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Kinetics Studies on Biological Treatment of Tannery Wastewater Using Mixed Culture

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***Abstract*—**In this study, aerobic digestion of tannery industry wastewater was carried out using mixed culture obtained from common effluent treatment plant treating tannery wastewater. The effect of pH, temperature, inoculum concentration, agitation speed and initial substrate concentration on the reduction of organic matters were found. The optimum conditions for COD reduction was found to be pH - 7 (60%), temperature - 30°C (61%), inoculum concentration - 2% (61%), agitation speed - 150rpm (65%) and initial substrate concentration - 1560 mg COD/L (74%). Kinetics studies were carried by using Monod model, First order, Diffusional model and Singh model. From the results it was found that the Monod model suits well for the degradation of tannery wastewater using mixed microbial consortium.

***Keywords*—**Tannery, Wastewater, Biological treatment, Aerobic, Mixed culture, Kinetics.

I. INTRODUCTION

TANNERY wastewater treatment is complex due to the variety of chemicals added at different stages of processing of hides and skins. Major problems in tanneries are due to wastewater containing heavy metals, toxic chemicals, chloride, lime with high dissolved and suspended salts and other pollutants [1]. The tanning process and the effluents generated have already been reported in literature [2-4].

Many conventional processes were carried out to treat wastewater from tannery industry such as biological process [5-9], oxidation process [10-12] and chemical process [13-15] etc. Among these, physical and chemical methods are considered very expensive in terms of energy and reagents consumption [16,17]. And generation of excessive sludge [18]. The main advantages of biological treatment methods are (i) Low capital and operating costs compared to alternatives such as chemical-oxidation processes (ii) True destruction of organics, versus mere phase separation, such as with air stripping or carbon adsorption (iii) Oxidation of a wide variety of organic compounds (iv) Removal of reduced inorganic compounds, such as sulphides and ammonia, and total nitrogen removal possible through denitrification (v) Operational flexibility to handle a wide range of flows and wastewater characteristics (vi) Reduction of aquatic toxicity. In this study batch experiments are conducted for the removal of organic matters from the tannery wastewater using mixed culture obtained from tannery wastewater treatment plant.

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II. MATERIALS AND METHODS

A. Materials

The tannery wastewater was collected from Ranipet tannery effluent treatment Co. Ltd., Walajah, India. The mixed culture was obtained from CETP sludge, Ranipet, India. The wastewater was analyzed in the laboratory for the parameters such as Colour, Chemical Oxygen Demand (COD), pH, Biological Oxygen Demand (BOD), etc., as per Standards Methods of Analysis [19] and it was reported in Table I.

B. Experimental Procedure

Experiments were conducted in a 250 mL Erlenmeyer flask. The effect of pH on degradation of tannery wastewater was studied. 100 cc of wastewater obtained from tannery industry was taken in the batch reactor and seed sludge 2 % (v/v) was added to it. The pH of the wastewater was adjusted to 5, 6, 7 and 8 by adding acid or base as required. Sulfuric acid and sodium hydroxide were used as acid and base respectively. The COD of the wastewater in each batch reactor were measured at regular time intervals.

The effect of temperature was studied in the range of 20-35°C. The effect of inoculum concentration was studied by adjusting the concentration by 1% to 4%. The effect of agitation speed was carried out in the range of 125 – 200 rpm. The initial concentration of tannery wastewater was varied to give approximately 1560, 3220, 4680, and 6240 mg COD/L. 150 cc of each sample is taken in separate batch reactor and 2% (v/v) seed sludge was added to each flask. The reduction in COD was recorded at regular time intervals and reported in terms of % COD reduction.

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C. Kinetics

Experimental data obtained from the batch degradation studies were fitted to four models namely, Monod model, First order, Diffusional and Singh model.

Monod Model

$$-\frac{dC_s}{dt} = \frac{k_1 C_x C_s}{Ks + Cs}$$

$$\frac{1}{r} = \left(\frac{1}{\left(\frac{dC_s}{d_t}\right)}\right) = -\left(\frac{K_s}{K_1 C_x}\right)\left(\frac{1}{C_s}\right) - \frac{1}{K_1 C_x}$$

Where dC_s/dt – Substrate degradation rate, mg COD/L.h. K_s – Half saturation constant of Monod's equation, mg COD/L. K_1 – Maximum specific degradation rate, mg COD/mg TVS h. C_x – Biomass concentration,mg/L.
C_s – Substrate Concentration, mg COD/L

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}

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

Singh model

The Singh model is given by,

$$-\frac{dC_s}{dt} = \frac{k_{si} C_s}{1+t}$$

Integrating the above equation between the proper limits, it becomes

$$\ln\left(\frac{C_s}{C_{so}}\right) = -k_{si} \ln(1+t)$$

Where k_{si} – Rate constant for Singh model.

III. Results and Discussions

Characterization of the tannery wastewater

Tannery wastewater is 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 given in Table 1. In general, tannery wastewaters are basic, have a dark brown colour and have a high content of organic substances that vary 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 a 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 $PO4^{3-}$ averaged 168, 115 and 21mg/L, respectively. The pH of the tannery wastewater ranges between 7.7-7.9. It showed that the influent was characterised by high alkalinity content (3150 mg/L) due to the chemicals used in leather processing. Influent total N concentration was 827 mg/L, 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 feeding stages. It is also observed that tannery effluents are 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. Several problems have been encountered during the biological treatment of tannery wastewater because of high toxicity. The inhibition of biodegradation due to the presence of chromium and sulfides demonstrates the antibacterial activity. High concentrations of these constituents make the possible discharge of tannery wastewaters into water bodies problematic, as they cause eutrophication and other adverse environmental effects (Durai and Rajasimman, 2011).

TABLE I
PHYSICO-CHEMICAL CHARACTERISTICS OF TANNERY WASTEWATER

Sl.No	Parameters	Values
1.	pH	7.7-7.9
2.	Colour	Dark Brown
2.	Total Suspended Solids	1150
3.	Total Dissolved Solids	12880
4.	Turbidity	150 NTU
5.	Alkalinity	3150
6.	BOD	1746
7.	COD	6240
8.	Sulphide	232
9.	Total Nitrogen	327
10.	Ammonical Nitrogen	115
11.	Total Chromium	13.3
12.	Total Phosphate	21
13.	Total Kjeldahl Nitrogen	168

Except pH and turbidity all the values are in mg/L

Effect of pH

pH is one of the important factor in the degradation of organic matters present in wastewater by microbes. Fig.1 shows the effect of pH on the degradation of tannery wastewater using mixed microbes. In the acidic conditions, the reduction in COD was found to be low. From the figure, pH of 7 was found to be optimum for the maximum COD

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reduction (60%) and it was maintained for further studies.

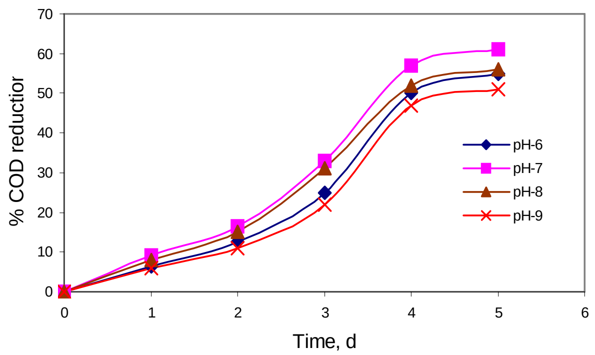

Fig.1. Effect of pH on the degradation of tannery wastewater

Effect of Temperature

Temperature not only affects the metabolic activities of the microbial population but also influences the gas-transfer rates and the settling characteristics of activated sludge. In general, the rate of biochemical reactions and of substrate transfer process increases with higher temperature. However, the solubility of oxygen decreases in the mixed liquor as temperature increase, resulting in poor biodegradation conditions for aerobic microbes. Thus, increase in temperature generates two reciprocal effects on biochemical reactions. Furthermore, sludge is difficult to settle as higher temperature maintained. The average temperature for the process should be determined by the consideration of these effects. Experiments were conducted at different temperatures, 20°C, 25°C, 30°C and 35°C at a pH of 7. From the Fig.2, it was observed that a temperature of 30°C was found to be optimum for the maximum degradation of tannery wastewater and hence it was maintained for further studies.

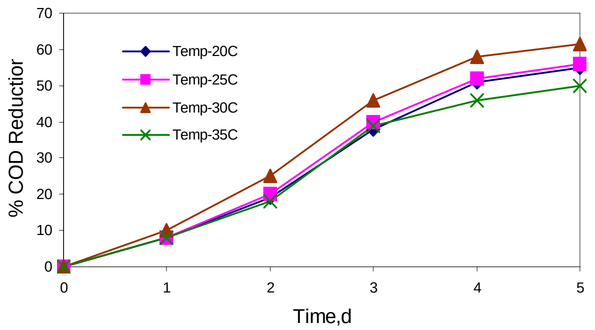

Fig.2. Effect of temperature on the degradation of tannery wastewater

Effect of inoculum Concentration

Inoculum concentration was changed from 1% - 4 %(v/v) for the mixed culture, keeping pH (7) and temperature (30°C) constant. Samples were withdrawn for COD analysis and it was found to be 2 % Inoculum concentration was optimum and hence it was maintained for further studies (Fig.3).

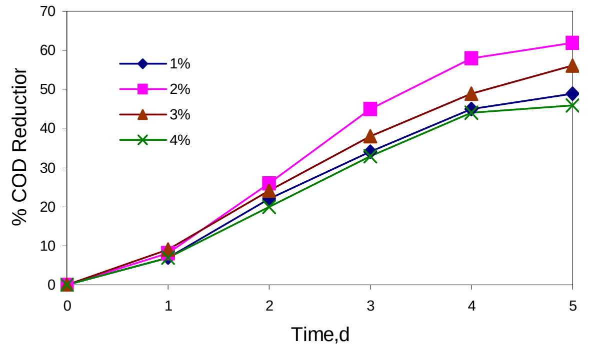

Fig.3. Effect of inoculum concentration on the degradation of tannery wastewater

Effect of Agitation Speed

Optimization of agitation speed for the COD reduction of tannery wastewater was carried out at different speeds viz., 125 rpm, 150 rpm, 175 rpm and 200 rpm. This difference in agitation speed has significant variation in COD reduction. These mixed consortia have maximum COD reduction of 65% at 150 rpm and further increase in agitation rate caused observable fall in COD reduction. This is clearly shown in Fig.4. This could be attributed to the effect of shear rate on the cell wall, resulting in cell damage.

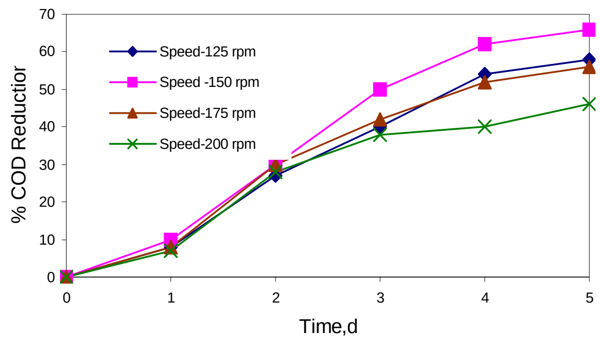

Fig.4. Effect of agitation speed on the degradation of tannery wastewater

Effect of Initial Substrate Concentration

The Initial concentration of the wastewater was varied to give approximately 1560, 3220, 4680 and 6240 mg COD/L. 150 cc of each sample was taken in separate batch reactor and 2 % (v/v) seed sludge was added to each flask. The reduction in COD was recorded at regular tie intervals and reported in terms of % COD reduction. The observations were shown in Fig.5. The results show that as the time progresses the substrate concentration decreases for all the initial substrate concentrations and reaches a final value after degradation stops. The maximum percentage COD removal of 61%, 65%, 69%, and 74% are obtained for the initial concentrations of 1560, 3220, 4680 and 6240 mg COD/L respectively. From the

Figure it is also observed that the degradation rate is high at lower substrate concentration when compared to higher concentrations.

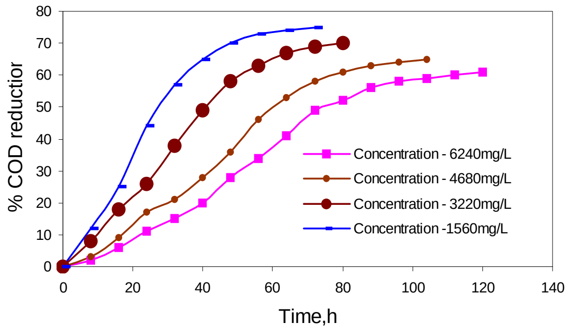

Fig.5. Effect of initial substrate concentration on the degradation of tannery wastewater

IV. Kinetics

Monod Model

The experimental values were used to determine the parameters and to verify the performance of the Monod model. Time vs Cs data were plotted and dC_s/dt values were obtained from the plot. A plot of $1/C_s$ vs $1/(dC_s/dt)$ for various initial substrate concentrations was shown in Fig.6. The COD reduction profile was well explained by Monod Model with high values of R^2 (0.9) for all the initial substrate concentrations. The values of the kinetic parameter present in the batch model for all initial substrate concentrations were estimated from the slope of the best-fit lines and it was given in Table II. It was observed that as the initial substrate concentration increases the rate constant decreases. The high R^2 values show the ability of this model in describing the batch kinetics of the degradation of tannery wastewater.

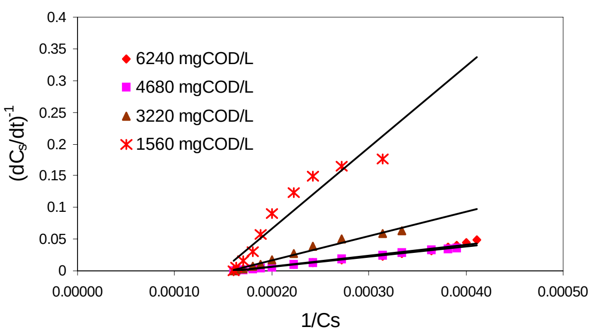

Fig.6. Monod model in batch degradation kinetics of tannery wastewater

The First Order Model

The First order model was applied to the experimental data to verify the performance of the model and it was shown in Fig.7. Time vs ln (C_s/C_{so}) data were plotted for various initial substrate concentrations. The values of the constants in first order model were found to be decreases with increase in initial substrate concentration. The R^2 values were also found to be good (>0.9) for all cases. Hence the degradation of tannery wastewater using mixed culture follows the first order system.

TABLE II
PHYSICO-CHEMICAL CHARACTERISTICS OF TANNERY WASTEWATER

Kinetic Model	Initial Substrate Concentration, mgCOD/L			
	1560	3220	4680	6240
Monod Model				
K_1, mgCOD/mg TVS,L	-0.0057	-0.0083	-0.0051	-0.0034
K_s, mg COD/L	6765.5	6343.7	6225.4	6221
R^2	0.9008	0.9806	0.9985	0.9769
First Order Model				
K_1,h^{-1}	0.0209	0.0172	0.012	0.0094
R^2	0.9341	0.9751	0.9742	0.9733
Diffusional Model				
K_D,mg $COD^{0.5}/L^{0.5}h$	-36.772	-33.046	-29.368	-15.275
R^2	0.8594	0.8121	0.8552	0.8321
Singh Model				
Ksi,h-1	0.6778	0.5769	0.4832	0.4225
R^2	0.8420	0.8839	0.8861	0.8703

Diffusional Model

The experimental data were plotted for diffusional model and it was shown in Fig.8. The values of the rate constant and R^2 were represented in Table II. The Biodegradation rate does not depend on diffusion phenomenon. Hence, Diffusional model failed miserably in representing the batch biodegradation of tannery wastewater. This fact is also complimented by the poor values of R^2 obtained with the diffusional model.

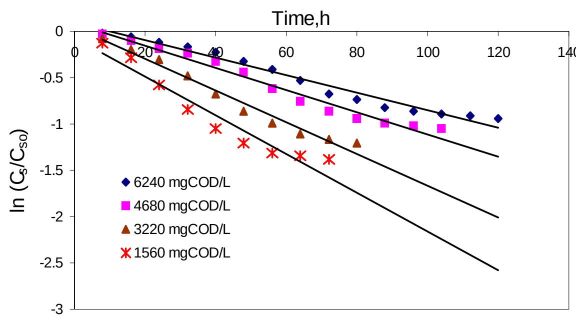

Fig.7. First order model in batch degradation kinetics of tannery wastewater

The Singh Model

The experimental data were plotted for Singh model and shown in Fig.9. From the best-fit lines the value of rate constant and R^2 were found and they were given in Table II. The kinetic constant decreases with increase in initial substrate concentration. But the low R^2 values show the inability of this model in describing the degradation of tannery industry wastewater in a batch reactor.

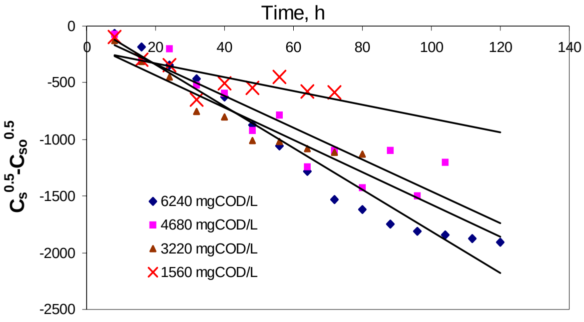

Fig.8. Diffusional model in batch degradation kinetics of tannery wastewater

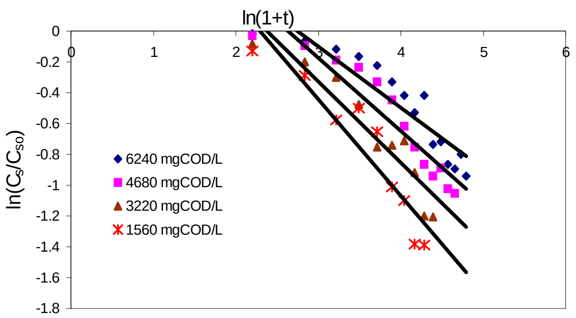

Fig.9. Singh model in batch degradation kinetics of tannery wastewater

V. Conclusion

Tannery wastewater was treated in a batch reactor using mixed microbial consortium. The process parameters viz. pH, temperature, inoculum concentration, agitation speed and initial substrate concentration were optimized for the maximum COD reduction. A maximum COD removal of 74% was achieved at the optimized condition. The kinetics studies were carried out by various models like, Monod model, First order, Diffusional model, Singh model. The rate constants were found to be decrease with increase in concentration. From the results it was found that the Monod model and First order model suits well for this system. Where as Diffusional and Singh Models fail to represent the batch study. This is proved by their low R^2 values.

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References

[1] N. K. Uberoi, Environmental Management, Excel Books, New Delhi. 2003, pp. 269.

[2] W. M. Wiegant, T.J.J. Kalker, V.N. Sontakke and R.R. Zwaag, “Full scale experience with tannery water management: an integrated approach”, Water Sci. Technol, vol.39(5), 1999, pp.169–176.

[3] K. J. Sreeram, T. Ramasami, “Sustaining tanning process through conservation, recoveryand better utilization of chromium”, Resourc. Conserv. Recycling, vol.38 (3), 2003, pp. 185–212.

[4] M. L. M. Stoop, “Water management of production systems optimised by environmentally oriented integral chain management: case study of leather manufacturing in developing countries”, Technovation, vol.23 (3), 2003, pp. 265–278.

[5] D. H. Ahn, Y. C. Chung, Y. J. Yoo, D. W. Pak and W.S.Chang, “Improved treatment of tannery wastewater using *zoogloea ranigera* and its extracellular polymer in an activated sludge process”, Biotechnol. Let, vol.18 (8), 1996, pp. 917 – 922.

[6] K. Vijayaraghvan, and D.V. H. Murthy, “Effect of toxic substances in anaerobic treatment of tannery wastewater”, Bioprocess Biosys. Eng, vol.16, 1997, pp. 151-155.

[7] M. Wiemann, H. Schenk, and W. Hegemann, “Anaerobic treatment of tannery wastewater with simultaneous sulphide elimination”, Water Res, vol.32(3), 1998, pp. 774-780.

[8] C. Di Iaconi, A. Lopez, R. Ramadori, and R. Passino, “Tannery wastewater treatment by sequencing batch biofilm reactor”, Environ. Sci.Technol, vol. 37(14), 2003, pp. 3199 – 3205.

[9] G. Farabegoli, A. Carucci, M. Majone and E. Rolle, “Biological treatment of tannery wastewater in the presence of chromium”, Journal of Environmental Management, vol.71(4), 2004, pp. 345-349.

[10] S.G. Schrank, H. J. Jos, R. F. P. M. Moreira and H. Fr. Schroder, “Fentons oxidation of various – based tanning materials”, Desalination, vol.50, 2003, pp. 411-423.

[11] G. Sekaran, K. Chitra, K. Mariappan, and K. V.Raghavan, “Removal of sulphide in anaerobically treated tannery wastewater by wet air oxidation”, Journal of environmental science and health, vol. 31, 1996, pp. 579-598.

[12] S. Dogruel, G. E. Ates, B. F. Germirli, and D. Orhon, “Ozonation of nonbiodegradable organics in tannery wastewater”, J. Environ. Sci. Health. Part-A, vol. 39, 2004, pp. 1705 – 1715.

[13] C. Di Iaconi, A. Lopez, G. Ricco, and R. Ramadori, J. Anal. Environ.Cultur. Herit. Chem, vol. 91, 2001, pp. 587.

[14] D. Orhon, S. Sszen, E. Ubay Cokgsr, and E. Ates, IAWQ 19th Biennial International Conference, 1998, pp. 256 -363.

[15] Z. Song, C. J. Williams and R.G. J. Edyvean, ‘Treatment of tannery wastewater by chemical coagulation”, Desalination, vol.164, 2004, pp.249 - 259.

[16] J. H. Churchley, “Removal of sewage effluent- the use of a fullscale ozone plant”, Water Science and Technology, vol. 30(3), 1994, pp. 275-284.

[17] S. R. Stern, Azpyrkowicz, and I.Rodighiro, “Aerobic treatment of textile dyeing wastewater”, Water Science and Technology, vol. 47(10), 2003, pp. 55-59.

[18] W. Chu, “Dye removal from textile dye wastewaters using recycled alum sludge”, Water Research, vol.35 (13), 2001, pp. 3147-3152

[19] APHA.1998.Standard Methods for Water and Wastewater Examination, 20th Ed. American Public Health Association, Washington

[20] G. Durai, and M. Rajasimman, “Biological treatment of tannery wastewater –a review”, Journal of Environmental science and Technology, vol. 4(1) 2011, pp. 1-17.