L

Figure 6 shows the Respirograms of the mixed liquor with the syntan concentrations 150 and 200mg/L .In this case, on the contrary, a long lag phase of 6.5 hrs was observed and is mainly due to the increased toxic effect with an increase in syntan concentration. At the end of 10 hrs the oxygen uptake rate is 48 mg/L h with 150mg/L syntan concentration and 24 mg/L h with the 200 mg/L concentration indicate potential toxic impact or very low rates of biodegradability.

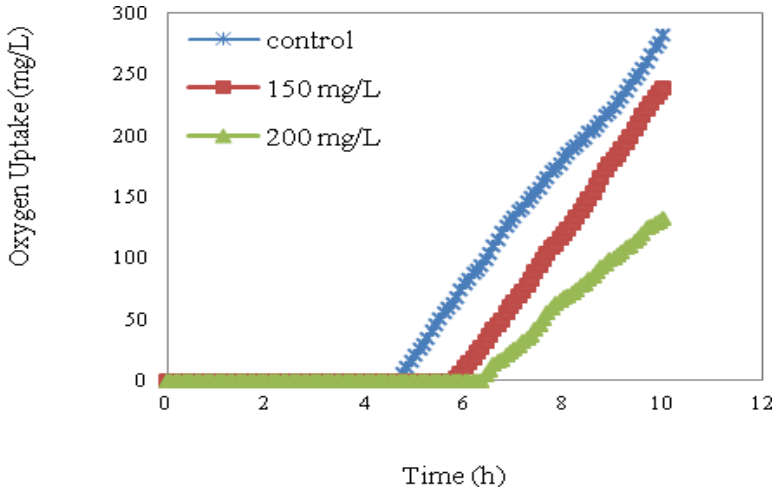

Fig.6a. Oxygen uptake profile

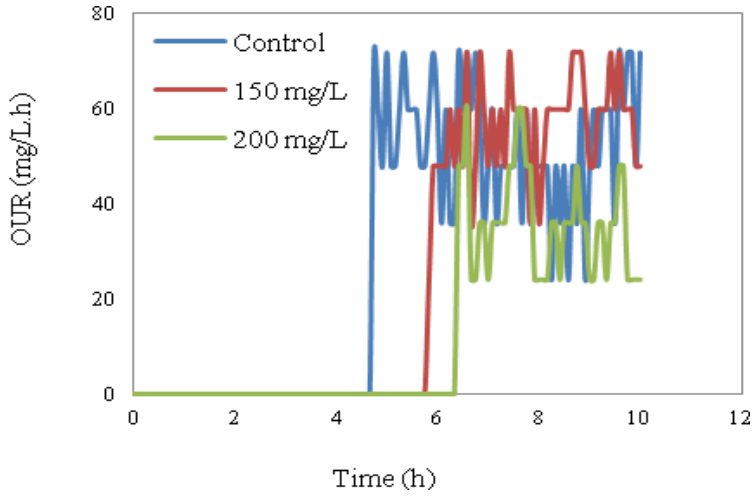

Fig. 6b. OUR profile

Figure 6: Respirograms of mixed liquor with nitrogen containing resin concentrations 150 and 200m g/L

The COD removal efficiency of nitrogen containing resin was given in the table 2.In this case also, a decrease in COD removal with an increase in syntan concentration from 50 to 200mg/L was observed. But a very low % COD removal was found to be 5, 4.7, 1.5 and 0.1 at concentrations 50, 100, 150 and 200 mg/L respectively. This shows the low rates of biodegradability of syntan.

TABLE 2. MEASURED CHARACTERISTICS OF COD REMOVAL WITH THE NITROGEN CONTAINING RESIN

Concentration	Initial COD(mg/L)	Final COD(mg/L)	% COD removal
50 mg/L	80	76	5
100 mg/L	82.9	79	4.7
150 mg/L	131.9	129.8	1.5
200 mg/L	138.05	137.9	0.1

IV. CONCLUSION

Respirometric method for biodegradability assessment of two synthetic tanning agents was proposed and evaluated. It was based on comparison of oxygen uptake rate curves with the control and COD removal measurement. The method was shown to be able to detect biodegradability and inhibition effect of syntans on the oxygen uptake rate.

The Respirometry showed that phenol condensation product was biodegradable up to 50mg/L. The biodegradability was inhibited as the concentration of phenol condensed product increased from 100 to 200mg/L. But studies with nitrogen containing resin showed low oxygen uptake rates and very low COD removals as well, indicating the inhibition effect on the biodegradability. The results reported in this paper

pertain to short term experiments in the order of 10hrs conducted with mixed cultures. It is perceivable that with the increased experimental time may exhibit different biodegradation capabilities.

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