Degradation of tannery waste water by SBR using salt tolerant microorganisms with wheat bran sorbent

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Abstract
Sequencing batch reactor is a type of activated process operated by a fill and draw manner which has been successfully used to treat municipal and industrial wastewater because of its simple configuration. In this study, tannery waste water was treated by SBR using salt tolerant microorganisms and the influence of sorbent addition on the performance of SBR was investigated. Wheat bran was added (10g/L) as sorbent. The initial substrate concentration was varied to give approximately 1560 mg COD/L, 3120 mg COD/L, 4680 mg COD/L and 6240 mg COD/L. The results showed the variation of COD removal efficiency with sorbent for the initial COD concentration of 1560 mg COD/L as 86.0% for the HRT of 5 days with an organic loading rate of 0.312 kgCOD/m^{3}d.Then OLR was increased to 0.390 kgCOD/m^{3}d, 0.520 kgCOD/m^{3}d and 0.780 kgCOD/m^{3}d by decreasing the HRT to 4, 3 and 2 days.

Consequently, COD reduction was found to be 82.50%, 78.2% and 71.60%. Similar trend was obtained for the influent concentration of 3120 mg COD/L, 4680 mg COD/L and 6240 mg COD/L. From the results it was observed that the addition of sorbent increases the COD removal efficiency for all the initial COD concentrations.

Keywords: SBR, Tannery waste water, Salt tolerant microorganisms, HRT and OLR.

Introduction

Sequencing batch reactor is an activated sludge process in which entire operations are carried out by time sequence in a single basin rather than space sequence in separate tanks as such in conventional activated sludge (CAS) system[1]. Study on SBR was conducted at the University of Notre Dame[2] in spite of substantial attention given to SBR from 1971. Process operation and performance have been thoroughly described by Irvine et al.[3-5]

They are uniquely suited for wastewater treatment applications characterized by low or intermittent flow conditions of 0 to 5 mgd[6]. Small - size structure, operating by flexible modes, minimum manufacturing and operation costs and simultaneous removal of phosphorous and nitrogen are the main advantages of using SBR. The different types of waste waters have been treated by SBR including wastewater from industrial and domestic sources, removal of phosphorous and nitrogen and landfill leachate etc. SBR process has been used by several researchers for the treatment of different waste water[7-12] including various heavy metals and contamination of both biodegradable and non-biodegradable wastes. Many researchers studied sequencing batch reactor process for both biodegradable and non-biodegradable contamination and also for treatment of wastewater containing different types of heavy metals. Sequencing batch reactors (SBR) were mainly incorporated for COD removal from wastewaters[13, 14].

Waste water is generated during tanning process by soaking salt-laden skins and hides in fresh water for removing excess salt causing excess salinity. Many conventional processes were carried out for tannery industry wastewater including biological process[15], oxidation process[16] and chemical process[17] etc. Aerobic or anaerobic biological treatment process by bacteria produces the inorganic substances which are harmless in nature by decomposition of waste. ASP (Activated sludge process) [19] and UASB (upflow anaerobic sludge blanket) are the commonly used biological process for the waste water in tanneries[18]. Energy-intensive and low cost are the main reasons for using ASP in the operation and maintenance point of view.

The presence of high salinity in the range of 1–10% NaCl by wt hinders biological treatment methods[20]. However dissolved organics of tannery waste water can be effectively degraded by the salt tolerant microbes of varying saline concentrations.

In this work, mixed salt tolerant microbes were employed for the treatment of wastewater produced in tanneries by SBR. Senthilkumar et al[21] tested the ability of these salt tolerant microorganisms for the degradation of tannery wastewater in a batch reactor under different salinity. In tannery wastewater treatment, various disturbances have been encountered in the growth of biomass and inhibition of nitrification. Combining pre- and post-treatment by physical/chemical methods with biological methods produces better results compared to the individual process. Report suggests that adsorption can remove the colour and metals efficiently[22].

Subramaniam et al[23] studied the COD removal from a slaughter house wastewater using combined anaerobic pond-sequencing batch reactor treatment and achieved more than 95% COD removal. Activated carbon could be used together with biological treatment processes for increasing the removal efficiency which could be utilized as the media for microorganisms in attached growth system. Wastewater can be treated in various conventional treatment methods and adsorption process is considered as effective and economical method[24].

Adsorption is a sludge-free process and it has a low investment to set up, which gives the cost-effective advantage compared to the other treatment methods[25]. Low-cost alternative adsorbents can be classified in two ways based of their availability and their nature[26]. FTIR analysis has been used as a useful tool to identify the presence of certain functional groups of the bioadsorbent.[27]

SBR performance can be enhanced by simultaneous biodegradation and adsorption processes with the addition of adsorbents during tannery waste water treatment. Sorbent addition has the following benefits over the conventional process:

- Enhanced COD and BOD removal efficiency
- Enhances the shock loads stability and toxic upsets
- Improvement toxic substances and priority pollutants removal
- Removal of colour effectively
- Enhancement of the settling and dewatering of sludge
- Suppression of stripping of volatile organics
- Less tendency to foam in aerator.

Material and Methods

All the chemicals used in this study are of the best quality and grade available. Double distilled water was used throughout the experimental work. Tannery wastewater was collected from Ranipet Tannery Effluent Treatment Co. Ltd., Walajah, South India. The combined wastewater was stored at 5°C in a freezer. The wastewater was analyzed in the laboratory for the parameters such as pH, total suspended solids (TSS), total dissolved solids (TDS), turbidity, alkalinity, BOD, COD, sulphide, total nitrogen (TN), ammonical nitrogen, chromium (Cr), total phosphate, total Kjeldahl nitrogen (TKN) based on Standard Methods of Analysis.[28] The wastewater was collected during different seasons and hence variation occurs in the characteristics of the tannery wastewater.

In general, tannery wastewater was basic, dark brown in colour and had a high content of organic substances varying according to the chemicals used. The tannery wastewater was characterized by substantial organic matter content and high SS content, resulting in total COD concentration of 6240 mg/L and SS concentration of 1150 mg/L. Very high salinity was reflected by TDS concentration of 12, 880 mg/L. TKN, $N\text{-}NH_3$ and PO_4^{3-} averaged 168, 115 and 21mg/L respectively.

The pH value of the wastewater was 7.7 which showed that the influent is characterized by high alkalinity content (3150 mg/L) due to the chemicals used in leather processing. Influent total N and COD concentrations were 827 mg/L and 6240 mg/L respectively whereas influent ammonical N was 115 mg/L. Sulfide and total chromium concentrations were 232 mg/L and 13.3 mg/L respectively during the process of feeding stages. It was also observed that tannery effluents were rich in nitrogen, especially organic nitrogen, but very poor in phosphorus. In addition to organic and nitrogen compounds, tannery wastewaters contain sulfide, chromium, which impart high antibacterial activity.

Seed Sludge: The seed sludge for the degradation in sequential batch reactor was brought from the secondary basin treating the tannery wastewater. It was also stored at 5°C in a freezer and used for batch and continuous study.

Salt Tolerant Microorganisms: The salt tolerant bacterias used in this work are *Pseudomonas aeruginosa*, *Bacillus flexus*, *Exiguobacterium homiense* and *Styphylococcus aureus*. They were obtained from Microbial Type Culture Collection Centre (MTCC), Chandigarh, India. Senthilkumar et al[21] used these salt tolerant organisms for the treatment of tanning industrial wastewater in a batch reactor and found that they are efficient for the degradation process. Hence these organisms were used to treat the leather industrial wastewater in a SBR. At aseptic conditions, frozen cultures of pure salt tolerant bacterial microbes were stored in agar slants and inoculated on 5 ml nutrient broth media. Orbitary shaker (Remi, India) was used for the incubation of broth at 150 rpm and 37°C for 24 h. Well-grown culture suspensions of uniform concentration were used as sources of inoculum for all the experiments.

Sorbent: In this study, 21 various sorbents were screened for degradation of tannery wastewater using Plackett-Burman design. They are Enteromorpha prolifera, Hydrilla verticillata, Hypnea valentiae, Tamarind seed, Wheat bran, Rice husk, Paddy straw, Hardwood sawdust, Plant leaves, Turbinaria ornate, Press mud, Turninaria Conoids, Sugarcane baggasse, Cocnut Shell, Bamboo Waste, Grain Sorghum, Tamarin Wood, Sargassum Tennnrsinnum, Chlorella bulgaris, Synechocystis sp and Scenedesmus Obliquus. Among these sorbent, wheat bran was selected as a suitable sorbent based on the pareto chart and it was used for the further study in SBR.

Experimental Setup

Sequential Batch Reactor (SBR): Two laboratory-scale plexiglass reactors (SBR-1 and SBR-2), each with a total volume of 10L were used as reactor. The schematic diagram of the experimental set up is shown in fig. 1. Tubes were inserted into the reactors to carry out the inlet and outlet of the waste water using peristaltic pumps. Oxygen was supplied to the reactor by fine bubble air diffuser. The mixing inside the reactors was achieved with a mechanical stirrer at the speed of 150 rpm. Each cycle lasted for 24h: Filling - 1h, Reaction – 20h, Settling - 2h, Withdrawal - 0.75h and Idle - 0.25h. The reactor (SBR-1) was inoculated with the mixed consortia obtained from the sludge.[29]

Experimental Procedure: The reactor (SBR-1) was operated for various initial concentrations of 1560 mg COD/L, 3120 mg COD/L, 4680 mg COD/L and 6240 mg COD/L at different OLR. Initially an OLR of 0.319 kgCOD/m^3day was applied for 15 days. Then the OLR wa increased to 0.39 kgCOD/m^3 on 16^{th} day. From 32^{nd} day, the OLR was maintained at 0.52 kgCOD/m^3 till 40^{th} day. Finally, an OLR of 0.78 kgCOD/m^3 was applied until the end of the experiment. Consequently, the HRT in the reactor was maintained as 5, 4, 3 and 2 days. During the feeding (1 h) of tannery wastewater, the reactor has to be fully aerated. The aeration was then continued for another 20 h (react step: aeration).

Settle step (sedimentation) was achieved by shut down the reactor for 2 hours. Once the bio-sludge was completely settled, the supernatant had to be removed within 0.75 hr by decanting step and the system was ideally kept for 0.25 hours. The above operation was repeated by introducing the fresh tannery water. In idle step, the excess bio sludge was removed from the bottom of the reactor to maintain the stable bio-sludge concentration of the reactor. APHA's standard method was used for analyzing COD of waste water by operating the reactor for 50 days. From the Plackett-Burman design, it was found that the sorbent wheat bran was most effective for the degradation.

Performance of SBR using Salt tolerant micro organisms with Sorbent: In this study, the influence of sorbent addition on the performance of SBR was investigated. Wheat bran was added (10g/L) as sorbent. The initial substrate concentration was varied to give approximately 1560 mg COD/L, 3120 mg COD/L, 4680 mg COD/L and 6240 mg COD/L and the results are given in table 1.

The variation of COD removal efficiency with sorbent for the initial COD concentration of 1560 mg COD/L is shown in fig. 2. During the initial concentration of 1560 mg COD/L, the COD removal efficiency was found to be 86.0% for the HRT of 5 days with an organic loading rate of 0.312 kgCOD/m^3d. Then OLR was increased from 0.312 kgCOD/m^3d to 0.390 kgCOD/m^3d by reducing the HRT from 5 days to 4 days. On sixteenth day, the reactor performance was measured continuously by determining effluent COD from the reactor.

It was observed that a maximum COD reduction of 82.50% was obtained. After reaching the steady state, the OLR was increased from 0.390 kgCOD/m^3d to 0.520 kgCOD/m^3d by reducing the HRT to 3d and the performance was noted. After nine days of operation, the maximum percentage COD removal was 78.2%.

OLR was increased from 0.520 kgCOD/m^3d to 0.780 kgCOD/m^3d by decreasing the HRT from 3 days to 2 days. At this stage it was observed that a maximum degradation of COD was found to be 71.60%. Even though decrease in HRT causes instantaneous increase in OLR, a low effluent COD level was recovered in a short period of time. COD reduction was found to decrease with decrease in HRT. However, a major reduction of these parameters occurs for the HRT between 3 days and 2 days. It was also seen that there was no significant improvement in the degradation above 3 days.

Similar trend was obtained for the influent concentration of 3120 mg COD/L, 4680 mg COD/L and 6240 mg COD/L. This was shown in figs. 2 to 5. From the results it was observed that sorbent addition significantly increases the COD removal efficiency for all the initial COD concentrations.

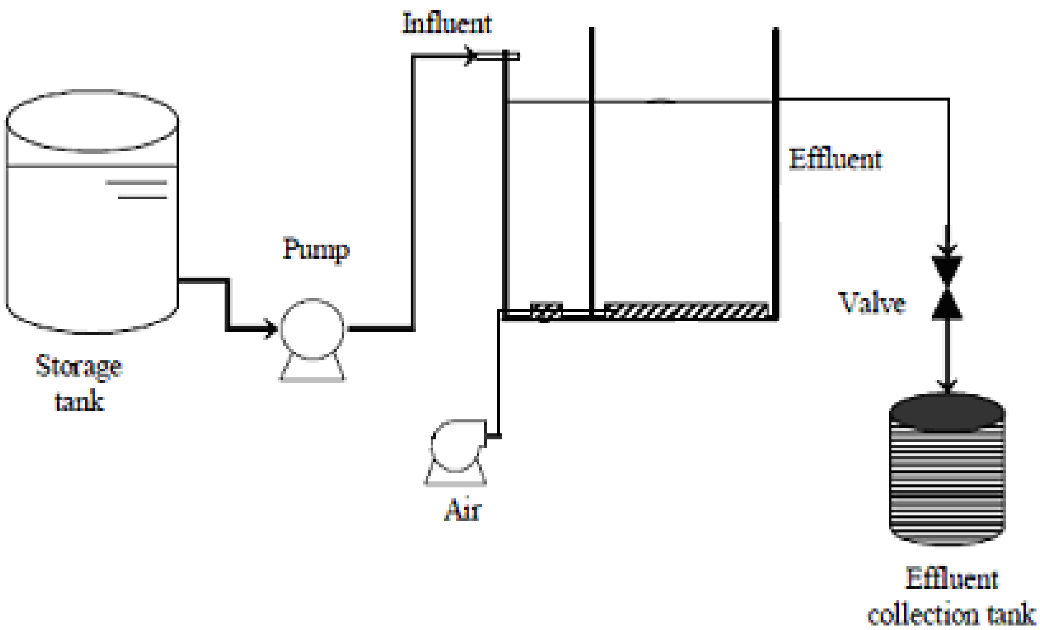

Fig. 1: Scheme of sequential batch Reactor set up

Table 1
Performance of SBR using Salt tolerant micro organisms with Sorbent

Substrate Concentration, mg COD/L	HRT, d	OLR, $KgCOD/m^3.d$	%COD Reduction STMS
1560	5	0.312	94.20
	4	0.390	91.50
	3	0.520	89.00
	2	0.780	82.50
3120	5	0.644	88.35
	4	0.805	85.12
	3	1.070	83.00
	2	1.610	76.00
4680	5	0.936	86.75
	4	1.170	83.58
	3	1.560	80.15
	2	2.340	73.10
6240	5	1.308	78.50
	4	1.635	77.25
	3	2.180	74.10
	2	3.270	62.00

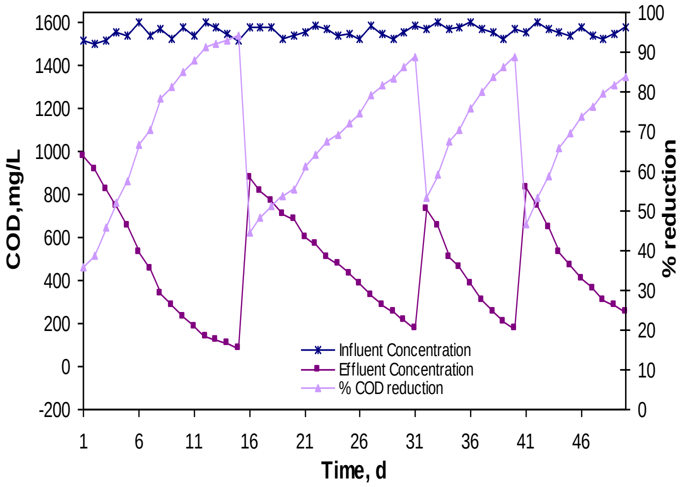

Fig. 2: Performance of SBR in treating tannery wastewater using STMS – 1560 mg COD/L

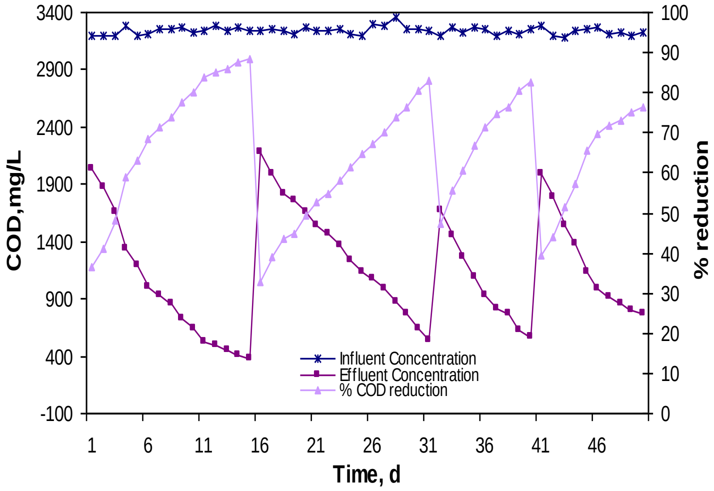

Fig. 3: Performance of SBR in treating tannery wastewater using STMS - 3120 mg COD/L

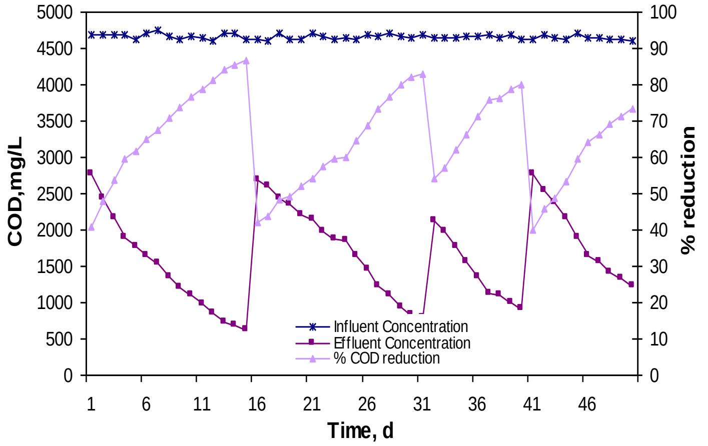

Fig. 4: Performance of SBR in treating tannery wastewater using STMS - 4680 mgCOD/L

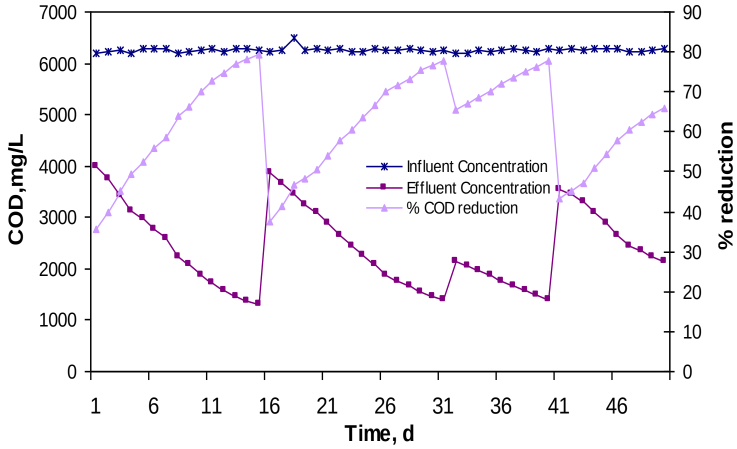

Fig. 5: Performance of SBR in treating tannery waste water using STMS -6240 mg COD/L

Effect of HRT on COD reduction: HRT, one of the vital operating parameters to be optimized in continuous degradation study, was varied in the range of 5 days to 2days. From fig. 6, it was inferred that at high HRT, the degradation was found to be maximum irrespective of microorganisms and initial substrate concentration. When HRT was reduced, the percentage COD reduction was also reduced, but the significant drop in reduction occurs when the HRT was reduced from 3d to 2d for all the cases. For lower and higher initial concentrations, the optimal HRT for better percentage COD removal efficiency was found to be 3 days.

Effect of Organic Loading Rate on COD reduction: Figure 7 shows the relationship between the organic loading rate and the COD removal efficiency for overall performance of the reactor. During the initial stages, at low organic loading rate, the removal efficiency was found to be high (over 90 %).

It was also observed that SBR has an excellent ability to overcome sudden disturbance in input organic loading. Some immediate decrease in COD removal efficiency was followed, but the high removal efficiency was recovered in a short period of time. In the figure 7, for the same organic loading rate, a difference in percentage COD reduction was observed and it was due to the fact that the reactor was operated at different initial substrate concentrations.

Kinetic Modeling of Continuous Study: The biodegradation kinetics was studied for the continuous degradation of tannery wastewater at different initial substrate concentration and various hydraulic retention times. The experimental data obtained from SBR were used to fit the first order and diffusional model.

First Order Model: The experimental data was 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 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 al.[30] 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) was defined as the ratio of explained variance to the total variance. Figs. 8-11 show the fit of the model for the experimental data obtained at various HRT's for different initial substrate concentrations.

Diffusional Model: The experimental data obtained from the SBR were represented by the diffusional model in figs. 12-15. The kinetic rate constants and R^2 values obtained from the graph are shown in table 2. The lower values of R^2 and the values of kinetic constant imply the inadequacy of diffusional model for the degradation process under consideration. 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 figs. 12-15.

Conclusion

The treatment of tannery industry wastewater was carried out in a sequential batch reactor with the addition of wheat bran as sorbent along with the salt tolerant microorganisms namely *Pseudomonas aeruginosa*, *Bacillus flexus*, *Exiguobacterium homiense* and *Styphylococcus aureus*. The results showed that this treatment to be an efficient biological process, producing low COD effluent under optimum aeration and HRT's for all the initial substrate concentrations. It was observed that the addition of wheat bran sorbent increases degradation efficiency.

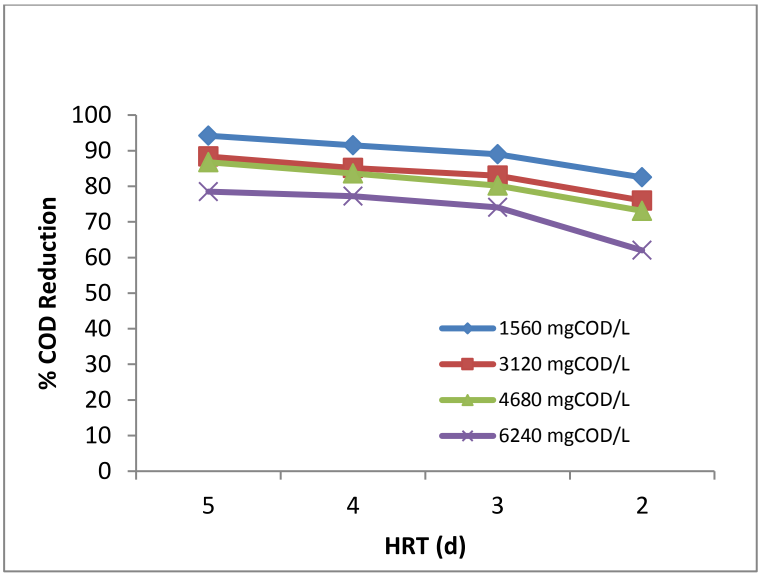

Fig. 6: Effect of HRT on COD reduction on addition of sorbent

Table 2
Kinetic parameter values for the degradation of tannery wastewater in SBR using mixed culture with sorbent

kinetic Model	HRT, d	Average Initial Substrate Concentration, mg COD/L			
		1560	3120	4680	6240
First Order Model	5	0.8121	0.0975	0.0926	0.074
k_1, h^{-1}	4	0.1114	0.1017	0.0956	0.0839
	3	0.1583	0.1512	0.1351	0.1313
	2	0.1409	0.1304	0.1060	0.0885
R^2	5	0.8981	0.9234	0.9628	0.9543
	4	0.9298	0.8998	0.9118	0.9364
	3	0.9057	0.9200	0.9412	0.9019
	2	0.8977	0.9421	0.8936	0.9413
Diffusional Model	5	-2.8126	-3.9600	-4.7654	-4.7762
k_D,$mgCOD^{0.5}/L^{0.5}h$	4	-3.1708	-4.3098	-4.9330	-5.1966
	3	-4.7628	-6.5650	-7.2106	-8.462
	2	-4.2600	-5.7672	-5.8824	-6.0034
R^2	5	0.9021	0.8432	0.8345	0.9000
	4	0.5478	0.4928	0.7732	0.5969
	3	0.5276	0.5326	0.7002	0.4164
	2	0.3868	0.1146	0.7945	0.2801

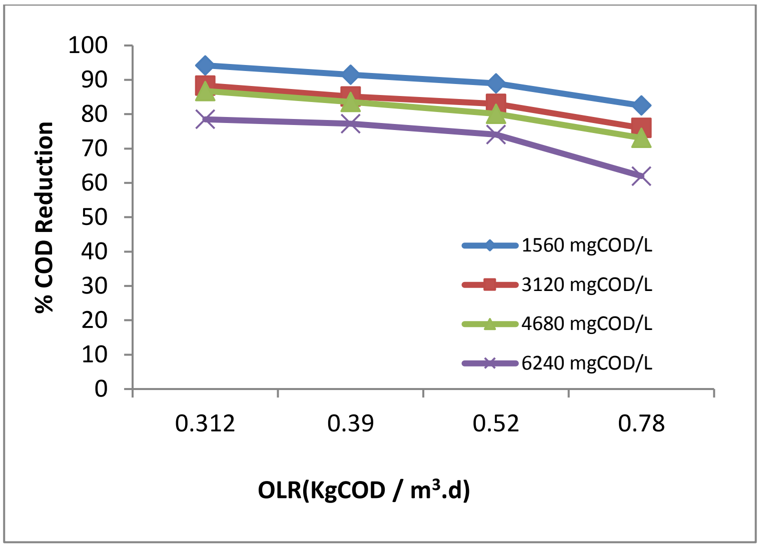

Figure 7: Effect of OLR on COD reduction on addition of sorbent

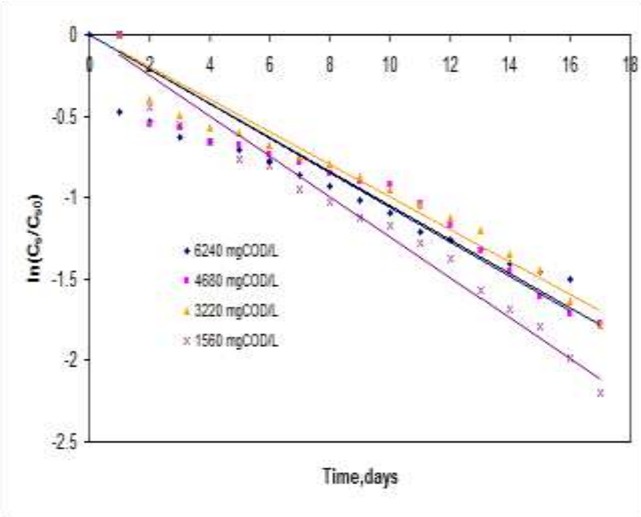

Fig. 8: First order model in continuous degradation kinetics using STMS for HRT 5 d

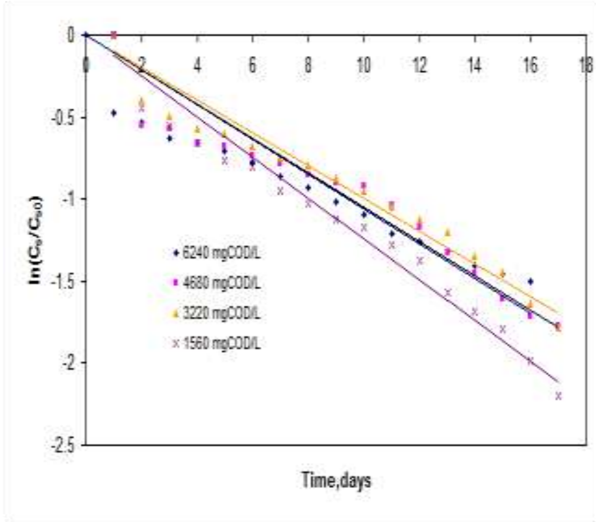

Fig. 9: First order model in continuous degradation kinetics using STMS for HRT 4 d

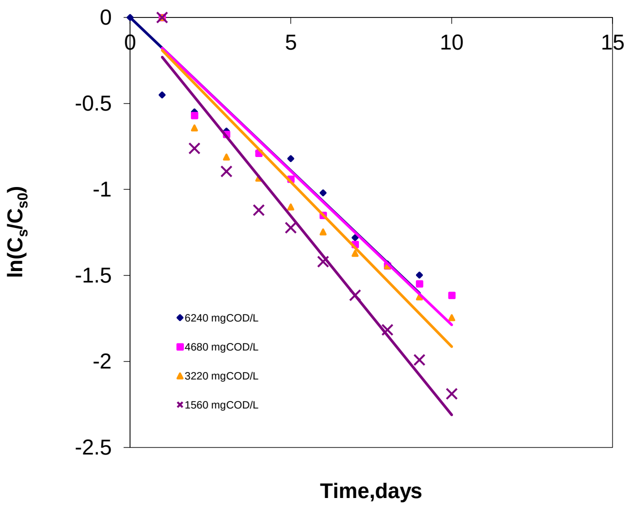

Fig. 10: First order model in continuous degradation kinetics using STMS for HRT 3d

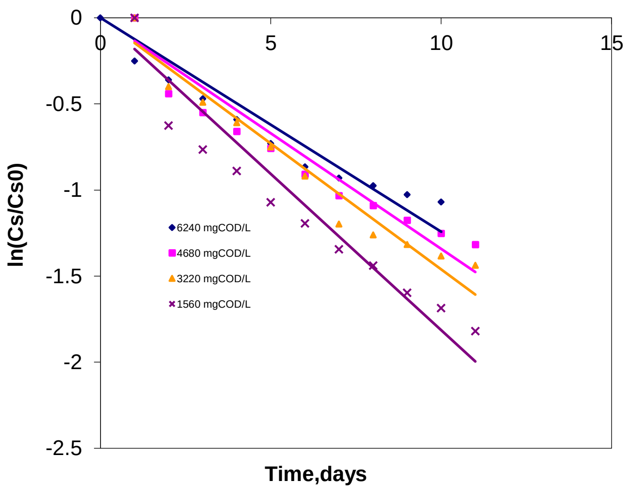

Fig. 11: First order model in continuous degradation kinetics using STMS for HRT 2 d

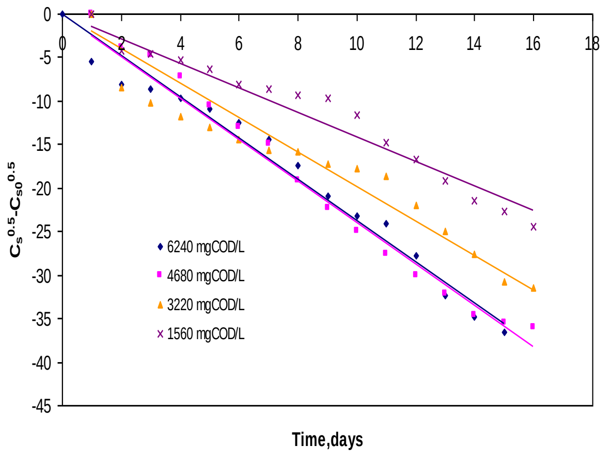

Fig. 12: Diffusional model in continuous degradation kinetics using STMS for HRT 5 d

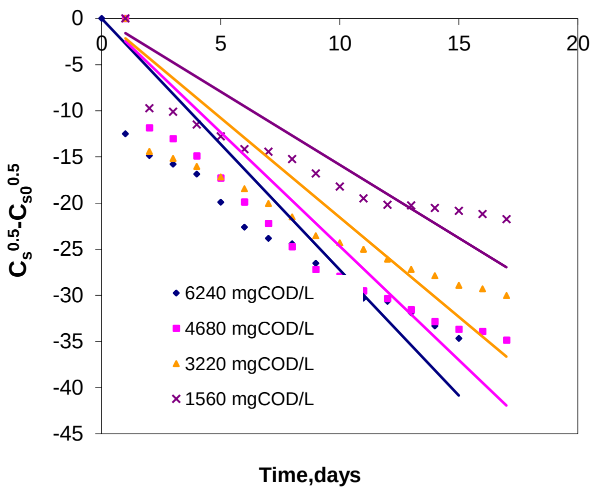

Fig. 13: Diffusional model in continuous degradation kinetics using STMS for HRT 4

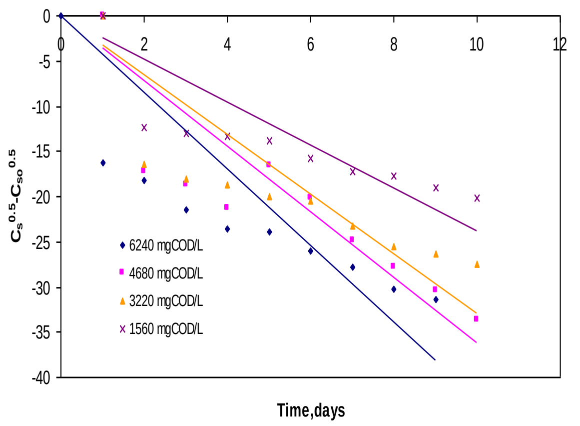

Fig. 14: Diffusional model in continuous degradation kinetics using STMS for HRT 3 d

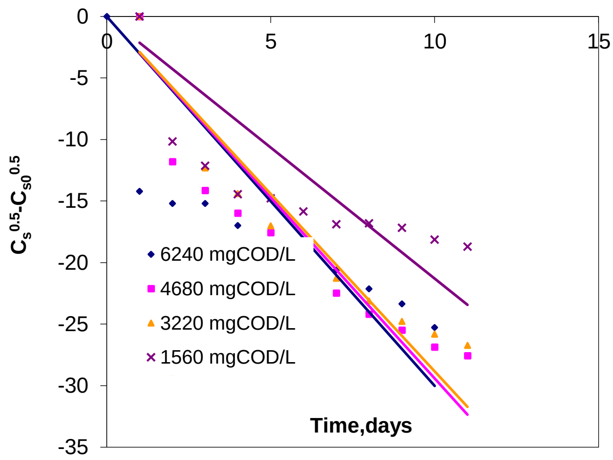

Fig. 15: Difffusional model in continuous degradation kinetics using STMS for HRT 2 d

It can be concluded that the sequential batch reactor inoculated with salt tolerant microorganisms along with wheat bran as sorbent can be utilized for the treatment of tannery wastewater. Various benefits like small space requirements, operating flexibility and potential capital cost savings by eliminating clarifiers and other equipment rather than in activated sludge processes are clearly depicted during the study.

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