

Kinetic Analysis of Sequencing Batch Reactor for the Treatment of Tannery Wastewater

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ABSTRACT

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- 5,4,3 and 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 color were found to be 84% and 58% 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 R² value calculated the first order model fits the data well. In the kinetic studies, modified Stover-Kincannon, Diffusion Model, Michaelis-Menten model and second-order models, and were found to be the most appropriate model for ASBR reacting tannery wastewater than first order model.

Key words : Sequencing Batch Reactor (SBR), Chemical Oxygen Demand (COD) Removal, Michaelis- Menten, Second Order, Modified Stover-Kincannon.

1. INTRODUCTION

During tanning process at least about 300kg 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 30-35L/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(SBR) 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].

1.1 Model Development

Mass balance for substrate: feed step

Substrate concentration and reactor fluid content in SBR system are at their respective lowest value at the beginning of feeding. During feeding, the change in waste concentration and the change in reactor waste volume occur simultaneously. A mass balance on waste (accumulation rate = input rate-output rate- decay rate) gives:

$$\frac{d(VC)}{dt} = QC_0 - 0 - V_r \quad (1)$$

1.2 Analysis and Kinetics of the Sequencing Batch Reactors

Where Q is influent flow rate, t is time; C is waste concentration, r is waste conversion or decay rate, and other terms are as presented in Fig. 1. A list of variables used in this report are presented under nomenclature.

Applying the product rule of differentiation, Equation (1) gives:

$$V \frac{dC}{dt} + C \frac{dV}{dt} = QC_0 - V_r$$

$$\text{or } \frac{dC}{dt} + \frac{C}{V} \frac{dV}{dt} = \frac{Q}{V} C_o - r \quad (2)$$

Knowing that

$$\frac{dV}{dt} = Q,$$

Equation (2) becomes:

$$\frac{dC}{dt} + \frac{C}{V} Q = \frac{Q}{V} C_o - r$$

$$\text{or } \frac{dC}{dt} = \frac{Q}{V} (C_o - C) - r \quad (3)$$

Observing that $V = V_o + V_t$ and that $V_t = Qt$, Equation (3) can be written as in the form:

$$\frac{dC}{dt} = \frac{Q}{V_o + Qt} (C_o - C) - r \quad (4)$$

Mass balance for substrate: react step

For short feeding time in comparison to react time, we may assume that the reaction time controls waste decay. During the react step, flow into and out of the system are zero. Therefore, Equation (4) gives:

$$\frac{dC}{dt} = -r \quad \text{or} \quad dt = \frac{dC}{r} \quad (5)$$

1.3 Integration Limits

Waste concentration in the reactor at any time during the feed step (C_F) can be represented by:

$$C_F = [V_o C_o + V_t C_o] \left(\frac{1}{V_o + V_t} \right)$$

$$= \left[V_R - V_D C_D + V_t C_o \left(\frac{1}{V_o + V_t} \right) \right] \quad (6)$$

Where V_t is the volume of raw waste fed to the reactor at the time of interest, V_R is the total reactor volume, and V_o is the volume of waste in the reactor at the end of decant ($V_R - V_D$).

The lower integration limit for Equation (5) is the waste concentration at the beginning of react step. It is the waste concentration at the end of feed step (C_{EF}), and is given by:

$$(C_{EF}) = [V_D C_o + V_o C_D] \left(\frac{1}{V_R} \right)$$

$$= [V_D C_o + (V_R - V_D) C_D] \left(\frac{1}{V_R} \right) \quad (7)$$

The upper integration limit for Equation (5) is the waste concentration at the react step or the decant concentration (C_D). With the integration limits, Equation (5) may be written as:

$$\int_0^R dt = - \int_{\frac{V_D C_o + V_R - V_D C_D}{V_R}}^{\frac{C_D}{V_R}} \frac{dC}{r} \quad \text{or}$$

$$t_R = - \int_{\frac{V_D C_o + V_R - V_D C_D}{V_R}}^{\frac{C_D}{V_R}} \frac{dC}{r} \quad (8)$$

1.4 Zero- Order Kinetics

For zero order reaction kinetics, $r = K$. Therefore, Equation (8) becomes:

$$\int_0^R dt = - \int_{\frac{V_D C_o + V_R - V_D C_D}{V_R}}^{\frac{C_D}{V_R}} \frac{dC}{k} \quad \text{or}$$

$$t_R = - \frac{1}{K} \int_{\frac{V_D C_o + V_R - V_D C_D}{V_R}}^{\frac{C_D}{V_R}} dC \quad (9)$$

Integrating Equation (9), we have:

$$t_R = - \frac{1}{K} \left[C_D - \left(\frac{V_D}{V_R} C_o + \frac{V_R - V_D}{V_D} C_D \right) \right]$$

$$= - \frac{1}{K} \left[C_D - \left(\frac{V_D}{V_R} C_o + \frac{V_R}{V_D} C_D - C_D \right) \right] \quad (10)$$

That is:

$$t_R = \frac{1}{K} \left[-C_D + \left(\frac{V_D}{V_R} C_o + \frac{V_R}{V_D} C_D - C_D \right) \right]$$

$$= \frac{1}{K} \left[-C_D + \left(\frac{V_D}{V_R} C_o + \frac{V_R}{V_D} C_D - C_D \right) \right] \quad (11)$$

That is:

$$t_R = \frac{1}{K} \left[\left(\frac{V_D}{V_R} C_o + \frac{V_R}{V_D} C_D - 2C_D \right) \right]$$

$$\text{or } Kt_R = \left[\left(\frac{V_D}{V_R} C_o + \frac{V_R}{V_D} C_D - 2C_D \right) \right] \quad (12)$$

1.5.1 First-Order Kinetics

For first order kinetics, $r = KC$. Therefore, Equation (8) becomes:

$$\int_0^{t_R} dt = - \int_{\frac{V_D C_o + V_R - V_D C_D}{V_R}}^{\frac{C_D}{V_R}} \frac{dC}{r} \quad \text{or}$$

$$t_R = - \int_{\frac{V_D C_o + V_R - V_D C_D}{V_R}}^{\frac{C_D}{V_R}} \frac{dC}{KC} \quad (13)$$

Integrating equation (13), we have:

$$t_R = - \frac{1}{K} \left[\ln \ln C_D - \ln \ln \left(\frac{V_D}{V_R} C_o + \frac{V_R - V_D}{V_D} C_D \right) \right]$$

$$= - \frac{1}{K} \left[\ln \ln C_D - \ln \ln \left(\frac{V_D}{V_R} C_o + \frac{V_R}{V_D} C_D - C_D \right) \right]$$

$$t_R = \frac{1}{K} \left[-\ln \ln C_D + \ln \ln \left(\frac{V_D}{V_R} C_o + \frac{V_R}{V_D} C_D - C_D \right) \right]$$

$$= \frac{1}{K} \ln \ln \left[\left(\frac{V_D C_o + V_R - V_D C_D}{V_D C_D} \right) \right] \quad (15)$$

$$t_R = \frac{1}{K} \ln \ln \left[\frac{V_D C_o}{V_R C_D} - \frac{V_D}{V_R} + 1 \right]$$

$$\text{or } Kt_R = \ln \ln \left[\frac{V_D C_o}{V_R C_D} - \frac{V_D}{V_R} + 1 \right] \quad (16)$$

1.5.2 Second-Order Kinetics

For a second order reaction kinetic, $r = KC^2$. Therefore, Equation (8) becomes:

$$\int_0^{t_R} dt = - \int_{\frac{V_D C_o + V_R - V_D C_D}{V_R}}^{\frac{C_D}{V_R}} \frac{dC}{KC^2}$$

$$\text{or } t_R = - \frac{1}{K} \int_{\frac{V_D C_o + V_R - V_D C_D}{V_R}}^{\frac{C_D}{V_R}} \frac{dC}{C^2} \quad (17)$$

Integrating Equation (17), we have:

$$t_R = \frac{1}{K} \left[\frac{1}{C_D} - \frac{1}{\left(\frac{V_D}{V_R} C_o + \frac{V_R - V_D}{V_R} C_D \right)} \right]$$

$$= \frac{1}{K} \left[\frac{1}{C_D} - \frac{1}{\frac{V_D C_o + (V_R - V_D) C_D}{V_R}} \right] \quad (18)$$

That is

$$t_R = \frac{1}{K} \left[\frac{[V_D C_o + (V_R - V_D) C_D] - V_R C_D}{C_D [V_D C_o + (V_R - V_D) C_D]} \right]$$

$$= \frac{1}{K} \left[\frac{V_D C_o + V_R C_D - V_D C_D - V_R C_D}{C_D [V_D C_o + (V_R - V_D) C_D]} \right] \quad (19)$$

$$t_R = \frac{1}{K} \left[\frac{V_D C_o - V_D C_D}{C_D [V_D C_o + (V_R - V_D) C_D]} \right]$$

$$\text{or } K t_R = \left[\frac{V_D C_o - V_D C_D}{C_D [V_D C_o + (V_R - V_D) C_D]} \right] \quad (20)$$

$$= \left[\frac{V_D C_o - V_D C_D}{C_D [V_D C_o + (V_R - V_D) C_D]} \right] \quad (21)$$

1.6 Grau Second-Order Model

The second order model was employed to the experimental results for SBR system treating tannery wastewater. The general equation of Grau Second Order Kinetics Model is shown below:

$$\frac{ds}{dt} = k_2 X \left(\frac{s}{S_0} \right)^2 \quad (22)$$

Where, $\frac{ds}{dt}$ is the substrate removal rate (g/L-day), k_2 is kinetic constant (g COD/gVS- day), X is the concentration of microorganisms (gVS/L), S is substrate concentration at any time, and S_0 is the concentration of initial substrate (g/l), integrating the above equation within the boundary conditions ($S = S_i$ to S_e and $t = 0$ to H), and then linearized, the following equation is obtained.

$$\frac{S_0 \theta_H}{S_0 - S} = \theta_H + \frac{S_0}{k_2 X} \quad (23)$$

Holding the term " $\frac{S_0}{k_2 X}$ " in the above equation constant leads to

$$\frac{S_0 \theta_H}{S_0 - S} = a + b \theta_H \quad (24)$$

The term $\frac{S_0 - S_i}{S_0}$ is the substrate removal efficiency (E) and it can be used in the equation as shown below:

$$\frac{\theta_H}{E} = a + b \theta_H \quad (25)$$

If $V/Q(S_i - S_e)$ is plotted against $1/OLR$, KB/U_{max} is the slope and $1/U_{max}$ is the intercept point of the line. Figure 4 shows the plot of the Grau second-order multicomponent model for SBR. The value of a and b were determined from the intercept and slope of the straight lines. The values of a and b were obtained to be 0.87 and 1.019, respectively, with high correlation coefficient ($R_2 = 0.99$). This confirms the validity of the application of this model for SBR treating tannery wastewater. Hence, the formula for predicting substrate concentration in the effluent can be given as:

$$S = S_0 \left(1 - \frac{\theta}{0.87 + 1.019\theta} \right) \quad (26)$$

1.7 Diffusion Models

The Diffusional model is given by

$$\frac{-DCS}{dt} = kDC0.5 \quad (27)$$

When integrated between the known limits, the above equation becomes

$$\sqrt{Cs} - \sqrt{Cs0} = -2kDt \quad (28)$$

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.

1.8 Modified Stover-Kincannon Model

The Stover-Kincannon was developed first for rotating biofilm reactor (Sandhye and Swaminathan, 2006). It is assumed that the organic loading rate can be correlated with substrate utilization rate using mono-molecular kinetics. The substrate removal rate is defined in two different forms as shown below:

$$\frac{ds}{dt} = \frac{Q}{V} (S_i - S_e) \quad (29)$$

$$\frac{ds}{dt} = \frac{U_{max}}{K_B} \left(\frac{QSi/V}{\left(\frac{QSi}{V} \right)} \right) \quad (30)$$

This can be linearised as

$$\frac{ds}{dt} = \frac{U_{max}}{K_B} \left(\frac{QSi/V}{\left(\frac{QSi}{V} \right)} \right) \quad (31)$$

Where ds/dt is the substrate removal rate (g/L-day), U_{max} is the maximum utilization rate constant (g/L-day), K_B is saturation value constant (g/L-day), Q is the flow rate (L/day) and V is the effective volume of reactor (L). Since dS/dt approaches U_{max} as the organic loading rate, qSi/V approaches infinity.

2. Materials and methods

Substrate: The tannery effluent and the mixed culture were collected from the Pallavaram Tannery Effluent Treatment Co. Ltd., Pallavaram, Chennai. India and used as an influent for the bioreactor during the experimental period.

2.1 Experimental Setup

Tannery Substrate obtained from Pallavaram Tannery Effluent Treatment plant (Chennai, Tamilnadu) the activated sludge process treating tannery wastewater was used in the reactor [1]. SBR was operated at different operating conditions by changing the hydraulic retention time (HRT- 5,4,3 and 2 days) and initial substrate concentration (6240mgCOD/L, 4680mgCOD/L, 3220mgCOD/L and 1560mgCOD/L). Two unique reactors, each with a total volume of 10litre, were used in this research. Rubber tubes were inserted into the reactors to ensure the filling and removal of the tannery effluent using peristaltic pumps. The reactors were supplied with sufficient oxygen by fine bubble air diffuser. The operating conditions in the reactors were maintained at the temperature of 30°C (Room Temperature) and pH of 7. The mixing inside in our reactors was achieved with a mechanical stirrer at the speed of 150 rpm. Each cycle lasted for 24hours: the filling in 1hour, the reaction took place in 20 hours, the settling in 2 hours, the withdrawal in 0.75 hour and the idle in 0.25 hour as prescribed. The reactors were operated for 50 days for various

initial concentration of 6240mg COD/L, 4680mg COD/L, 3220mgCOD/L and 1560mg COD/L at different OLR, initially 2kgCOD/m³ day for 15 days followed by 2.5kgCOD/m³ from the day of 16-30, 3.3kg COD/m³ from the day of 31-40 and finally 5kgCOD/m³ until the end of the experiment. For this reason 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 tannery wastewater. In this innovative method, sample was centrifuged at 10,000 rev/min for 30 min and the pH was adjusted to 7.8.

3. EXPERIMENTAL RESULTS

These results show that Modified Stover-Kincannon model, First Order Model, Diffusiom Model and Grau Second-Order can be applied successfully for modeling of the experimental results of SBR treating tannery wastewater with high correlation coefficient. On the other hand, the first order model appeared to be less successful ($R^2=0.83$) on predicting substrate and color removal from tannery wastewater in SBR system.

Table 1: Kinetic parameter values for the degradation of tannery wastewater in SBR

Kinetic Model	HRT, Days	Average Initial Substrate Concentration, mg/L			
		1560mg/L	3220mg/L	4680mg/L	6240mg/L
First Order Model k_1, h^{-1}	5	0.1436	0.1231	0.1128	0.0971
	4	0.1204	0.1147	0.1056	0.0836
	3	0.2249	0.1932	0.1908	0.1735
	2	0.0942	0.1196	0.1392	0.1542
R^2	5	0.9568	0.9519	0.9177	0.9124
	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
Modified Stover-Kincannon Model	5	0.5725	0.5541	0.5435	0.6134
	4	0.8254	0.8512	0.8445	0.8614
	3	0.9987	0.9957	0.9847	1.2724
	2	1.4361	1.4534	1.4523	2.0412
R^2	5	5.0006	4.5805	5.0006	5.0139
	4	5.0105	5.0439	5.0402	5.0302
	3	5.0668	5.0556	5.0512	5.0515
	2	5.0806	5.0695	5.0812	5.0827
Diffusion Models $kD, mgCOD0.5/L0.5h$	5	1.9153	2.5098	2.8512	2.9583
	4	1.6781	2.3566	2.6862	2.6097
	3	3.1236	4.0354	4.8516	5.2667
	2	2.3262	3.0913	3.2952	3.1495
R^2	5	0.9055	0.8506	0.6535	0.7092
	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
Grau Second-Order	5	19.300	19.540	16.200	10.240
	4	24.800	25.410	24.855	17.640
	3	32.700	32.640	29.810	23.140
	2	42.500	43.500	36.200	24.180
R^2	5	5.5106	5.5422	5.4865	5.8013
	4	5.5668	5.5638	5.5528	5.8405
	3	6.0033	6.0208	6.0102	5.8915
	2	6.0042	6.0215	6.0204	6.6093
Michaelis-Menten Model	5	0.6215	0.5863	0.5784	0.5834
	4	0.8841	0.9221	0.8435	0.9525
	3	1.4352	1.4527	1.4421	1.3234
	2	1.4358	1.4284	1.4739	2.0547
R^2	5	1.1728	1.1679	1.1337	1.1284
	4	1.1762	1.1858	1.1177	1.1159
	3	0.1355	0.1172	0.1159	0.1162
	2	1.1272	1.1161	1.1162	1.1163

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. 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 1-4 shows the fit of the model for the experimental data when the HRT is 5 days.

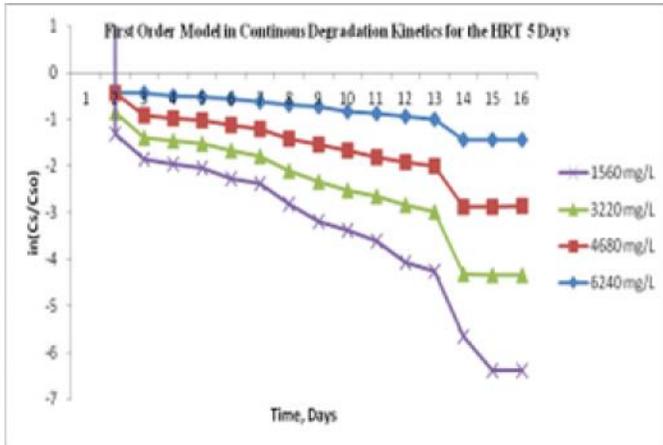


Figure 1: First Order Model in Continuous Degradation Kinetics for the HRT 5 Days

The experimental data is compared with the values predicted by first order model in continuous degradation kinetics for the HRT 5 days. 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 computed in Table 2. As the initial concentration of substrate increases, the rate constant k_1 decreases as in the table. This can be described to a growing importance of the recalcitrant fraction in reducing the diffusivity of the biodegradable substance.

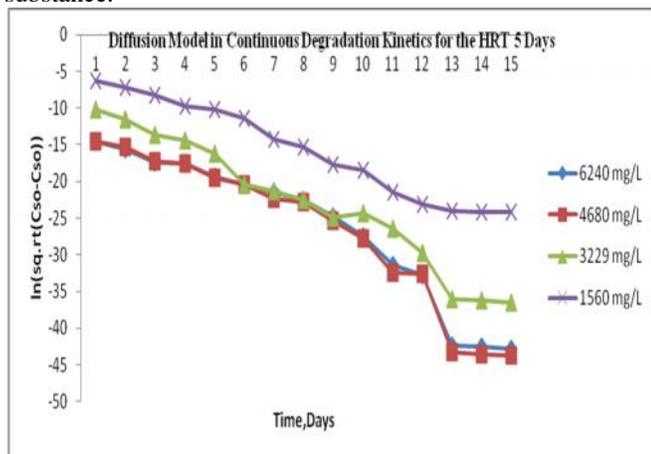


Figure 2: Diffusion Model in Continuous Degradation Kinetics for the HRT 5 Days

From the experimental data, the modified Stover-Kincannon Model in Continuous degradation for the HRT 5 days and rate constant k_D was determined through the LSQ fitting. From the R^2 values it was found that the Stover-Kincannon Model fails

to represent the experimental data. This is clearly depicted in Figure 3.

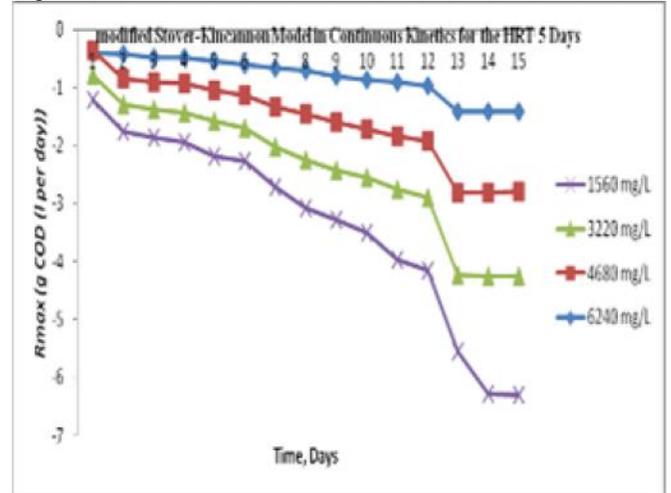


Figure 3: modified Stover-Kincannon Model in Continuous Kinetics for the HRT 5 Days

The experimental data is compared with the values predicted by Michaelis-Menten Model in Continuous Degradation Kinetics for the HRT 5 days. The Michaelis-Menten Model rate constant, R_{max} and 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 computed in Table 2. As the initial concentration of substrate increases, the rate constant k_1 decreases as in the table 2. and fig 3.

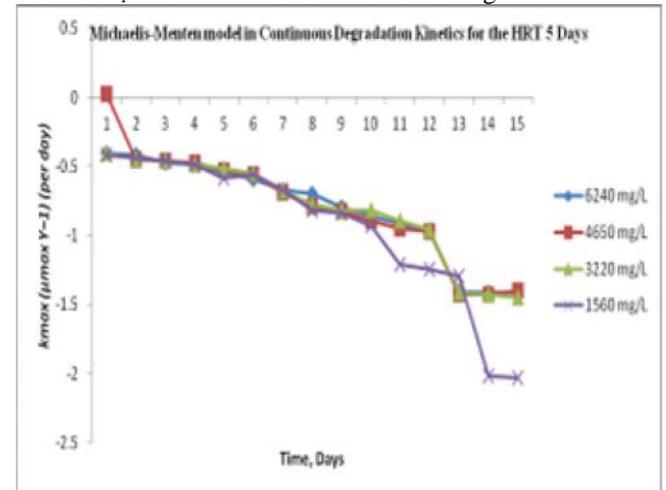


Figure 4 : Michaelis-Menten model in Continuous Degradation Kinetics for the HRT 5 Days

The experimental data is compared with the values predicted by Grau Second Order Model in continuous degradation kinetics for the HRT 5 days. The Grau Second Order Model rate constant, k_{max} and 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 computed in Table 2.

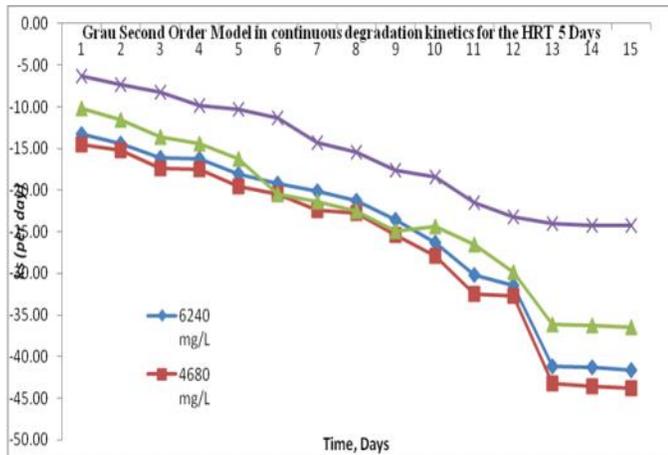


Figure 5 : Grau Second Order Model in continuous degradation kinetics for the HRT 5 Days

As the initial concentration of substrate increases, the rate constant k_1 decreases as in the table 2. and fig 5.

4. COMPARISON OF THE KINETIC PARAMETERS OBTAINED FOR THE VARIOUS SUBSTRATES

Table 2. Comparison of the kinetic parameters obtained for the various substrates.

Types of Wastewater	Reactor	U_{max}	K_B	References
Tannery Wastewater	MSBR	5.48	5.54	This study(2020)
Tannery Wastewater	ASBR	5.56	5.78	Andualem Mekonnen et al(2017)
Food Processing Wastewater	Anaerobic Contact	22.9 2	23.59	Senturk et al. (2010)
Formaldehyde containing Wastewater	UAFB	3.4	4.6	Priya et al. (2009)
Milk Permeate Wastewater	AMBBR	89.3	102.3	Wanga et al. (2009)
Paper Mill Wastewater	AF	86.2 1	104.1 5	Yilmaz et al.(2008)
Textile Wastewater	UAFB	31.6 9	45.37	Sandhye et al.,(2006)
Simulated Textile Wastewater	UASBR	7.5	8.2	Isik et al.,(2005)
Synthetic Saline Wastewater	UASBR	5.3	7.05	Kapdan (2005)
Corrugated Paper Wastewater	AF	3.86	0.80	Ahn et al.,(2002)

5. CONCLUSION

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 (84%) and color (58%) 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. The kinetic data and rate reaction constants could be used for the design of a field scale SBR for treating tannery wastewater. A design rationale can be evaluated on the basis of present experimental data for the purpose of application of this technology in similar plants. The outcome of the present investigation results would be helpful for making a design rationale for SBR treatment of tannery wastewater and a pilot

plant study can be conducted with real-life wastewater sample by application of derived data of present study. In the future scope of the study, microbial genomics study including phosphate removal aspects would be also considered. The influence of Solid Retention Time (SRT) should be explored also. A real-time kinetics profile with automatic data plotting could be derived for explaining the process in more rational way. It is also suggested that optimization of the process and operation variable may be examined with soft computing tools using various statistical approach.

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