Kinetic studies on biodegradation of tannery wastewater in a sequential batch bioreactor

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In this study, the performance of a bench scale aerobic sequencing batch reactor (SBR) was investigated for the treatment of tannery wastewater. Mixed culture obtained from the activated sludge process treating tannery wastewater was used in the reactor. SBR was operated at different operating conditions by changing the hydraulic retention time (HRT- 5 – 2 days) and initial substrate concentration (6240mgCOD/L, 4680 mgCOD/L, 3220 mgCOD/L and 1560 mgCOD/L). From the results it was found that a maximum reduction in COD and colour were found to be 79% and 51% respectively. In this study, first order and diffusional models are used to describe the kinetics of the degradation of tannery wastewater in SBR. The model parameters were calculated. From the R^2 value calculated the first order model fits the data well.

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Introduction

During tanning process at least about 300 kg chemicals are added per ton of hides [1]. Due to the variety of chemicals added at different stages of processing of hides and skins, the wastewater has complex characteristics. The tanning process and the effluents generated have already been reported in the literature [2-4]. Tanning industry also has one of the highest toxic intensity per unit of output [5]. 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 [6]. Major problems are due to wastewater containing heavy metals, toxic chemicals, chloride, lime with high dissolved and suspended salts and other pollutants [7].

The processes used most frequently for biological treatment of tannery wastewater in CETPs in India are the activated sludge process (ASP) and the upflow anaerobic sludge blanket (UASB) process [8-10]. Biodegradation of tannery wastewater using activated sludge process has been reported by many research workers [8, 11-13]. Several works have been carried out on tannery wastewater treatment using different reactors [14-18].

Sequencing batch reactor 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 [19, 20]. It is known to be a robust system that stands harsh conditions and often been used in order to treat the wastewater from industries [21]. The main advantages are easy operation, low cost, handling hydraulic fluctuation, no need for settling tank and sludge recycling as well as organic load without any significant variation in removal efficiency [22, 23]. The SBR process operates in a series of timed steps, reaction and settling can occur in the same tank, eliminating the need for a final clarifier [24]. The objective of this study is to treat the tannery wastewater in a SBR by varying the hydraulic retention time and initial substrate concentration for the maximum COD and color removal.

Materials and methods

Substrate

The tannery effluent and the seed sludge were collected from the Ranipet Tannery Effluent Treatment Co. Ltd., V. C. Mottur, Walajah, South India and used as an influent for the bioreactor during the experimental period.

Experimental setup

Two identical laboratory-scale plexiglass reactors, each with a total volume of 10 L, were used. Tubes were inserted into the reactors to ensure the filling and withdrawal of the effluent using peristaltic pumps. The reactors were supplied with oxygen by fine bubble air diffuser. The operating conditions in the reactors were maintained at the temperature of 30^{o}C and pH of 7 [25]. The mixing inside the reactors was achieved with a mechanical stirrer at the speed of 150 rpm. A schematic diagram of the experimental setup is shown in Figure 1. Each cycle lasted for 24h: the filling in 1 hr, the reaction took place in 20 hr, the settling in 2 hr, the withdrawal in 0.75 hr and the idle in 0.25 hr as prescribed in Figure 2.

The reactors were operated for 50 days for various initial concentration of 6240 mg COD/L, 4680 mg COD/L, 3220 mg COD/L and 1560 mg COD/L at different OLR, initially 2 kg COD/m^{3}day for 15 days followed by 2.5 kg COD/m^3 from the day of 16-31, 3.3 kg COD/m^3 from the day of 32-40 and finally 5 kg COD/m^3 until the end of the experiment. Consequently the hydraulic retention times in the reactors were maintained as 5, 4, 3, and 2 days. COD was analyzed by APHA's standard methods for the examination of water and wastewater. Color reduction was analyzed by the method suggested by Bajpai et al (1993) [26]. In this method, sample was centrifuged at 10,000 rev/min for 30 min and the pH was adjusted to 7.6. The absorbance was measured at 465 nm and transformed into color units.

Results and discussion

Tannery wastewater was characterized by the parameters like biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS) and total dissolved solids (TDS), chromium and sulfides etc. Typical characteristics of tannery wastewater were reported in our earlier article [25].

COD and Color reduction

In a SBR, COD removal efficiency and color reduction using the mixed culture obtained from the secondary sludge of tanneries were studied. The initial substrate concentration was varied to give approximately 6240 mgCOD/L, 4680 mg COD/L, 3220 mg COD/L and 1560 mg COD/L. The influent and effluent concentration of the reactor and percentage COD and color reduction for the initial COD 6240 mg/L was shown in Figure 3. At the initial stage the HRT of the reactor was maintained at 5 days with an organic loading rate of 2 kg COD/m^{3}d. At this stage, the percentage COD reduction is found to be low due to the fact that microbes need longer time for acclimatization. From the figure, it is observed that the maximum COD reduction of 66.5% and the color removal of 40% occur at the fifteenth day from the startup period.

The effect of organic loading rate (OLR) is investigated by varying HRT while maintaining the concentration of the influent constant. The HRT was varied from 5 days to 2 days. Organic loading rate is increased from 2 kg COD/m^{3}d to 5 kg COD/m^{3}d by reducing the hydraulic retention time from 5 days to 4 days with an organic loading rate of 2.5 kg COD/m^{3}d on sixteenth day and the reactor performance is monitored regularly by measuring effluent COD from the reactor. The influent COD concentration is maintained at an average concentration of 6240 mg COD/L from the beginning. The reactor reached steady state within sixteen days of operation and the

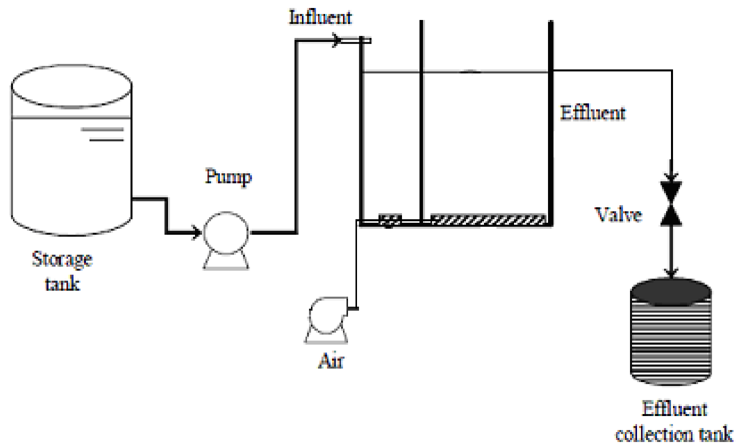

Figure 1. Schematic of sequential batch reactor

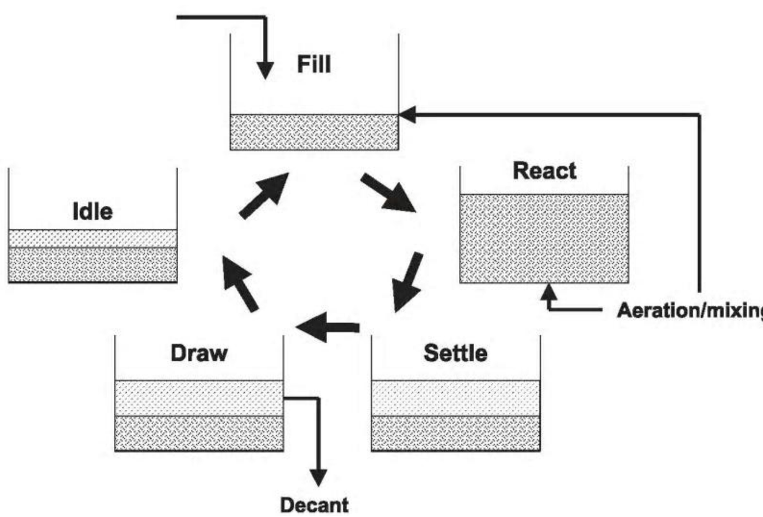

Figure 2. Operation of SBR in cycle

reduction in COD and color were found to be 64.8% and 35%.

After reaching the steady state, the organic loading rate is increased from 2.5 kg COD/m^3d to 3.3 kg COD/m^3d by reducing the hydraulic retention time to 3 days and the performance was noted. After nine days of operation the maximum percentage COD and color reduction is found to be 63% and 33%.

Then the organic loading rate is increased from 3.3 kg COD/m^3d to 5 kg COD/m^3d by decreasing the HRT from 3 days to 2 days. From the figure it was observed that a maximum degradation of COD and color was found to be 50% and 25%. Although there is an instantaneous increase in the organic loading rate while decreasing the HRT, a low effluent COD level is recovered in a short period of time. With decrease in HRT the percentage COD reduction is also found to decrease. However a significant drop in percentage COD and color reduction occurs for the HRT between 3 and 2 days. It is also seen that there is no significant improvement in the degradation of organic matter and color above

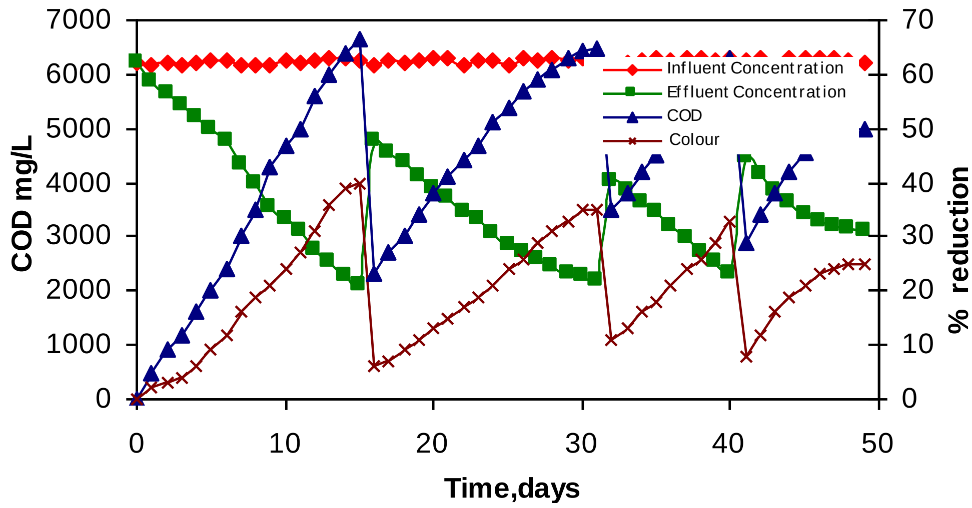

Figure 3. COD and color reduction profile in a SBR at an initial concentration of 6240 mg/L

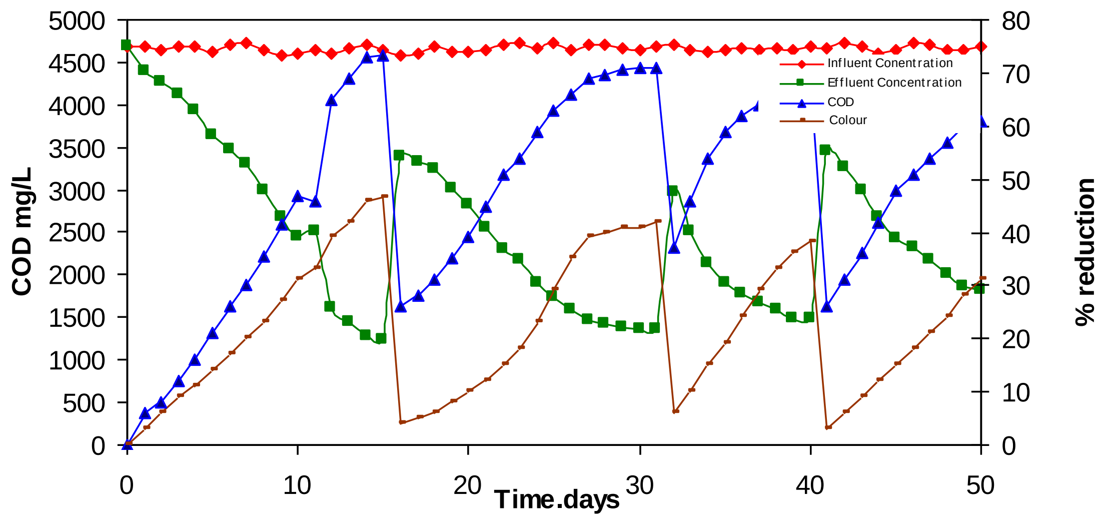

Figure 4. COD and color reduction profile in a SBR at an initial concentration of 4680 mg/L

3 days. The same trend is obtained for the influent concentration of 4680 mg COD/L, 3220 mg COD/L and 1560 mg COD/L. This is clearly depicted in Figures 4-6. The maximum COD and color removal were reported in Table 1.

Kinetics and modeling

First order model

The first order model is given by

$$-\frac{dC_s}{dt} = k_1 C_s$$

On integration between known limits, the model can be written as

$$\ln\left(\frac{C_s}{C_{so}}\right) = -k_1 t$$

Where

C_{so} - Initial substrate concentration, mg COD/L

Cs – Substrate concentration, mg COD/L

t - Degradation time, h

k_1 – First order rate constant, h^{-1}

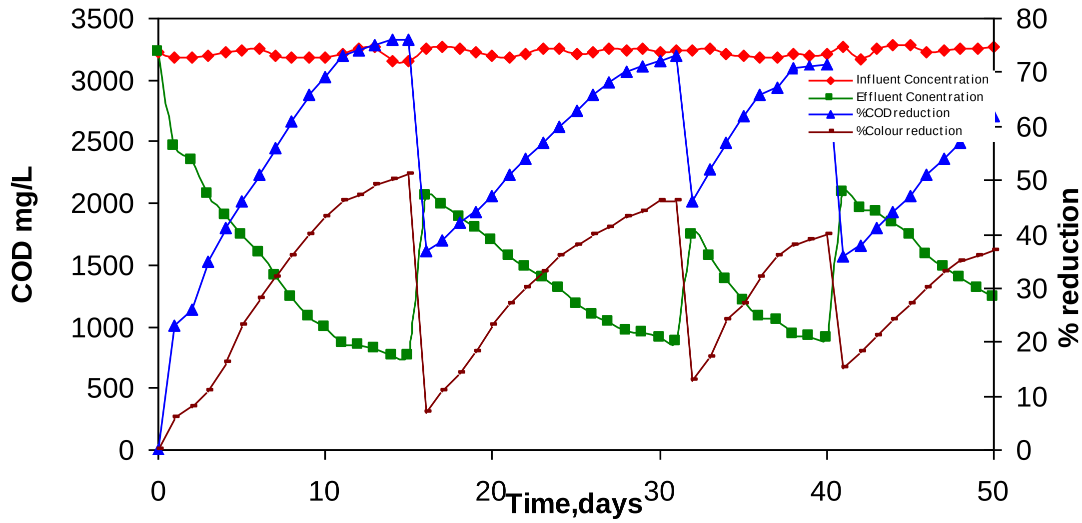

Figure 5. COD and color reduction profile in a SBR at an initial concentration of 3220 mg/L

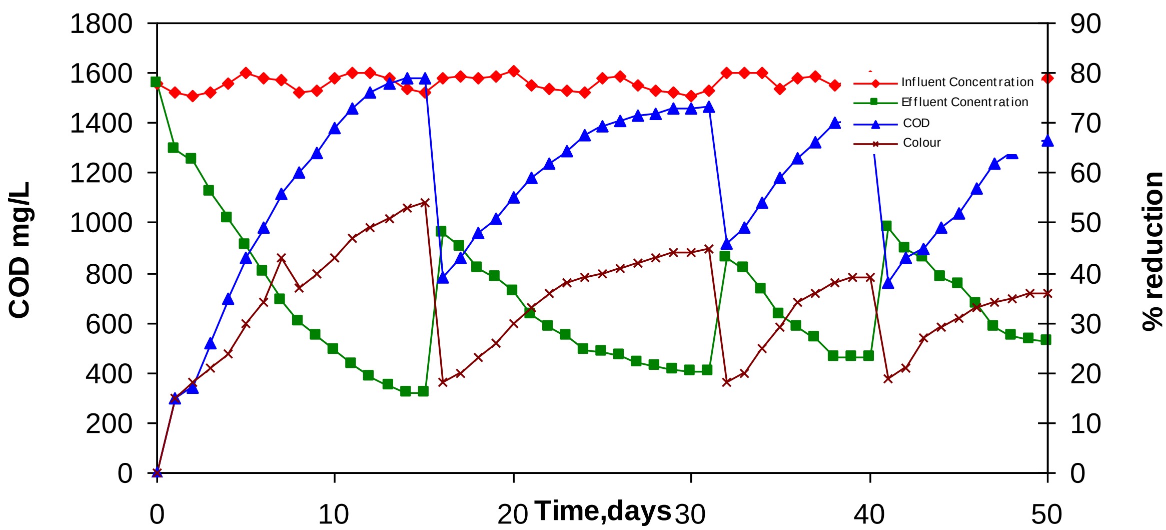

Figure 6. COD and colour reduction profile in a SBR at an initial concentration of 1560 mg/L

Table 1. Removal efficiency of COD and colour at various conditions in a SBR

HRT (days)	SBR performance with mixed culture							
	% COD Reduction				% colour reduction			
	6240 mg/L	4680 mg/L	3220 mg/L	1560 mg/L	6240 mg/L	4680 mg/L	3220 mg/L	1560 mg/L
5	66.5	73.4	76.0	79.0	40.0	46.4	51.0	54.0
4	64.8	71.0	73.0	78.4	36.0	42.0	46.0	45.0
3	63.0	68.4	71.6	73.8	33.0	38.0	40.0	39.0
2	50.0	61.0	62.0	66.5	25.0	31.0	35.0	36.0

Table 2. Kinetic parameter values for the degradation of tannery wastewater in SBR

Kinetic Model	HRT, Days	Average Initial Substrate Concentration, mg/L			
		1560	3220	4680	6240
First Order Model	5	0.1436	0.1231	0.1128	0.0971
	4	0.1204	0.1147	0.1056	0.0836
k_1, h^{-1}	3	0.2249	0.1932	0.1908	0.1735
	2	0.0942	0.1196	0.1392	0.1542
	5	0.9568	0.9519	0.9177	0.9124
R^2	4	0.9602	0.9698	0.9017	0.8999
	3	0.9195	0.9012	0.8999	0.9000
	2	0.9112	0.9001	0.9002	0.9003
Diffusional Model	5	1.9153	2.5098	2.8512	2.9583
	4	1.6781	2.3566	2.6862	2.6097
k_D,mgCOD$^{0.5}$/L$^{0.5}$h	3	3.1236	4.0354	4.8516	5.2667
	2	2.3262	3.0913	3.2952	3.1495
	5	0.9055	0.8506	0.6535	0.7092
R^2	4	0.8628	0.8625	0.5835	0.493
	3	0.2292	0.5196	0.0015	0.0001
	2	0.0754	0.3972	0.0438	0.3017

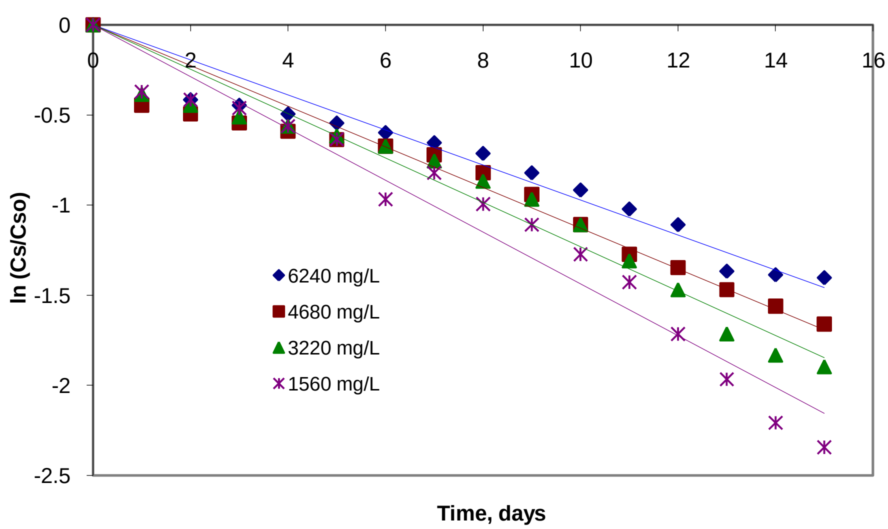

Figure 7. First order model in continuous degradation kinetics for the HRT 5 days

The experimental data is compared with the values predicted by first order model. The first order rate constant, k_1 was calculated from the slope of the straight line by the least square (LSQ) fit. The rate constants and the determination coefficient (R^2) are presented in Table 2. As the initial concentration of substrate increases, the rate constant k_1 decreases. This can be described to a growing importance of the recalcitrant fraction in reducing the diffusivity of the biodegradable substance. This is in confirmation with the results of Coverti *et*

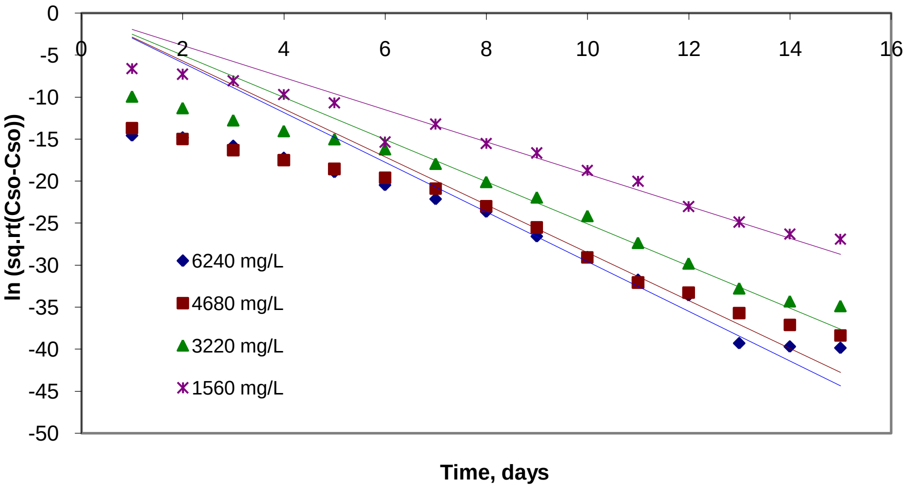

Figure 8. Diffusional model in continuous degradation kinetics for the HRT 5 days

al [27]. The satisfactory values of R^2 compliment the ability of the first order model in describing the kinetics of the present work. The determination coefficient (R^2) is defined as the ratio of explained variance to the total variance. Figure 7 shows the fit of the model for the experimental data when the HRT is 5 days. (Figure is not given for other HRT's)

Diffusional model

The Diffusional model is given by

$$-\frac{dC_s}{dt} = k_D C_s^{0.5}$$

When integrated between the known limits, the above equation becomes

$$\sqrt{C_s} - \sqrt{C_{so}} = -\frac{k_D}{2}t$$

Where k_D = Rate constant for Diffusional model

From the experimental data, the diffusional model rate constant k_D was determined through the LSQ fitting. From the R^2 values it was found that the diffusional model fails to represent the experimental data. This is clearly depicted in Figure 8.

Conclusions

The continuous degradation of tannery wastewater was carried out in a sequential batch reactor using mixed culture obtained from the tannery sludge. The parameters varied are initial substrate concentration, hydraulic retention time and organic loading rate. The performance of the system proved that the reduction in COD (79%) and color (51%) was high in SBR. Decrease in HRT leads to decrease in the percentage COD and color reduction. However significant drops in percentage COD and color reduction occurs for the HRT between 3 and 2 days. It is also observed that there is no significant improvement in the degradation of organic matter above 3 days. From the kinetic studies, it was found that the degradation of tannery wastewater in SBR follows first order model. This study shows the feasibility of treating a tannery wastewater in a SBR using sludge obtained from tannery wastewater treatment plant.

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