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Microbial kinetic analysis of a hybrid UASB reactor

Oktem Y.A.*
Istanbul University-Cerrahpasa, Faculty of Engineering, Department of Environmental Engineering, 34320, Turkey
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*to whom all correspondence should be addressed: e-mail: oktemy@istanbul.edu.tr
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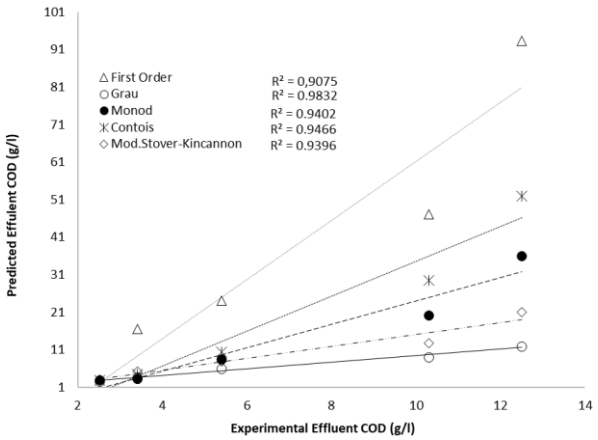
Graphical abstract



Abstract

Microbial kinetics of a hybrid upflow anaerobic sludge blanket (UASB) reactor were investigated when treating chemical synthesis–based pharmaceutical wastewater. Mathematical kinetics models have been tested with strong wastewater to reveal the relationship between substrate utilization rate and microbial population dynamics, depending on the hydraulic structure of the reactor. The data were collected for use in these models by operating at mesophilic temperature (37 ± 1°C), pH 6.8-7.2, at different HRT (3-0.17 days) at high OLR values from hybrid UASB. Monod, First-order, Grau second-order, Modified Stover-Kincannon, kinetic models were applied to the hybrid reactor. Grau second-order model and Modified Stover-Kincannon were found to be the most appropriate models for the hybrid UASB (R^2=0.99) and offers the best description of the process. The substrate removal rate constant (k_{2S}) was found to be 3.43 d^{-1} for Grau ve maximum substrate consumption rate (R_{max}) 1.016 g l^{-1}-day for Modified Stover-Kincannon.

Keywords: Hybrid UASB, microbial kinetic, anaerobic, Grau-second order, modified Stover Kincannon.

1. Introduction

Chemical synthesis-based pharmaceutical wastewater has a high chemical oxygen demand (COD) and a variable concentration of salts. Many researchers have tried different conventional methods for wastewater treatment such as biological oxidation, physico-chemical process; carbon bed adsorption, coagulation/flocculation, membrane separation, electrochemical treatment and oxidation etc. (Sakumoto and Miyata, 1984; Shubham *et al.*, 2020). But the reduction in the level of toxicity using these methods have been not meet the environmental regulations especially for the complex effluents (Chandak *et al.*, 2020). High rate reactors such as, upflow anaerobic sludge blanket (UASB) reactor or anaerobic filter (AF) have been successfully applied to the treatment of a wide variety of industrial wastewaters; pulp-paper liquor(Ahn and Forster, 2002), spent sulphide liquors (Jantsch *et al.*, 2002), swine wastewater (Perla *et al.*, 2020), chemical synthesis-based pharmaceutical wastewater (Oktem *et al.*, 2007), oilfield wastewater (Zhang, 2020), food industry wastewaters (Berardino *et al.*, 2000; Tsui *et al.*, 2020) and strong industrial wastewaters (Fernândez *et al.*, 2001; Shivayogimath and Ramanujam, 1999). The fundamental way to maintain optimum operating conditions of anaerobic digestion systems is to have a well understand the dynamic behaviours of the process. Therefore, a well-defined mathematical model of the process can be very useful from observing and estimating state of the process (Senturk *et al.*, 2013). Addition, mathematical models based on process kinetics can be used to understand the underlying biological and transport mechanisms also (Acharya *et al.*, 2011). Using kinetic model is a generally accepted approach in showing the system performance. Therefore, kinetic models can be used to find treatment performance of anaerobic digesters without real time operated. Process kinetics is essential tool for the improvement of treatment efficiency of biologically systems. It provides a rational basis for process analysis, control, and design, as well as relating with operational and environmental factors affecting substrate utilization rates (Alavi *et al.*, 2016; Andualem *et al.*, 2017; Feng *et al.*, 2020; Mengcheng, 2020; Saberia *et al.*, 2017). microbial kinetic studies reported in the literature have been for various types of reactors and wastewaters (Abtahi *et al.*, 2017; Tomar and Gupta, 2016; Zhou *et al.*, 2017). However, there is still lack of information in literature concerning substrate utilization rate, mo population dynamic and treatment efficiency at hybrid UASB reactors. OLR effect on the processes of substrate utilization, population dynamics,

etc. of microorganisms in hybrid UASB are of great importance. In this study, therefore, biokinetic models were tested at different OLR and HRT's at the hybrid UASB reactor.

2. Materials and methods

2.1. Hybrid UASB reactor

The lab-scale experiment was performed to assess the digestion ability of UASB system at different operating conditions. Reactor was designed and operated as an upflow anaerobic reactor with batch feeds. The reactor was made of glass that is sealed, has a working volume of 4 litre, and connected to the gas collecting bottle with a rubber tube. The environment and operating conditions of the reactor have been determined in accordance with anaerobic mo population. The pH of the reactor was controlled automatically at 6.8-7.2 by adding 1 N NaOH and 1 N HCL. The top half part of the reactor was filled with polypropylene pall rings (internal diameter, 25 mm; density 70 kg m^{-3}, and specific surface area, 206 m^2 m^{-3}). The reactor was placed in a water bath where the temperature is 37±1°C using a temperature controller. The temperature in the reactor was adjusted by an external, thermostatically controlled, hot water jacket.

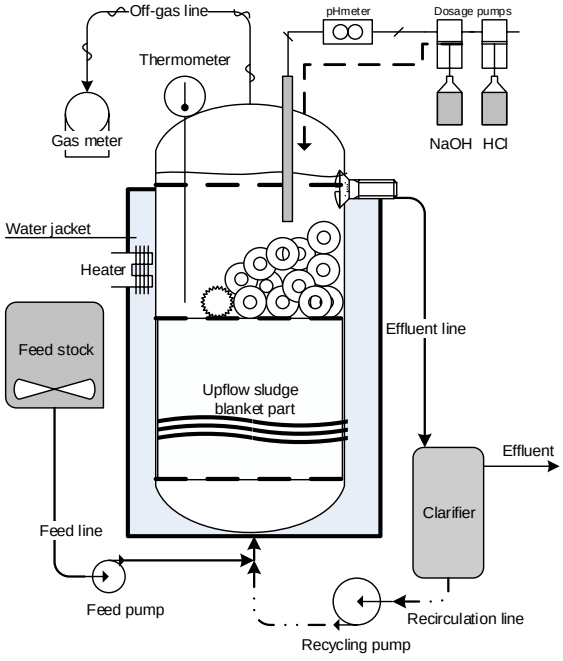


Figure 1. Hybrid UASB reactor (hUASB)

2.2. Wastewater and seed sludge

The wastewater was taken from a local chemical synthesis–based pharmaceutical facility. The general characteristics of the wastewater are given in Table 1. The hybrid reactor was seeded with an inoculation sludge taken from a UASB reactor treating effluents from a local alcohol distillery. The hybrid reactor was seeded inoculation granular sludge taken from the UASB (20% v/v). The reactor was then flushed with nitrogen gas for a period of 15 min in order to purge gaseous oxygen from inside the reactor.

Table 1. Characteristics of the chemical synthesis–based pharmaceutical wastewater (Oktem, 2004)

Parameter	Range
pH*	6.9-7.6
Total COD (mg L^{-1})	15000-51000
TSS (mg L^{-1})	6360-14900
NH_3-N (mg L^{-1})	100-120
TKN (mg L^{-1})	825-910
PO_4-P(mg L^{-1})	<1
C/N	18-56 (33)
BOD_5	3200-35600

**Unitless*

2.3. Analytical procedure

During the operation of the hybrid reactor, routine analyses were carried out determined. Biogas production, pH, alkalinity, volatile fatty acids (VFAs), TS and TVS, pH, total Kjeldahl nitrogen (TKN), ammonia nitrogen (NH_3–N), orthophosphate phosphorus (PO_4–P), alkalinity, and suspended solids (TS) such as parameters' analysis were carried out in accordance with to Standard Methods (APHA, 2017). Total solids (TS) and total volatile solids (TVS) parameters were used instead of suspended solids (SS) and volatile suspended solids (VSS) due to the granular characteristics of the sludge. The TS concentration of the seed sludge was approximately 100 g/l of which about 96% was TVS (Oktem, 2004). Effluent wastewater samples were centrifuged at 12000 rpm, and the soluble chemical oxygen demand (sCOD) concentration of the supernatant was measured. Chemical oxygen demand (COD) (5220 D-Closed Reflux, Colorimetric Method), 5-day biological oxygen demand (BOD-5210 B. 5-Day BOD Test) were analyzed according to Standard Methods (APHA, 2017). To determine Volatile Fatty Acids (VFAs), samples was centrifuged at 9900 rpm and 4°C for 20 min after well shaken. Supernatant was filtered through filter membrane filter, 0.22 μ_m pore size 47 mm diameter. The sample was used for analysis of soluble substances. 3% phosphoric acid solution was added to the filtrate to avoid degradation at a volume ratio of 1:9 for the analysis of volatile fatty acids (VFAs). Short Chain Fatty Acids (SCFA C2-C6) were measured using a HP Model 5890 Series II Gas Chromatograph (GC) (HP FFAP Column, 10 m/530 mm/1 mm) with used nitrogen as carrier.

2.4. Reactor operation

The C/N ratio, among other factors, should be set out at hold safety range to ensure process stability. The appropriate C/N ratio for effective metabolic processes of anaerobic microbial groups is in the 20-30 range (Athanasoulia *et al.*, 2012). The range for chemical synthesis-based pharmaceutical wastewater has been determined as 33. Solids retention (SRT) was achieved through control of the upflow velocity (UV) in the reactor, which was effected by control of the effluent recirculation flow rate. As stated in the previous study, the upflow speed was chosen as 0.5 m/h to ensure better contact of sludge and wastewater (Oktem *et al.*, 2007; Yue *et al.*, 2020). Macro nutrients (nitrogen and phosphorus as $(NH_2)_2CO$ and KH_2PO_4, respectively) were added to the nutrient balance in the feed solution according to the C:N:P ratio of 400:5:1.

The results obtained for steady state conditions during reactor operation at five different HRTs was used at kinetic models. The ratio of BOD_5/COD was determined that is almost same other reported studies with pharma wastewaters (Boroski *et al.*, 2009; Chen *et al.*, 2011; Farhadi *et al.*, 2012). Special feeding strategy was used in order to obtain a better reactor performance and allow microorganisms for acclimate to wastewater. It was recommended reported studies that start-up periods for treatment of pharmaceutical wastewater should be carried out with gradual replacement of readily degradable substrate. Therefore, in many experimental studies glucose was commonly used (Stronach *et al.*, 1986). The hybrid reactor was initially fed with glucose at an OLR of 5.8-6.2 kg COD m^{-3} d^{-1} with a hydraulic retention time (HRT) of 1-3 days. Then, with wastewater, up to 104.7 kg COD m^{-3} d^{-1} load was reached, in this process, HRT was between 0.17 - 3 days. For the alkalinity support to the reactor was added $NaHCO_3$.

2.5. Kinetic models

Modeling methods are useful tools for describing and predicting the performance of anaerobic treatment systems. There are various models for predicting effluent substrate concentrations in anaerobic treatment systems, including Monod (Monod, 1949), Contois (Contois, 1959), Grau second-order (Grau, 1975), Grau, and Stover-Kincannon Modified (Stover and Kincannon, 1982). The input data to all these models should be taken form at steady-state condition of reactor. In a recirculated UASB reactor, the rate of change of biomass and substrate is shown in the following equations (1 and 2).

$$V\frac{d_s}{d_t} = QS_0 + Q_rS - \frac{\mu.X}{Y} \quad (1)$$

$$V\frac{d_x}{d_t} = QX_0 + Q_rX_e + \mu X - k_dX \quad (2)$$

where X_0, X and X_e are the concentrations of biomass in the feed, reactor and effluent respectively (g VSS l^{-1}); Q is the inflow rate (l day^{-1}); V is the reactor volume (l); μ is the specific growth rate (d^{-1}); K_d is the death rate constant (d^{-1}); S_0 and S are the substrate concentrations in the feed and effluent (g COD l^{-1}); Y is the yield coefficient (g VSS g COD^{-1}). The ratio of the total biomass in the reactor to biomass wasted per given time represent the average time called as mean cell-residence time (Θc) and calculated from the equation (3) for AHR.

$$\theta_C = \frac{V.X}{Q.X_e} \quad (3)$$

2.6. Monod model

The relationship between the specific growth rate and the rate limiting substrate concentration can be expressed by the Monod (5) and Contois (6). In the Monod model, the concentration changes rate of substrate is expressed by equation 1. Using equation 3, the concentration of the substrate at the effluent (4) can be calculated.

$$\mu = \frac{\mu_m S}{K_s + S} \quad (4)$$

$$\mu = \frac{\mu_m S}{\beta.X + S} \quad (5)$$

If it is assumed that the concentration of biomass in the influent can be neglected at steady-state conditions and HRT (Θ_H) is defined as the volume of the reactor divided by the flow rate of the influent, following equations can be obtained by substituting and rearranging equations (3) and (4) into equations (1) and (2);

$$\mu = \frac{1}{\theta_c} + K_d \quad (6)$$

$$\mu = \frac{1}{\theta_c} = \frac{1}{\theta} = \frac{\mu_m S}{(K_s + S)} - k_d \quad (7)$$

The kinetic parameters Y and K_d for Monod model can be obtained equations (8) by rearranging equations and plotting Figure 2 as shown below:

$$\frac{S_0 - S}{\theta H.X} = \frac{1}{Y}.\frac{1}{\theta c} + \frac{K_d}{Y} \quad (8)$$

The values of μmax and K_S were determined from Figure 3 by plotting equation (9), which was derived by rearranging equation (7).

$$\frac{\theta c}{1 + \theta c.k_d} = \frac{K_S}{\mu_{max}}.\frac{1}{S} + \frac{1}{\mu_{max}} \quad (9)$$

2.7. Grau second-order kinetic model

The general expression for Grau second-order kinetics is given as follows (10), and the prediction of the substrate concentration at the effluent is given in equation 11.

$$-\frac{d_s}{d_t} = k_{2(S)}.X(\frac{S}{S_0})^2 \quad (10)$$

$$S = S_0\left(1 - \frac{\theta}{a + b\theta}\right) \quad (11)$$

where, $k_{2(S)}$: substrate removal rate constants. If equation 11 is integrated and linearized, then equation 12 will be obtained,

$$\frac{S_0\theta}{S_0 - S} = \theta + \frac{S_0}{k_{2(S)}.X} \quad (12)$$

Here, θ is the hydraulic retention time. If the second part of the equation is accepted as constant and first part of the equation is the substrate removal efficiency that will be obtained.

$$\frac{S_0\theta}{S_0 - S} = a + b\theta \quad (13)$$

$$\frac{\theta}{E} = a + b\theta \quad (14)$$

2.8. Contois model

By substituting equation (5) instead of the Monod equation into equations (2) and (15) can be obtained:

$$\mu = \frac{1}{\theta_c} + k_d \quad (15)$$

$$\frac{\theta_c}{1+\theta_c.k_d}=\frac{\beta}{\mu_m}.\frac{X}{S}+\frac{1}{\mu_m} \quad (16)$$

If equation 16 is arranged, β and μ_m are obtained from Figure 7 and the reactor effluent substrate concentration estimate can be expressed by equation (17).

$$S=\frac{\beta X(1+k_d\theta_c)}{\mu_m\theta_c-(1+k_d\theta_c)} \quad (17)$$

2.9. Modified Stover Kincanon model

Stover-Kincannon model has been used successfully various wastewater types in specially attached growth reactors (Faridnasr *et al.*, 2016; Kordkandi and Berardi, 2015; Noroozi *et al.*, 2014; Wang *et al.*, 2015). The M Stover - Kincannon model, developed for use in biofilm reactors, has yielded successful results in studies (Sandhya and Swaminathan, 2006). That model recognizes that based on mono-molecular kinetics, substrate utilization rate and organic matter loading rate can be correlated. Substrate removal can be shown in the following two forms.

$$\frac{d_S}{d_t}=\frac{Q(S_0-S)}{V} \quad (18)$$

$$\frac{dS}{dt}=\frac{U_m(^{QS_0}/_V)}{k_2+{}^{QS_0}/_V} \quad (19)$$

This equation can be linearized in the following form:

$$\left(\frac{dS}{dt}\right)^{-1}=\frac{V}{Q(S_0-S)}=\frac{k_BV}{R_{max}QS_0}+\frac{1}{R_{max}} \quad (20)$$

Where dS/dt is the substrate removal rate (g L^{-1} d^{-1}), R_{max} is the maximum utilization rate constant (g L^{-1} d^{-1}), K_B is the saturation value constant (g L^{-1} d^{-1}), Q is the flow rate (L d^{-1}) and V is the effective volume of reactor (L). Since dS/dt approaches R_{max} as the organic loading rate, qS_0/V approaches infinity. Then, by this equation, equation 33 is obtained to predict the effluent substrate concentration of the reactor.

$$S=S_0\frac{R_m(S_i)}{K_B+{}^{QS_0}/_V} \quad (21)$$

2.10. First order substrate removal model

The hydrolysis of organic pollutants was described by first order kinetics model. The mass balance equation for the substrate in the anaerobic system can be described as follows:

$$\frac{ds}{dt}=\frac{Q}{V}.S_0-\frac{Q}{V}.S-k_1.S \quad (22)$$

where, S_0 is substrate concentration in the influent (g l^{-1}): Se is substrate concentration in the effluent; Q is flow rate of influent to reactor (l d^{-1}); V is effective volume of the reactor and k_1 is first-order kinetic constant (per day). Under steady state conditions, (ds/dt)=0 and the above equation can be represented in the following form:

$$\frac{Q}{V}.(S_0-S)=k_1.S \quad (23)$$

3. Results and discussion

This study was carried out to determine of a hybrid UASB reactor' kinetic constants over two months of operation. Table 2 was prepared using experimental results for plot of kinetic models. Biokinetic models including Monod, Stover-Kincannon, Grau, second-order, etc. were applied to find the most suitable biokinetic model to describe the hybrid reactor.

3.1. Monod kinetic model

Five steady state sets of experimental data were used to determine the kinetic parameters. Figure 2 was plotted from equation (8) for determining the values of Y and K_d for Monod model and the corresponding values were 0.0095 g VSS $gCOD^{-1}$ and 0.00115 day^{-1}, respectively with high regression coefficient (R^2=0.9535). The decay coefficient value, Kd which was lower than the reported value (Hwang *et al.*, 1992; Singh and Ohja, 2002) might be due to low amount decay of cells. However, The higher yield coefficient obtained in the present investigation could be attributed to relatively larger proportion of biodegradable organic waste (disolved organic subtances) in pharmacetical wastewater. In general, the model parameters are specific to the configuration and operational mode of the reactor. Figure 3 was plotted from equation (9) for determining the values of μ_{max} and K_S for Monod model and the corresponding values were 0.017 d^{-1} and 16793 mg COD l^{-1}) day, respectively with high regression coefficient ($R2$=0.99).

Table 2. Experimental data for determining kinetic constants

Experimental setup	1	2	3	4	5
Feed (l day^{-1})	0.0272	0.0093	0.0047	0.0023	0.0016
COD Feed (mg L^{-1})	15400	15430	15400	15520	15225
Total gas yield (L g COD^{-1}-day)	0.47	0.44	0.39	0.37	0.3
Methane (%)	80	75	74	75	76
Methane Yield (L g COD^{-1}-day)	0.33	0.30	0.28	0.26	0.2
MLSS (kg m^{-3})	12.8	16.3	21.4	22.4	22.4
MLVSS (kg m^{-3})	7.53	9.32	11.90	12.70	12.90
HRT (day)	0.17	0.5	1	2	3.0
SRT (day)	28	50	120	310	580
OLR (kg COD m^{-3}-day)	104.76	35.98	17.99	8.99	6.03
SSUR (gCOD $gVSS^{-1}$-day)	0.120	0.412	1.057	2.294	3.615
SUR (gCOD $gVSS^{-1}$-day)	0.71	0.82	1.06	1.15	1.21
COD Removal (%)	0.30	0.3	0.70	0.81	0.86

Table 3 Comparison of kinetic constants in the *Modified Stover-Kincannon* model

Types of wastewater	Reactor	K_B (g COD l^{-1})	R_{max} (g l^{-1} d)	References
Chemical-based Pharmaceutical wastewater	hUASB	0.0247	1.016	This study
Pharmaceutical wastewater	AHR	115.66	108.69	(Pandian *et al.*, 2011)
Formaldehyde containing wastewater	UAFB	4.6	3.4	(Priya *et al.*, 2009)
Corrugated paper wastewater	AF	3.86	0.80	(Ahn and Forster, 2002)
Soybean wastewater	AF	83.3	85.5	(Yu *et al.*, 1983)
Simulated wastewater	MBBR	9.45	8.3	(Borghei and Hosseiny, 2002)
High-strength wastewater	UA-MBR	34.14	33.78	(Burman and Sinha, 2020)
Textile wastewater	UAFR	45.37	31.69	(Sandhye and Swaminathan, 2006)
Textile wastewater	Pilot UASB	16,12	23,17	(Gnanapragasam *et al.*, 2017)

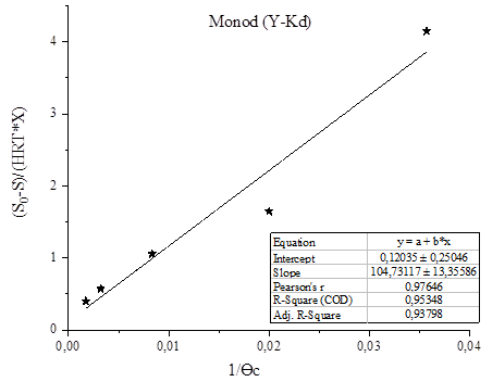


Figure 2. Monod model plot for (*Y*) and decay rate (K_d) constant

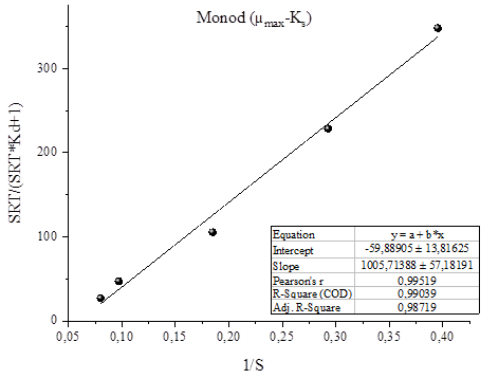


Figure 3. Monod model plot for (μ_{max}) and half saturation constant (K_S)

3.2. Modified Stover-Kicannon model

The maximum utilization rates increase the reactor efficiency. Stover- Kicannon model suggested that the substrate removal rates (COD_{rem}) were affected by the organic loading rate entering the reactor. Saturation value constant (K_B) and maximum utilization rate (R_{max}) were calculated from Figure 4 as 1,016 g COD l^{-1}-d and 0,0247 g COD l^{-1}-d with high regression coefficient (R^2=0.99). From R^2 value (Figure 4), the experimental data are found to align with this model. The R_{max} and K_B values obtained in this study were lower than values found by other studies (Table 4).

3.3. First order substrate removal model

The value of k1 was obtained from the slope of the line by plotting S_0-S/HRT versus S (Figure 5) in equation (23) with the low regression coefficient of 0.845. k_1 is first-order kinetic constant and was calculated from Figure 5 as 2,16 per day.

3.4. Grau second-order multicomponent substrate removal model

If equation (10) is integrated and then linearized, equation (14) will be obtained of *a* and *b* (dimensionless Grau second-order constant) were calculated from the intercept and slope of the straight line on the graph (Figure 6) as 0.503 and 0.9919 respectively, with high correlation coefficient (R^2) of 0.9916. The multicomponent Grau second-order substrate removal rate constant (k_{2S}:3.43 l d^{-1}) was calculated from the equation $a=S0/(k_S.X)$ (Table 4). Table 5 shows the constants determined in the previous studies using the Grau second order model. The possible reasons for the differences might be due to variation in reactor configuration, wastewater characteristics and microorganisms used in the study.

3.5. Contois kinetic model

Specific growth rate μ_{max} and kinetic parameter β coefficients were determined by using the data in Table 2 in the equation 16. these kinetic parameters, μ_{max} and β were calculated from the intercept and the slope of the straight line as 0.040 d^{-1} and 2.79 gCOD g VSS^{-1}, respectively.

Table 4. Calculated $k_{(2)S}$ values of the Grau second-order kinetic model

Θ (HRT) day	S_0 (g/l)	S (g/l)	X_0 (g VSS l^{-1})	X (g VSS l^{-1})	E(%)	$k_{2S}=S_0/a*X$
3	18,075	2,53	12,40	12,90	0,860	2,79
2	17,980	3,42	12,43	12,70	0,810	2,81
1	17,985	5,41	12,42	11,90	0,699	3,00
0,5	17,990	10,31	12,44	9,32	0,427	3,84
0,17	17,810	12,50	12,43	7,53	0,298	4,70
				(Avg) k_{2S}	**3,43**	

Table 5. Comparison of kinetic constants in the *Grau-second order* model

Types of wastewater	Reactor	a	b	k_{2s}	References
Pharmaceutical wastewater	hUASB	0,503	0,9919	3,43	This study
High-strength wastewater	An-HBR	0,517	0,838	0,53	(Burman and Sinha, 2020)
Textile dyeing wastewater	UASB	0,197	1,422	0,418	(Gnanapragasam *et al.*, 2017)
Simulated wastewater	MBBR	0,562	1,095	0,337	(Borghei and Hosseiny, 2002)
Formaldehyde containing wastewater	UAFB	0,64	9,36	3,2	(Priya *et al.*, 2009)
Seafood wastewater	UASB	0,27	1,009	1,3	(Jijai *et al.*, 2016)
Synthetic wastewater	UASB	0,558	1,043	0,8	(Puspendu and Ghangrekar, 2008)
Industrial wastewater	UASB	0,583	2,023	0,163	(Abtahi *et al.*, 2013)

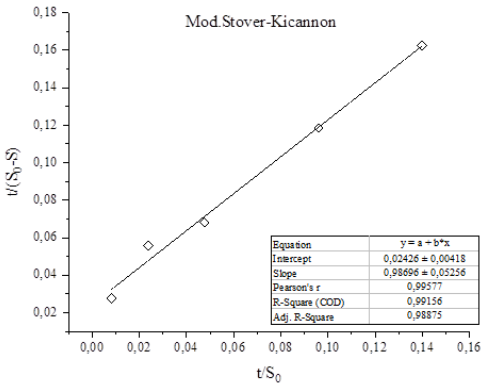


Figure 4. Modified Stover-Kincannon model plot for (R_{max}) and saturation constant (K_B)

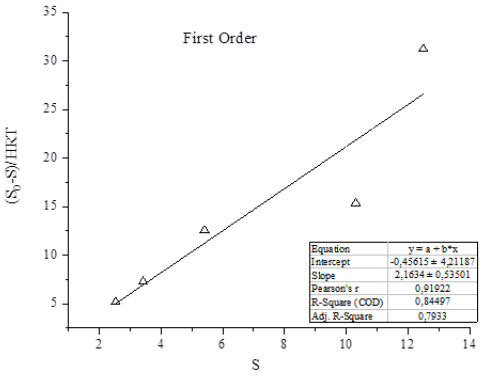


Figure 5. First order model plot for kinetic constant (k1)

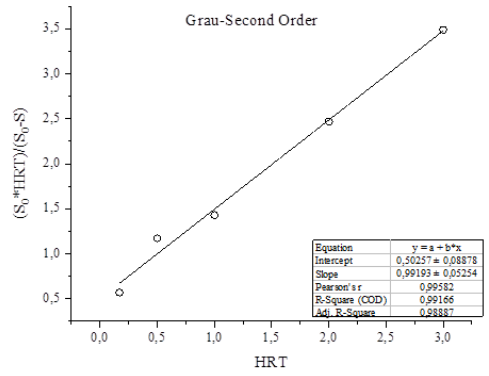


Figure 6. Grau **s**econd-order model for kinetic constants

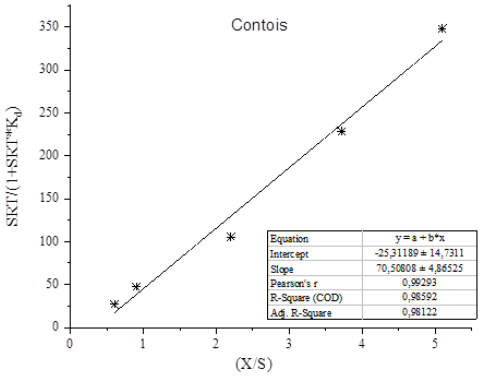


Figure 7. Contois model for kinetic constants

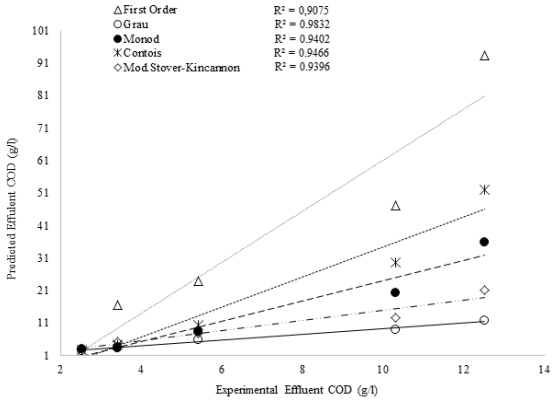


Figure 8. Comparison of predicted and experimental effluent COD

3.6. Prediction and validation

Validity of the models is the results obtained from the experimental effluent COD values were compared with the predicted values obtained from the models.The highest correlation of the modelling was determined Grau second-order (R^2: 0.98) and Contois (R^2: 0.99) kinetic models. But predicted values by models have different correlations. It could be think that predicted results are in good agreement with the experimental data in case of Grau second-order and Contois models Figure 8. The Monod, Mod.Stover-Kincannon and First Order models which have lower regression coefficient than others has not been suitable for predicting the COD values.

Among these, Modified Stover-Kicannon and Grau models gave the highest correlation coefficients, 99% and 99 % respectively. The substrate removal rate constant k_{2S} was calculated using different conditions at steady-state conditions and were shown in Table 5. As seen in the table, k_{2S} was determined 3,43 d^{-1} for hybrid UASB reactor. In the literature, kinetic studies conducted in UASB for the treatment of chlorinated ethane-containing wastewater indicated that this value varied between 1.12 and 7.53 d^{-1} (Basu and Asolekar, 2012). Figure 6 was plotted using the experimental data given in Table 2. The (a) and (b) values were calculated as 0.503 and 0.9919 respectively with the correlation coefficient (R^2=0.991). In a literature study, these values *a* and *b* were found to be 0.197 and 1.42 respectively during the treatment of textile dyeing wastewater in the UASB reactor (Gnanapragasam *et al.*, 2017). These values for UASB reactors is so close each other. Kinetic coefficients for Grau model at Different studies was illustrated in Table 6. Modified Stover-Kincannon is high correlation other model for this study also. By applying the Stover-Kincannon model which has high correlation, to the experimental studies, kinetic assessment was carried out. The value of K_B can be calculated from the intercept of the straight line and R_{max} can be obtained from the slope line of Figure 4. R_{max} and K_B were found to be 1,016 (g l^{-1} d) and 0.0247 (g COD^{-1}l) respectively. It is noteworthy that the Stover-Kincannon model have much lower kinetic (saturation constant (K_B) and maximum substrate consumption rate (R_{max}) than many studies in the literature. In studies conducted with toxic pharmaceutical wastewater, etc., such values are frequently encountered (Priya *et al.*, 2009). In addition, although the Monod equation has a high correlation, μ_{max} has a negative value. Figure 2 indicates negative Ks value with regression coefficient of 0.9904. Converti *et al.* (1999) reported that these constants can be attributed to the maximum degree of degradation of negative values. Since this issue could not be fully explained, the Monod equation and First order substrate removal kinetic equation were able not evaluated due to the relatively low correlation. Kinetic values of Grau model agree well with the values given in literature. As can be seen, applying Grau model's coefficients slightly lower values than reported in literature. Because wastewater contains a soluble substrate, the time for the substrate to hydrolyze is short. Chemical synthesis–based pharmaceutical wastewater includes important amount solvents, soluble substances, volatile fatty acids, heavy metals and toxic substances etc than other processes of pharmaceutical wastewater. Therefore, the substrate removal rate is a a little bit low. Studied with pharmaceutical wastewater, obtained coefficients from kinetic models may be change continously.

4. Conclusion

The Grau second-order model has given similar results in studies with wastewaters comparable to chemical synthesis wastewaters. In the literature, kinetic evaluations have been usually performed on the Stover-Kincannon model, in this study have a high correlation in the reactor also. The Grau second-order model for biofilm-suspended culture reactors seems more appropriate when the substrate removal efficiency is predicted in this type of wastewater containing highly dissolved organic matter.

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Abbreviations

Q: Inflow discharge to reactor (L/d)

V: Reactor volume (L)

S: Influent substrate concentration

S: Effluent substrate concentration

X: Total biomass concentration in reactor (g VSS/L)

X_0: Influent biomass concentration (g VSS/L)

Xe: Effluent biomass concentration (g VSS/L)

Θ_H: Hydraulic retention time (d)

Θ_C: Solids retention time (d)

Y: yield coefficient (g VSS/g COD)

K_d: Endogenous decay coefficient (d^{-1})

μ: Specific growth rate (d^{-1})

μ_{max}: Maximum specific growth rate (d^{-1})

Ks: Half-velocity constant (g COD/L)

K: Maximum substrate consumption rate in microorganis mass (g COD/g VSS.d)

β: Synthetic constant of Contois model (g COD/g VSS)

k_2 (S):Substrate removal rate of second-Order Grau model, Monod model (d^{-1})

α: Equals $S_0/K_2(S).X$ (g COD.d/g VSS)

b: Without unit

K_B: Saturation constant (g COD/L.d)

R_{max}: Maximum substrate consumption rate (g COD/L.d)

SSUR: Spesifik substrat Utilization rate (kgCOD/kgVSS.day)

SUR: Substrat utilization rate (kgCOD/kgVSS.day)

k_1: Kinetic constant for first order substrat removal model (gCOD/gSS.day)

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