

Kinetics of aerobic biodegradation of organic pollutants in moving bed biological reactor (MBBR)

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Received 20 August 2016; Accepted 21 October 2017

ABSTRACT

The main problem of sugar manufacturing plants is the production of high volumes of wastewater. In the last decades, the usage of chemical oxidation methods has gained importance to treat this type of waste water. Nowadays, the usage of biological technologies such as fixed and moving bed reactors has widely developed, being less expensive and more environmental friendly alternative. In this study, the process of kinetics of a lab-scale aerobic moving bed biological reactor (MBBR) by using simulated sugar-manufacturing wastewater as feed was investigated. The MBBR was consisted of a 30-L reactor filled with moving bed biofilm plastic particles (Kaldnes carriers K1). The MBBR was tested under different organic loads and different hydraulic retention times (HRT). The experimental substrate loading removal rate was compared with those estimated in the first order model, second-order (Grau) model, and Stover-Kincannon substrate removal model. After obtaining steady-state condition, organic loading rate was increased from 978 to 2615 g COD m⁻³ day and hydraulic retention time was decreased from 10 to 4 h, to resemble wastewater from sugar production lines. Ten different operational conditions were applied through changing these two parameters in a certain program. The results shown that the second-order removal model (Grau) and Stover-Kincannon model were demonstrated to be the most compliant models for this reactor. Therefore, these models were found applicable in predicting the behavior or design of the MBBR systems.

Keywords: Kinetic model; MBBR; Wastewater; Stover Kincannon; Grau; First order; Second order

1. Introduction

A significantly large volume of waste is generated during production of sugar and it contains a high amount of pollution load, particularly in terms of suspended solids, organic matter, press mud, bagasse and air pollutants. Several chemicals methods are used in sugar industries mainly for coagulation of impurities and refining of end products [1]. For example, SO₂ is bubbled through the defected raw sugar to remove color or lead. These methods, which are contributing towards increasing the organic strength, dissolved solid and suspended matter. On the other hand, a

variety of methods have been used to remove or reduce the concentration of organic compounds in industrial waste water among them, precipitation and coagulation, surface adsorption, ion exchange, advanced oxidation such as Fenton, aerobic biological methods as active sludge, and anaerobic biological methods could be highlighted. Thereby, the development of new biological processes has attracted extensive attention [2–8].

In this investigation, an aerobic moving bed biological reactor with Kaldnes carriers was used for treatment of the sugar manufacturing waste water. The MBBRs have gained much favor in recent years for organic waste water treatment due to their high performance, small volumes, low maintenances and operational costs [9,10].

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Nowadays, many advanced oxidation processes such as photocatalytic oxidation [11], Fenton [12–14], Photo-Fenton [15] and ozone oxidation [16–21] have been used to decolorize, detoxify and enhance the biodegradability of wastewater.

In addition, many different models for the biomass growth processes have been introduced in the wastewater treatment literature [22–24]. Generally, global parameters such as COD were used as a substrate for evaluation under assumption that the removal was exclusive due to aerobic biodegradation [25]. First order substrate removal model, Stover and kincannon model and second-order model (referred as optaken, Grau model) are some of those ones which were used to test the kinetics of organic removal in MBBR system of this work [26–29].

The main idea of this study was to determine the process kinetics of aerobic treatment and to compare kinetics among the models applied for the substrate removal of MBBR reactor.

2. Methodology

2.1. Sugar-manufacturing synthetic wastewater

The sugar-manufacturing synthetic wastewater, which was employed in this study, consisted of beet sugar molasses with tap water and some added materials resulting in a ratio of COD/N/P = 100/5/1. The initial parameters which were mentioned in Table 1 and were preserved at 22°C until used. The laboratory reagent (LR) grade chemicals were used in the experiments and the analytical grade (AR) chemicals were used for analysis. These LR and AR grade

chemicals were obtained from Merck chemical Ltd. The wastewater was prepared at various COD concentrations in the range between 978 and 2615 mg COD L⁻¹. Each gram of molasses used for preparing synthetic wastewater had a COD concentration equal to 978 mg L⁻¹.

2.2. MBBR reactor

The experiments were performed in lab-scale MBBR (Fig. 1). The reactor was fabricated from Plexiglas with an internal cross section of 24×25 cm and an external cross section of 25×26 cm, and a height of 60 cm. The effective height of the reactor was 50 cm. The total volume of the MBBR was 36 L. Wall thickness of reactor Plexiglas was 5 mm.

2.3. Kaldnes carriers K1

The reactor was filled with moving bed biofilm supports which were Kaldnes carriers K1 plastic particles. The Kaldnes carriers used in this research which were prepared from Norway (Fig. 2). The diameter and the length of these particles are 7 and 10 mm, respectively. Due to their microscopic structure, particles have a relatively high specific surface area.

Kaldnes carriers have also been tested and used in various environmental applications (mainly as an adsorbent) and for filtration media due to biological growth capability. Kaldnes carriers have 9.1 nominal diameters with a length of 7.2 mm and density of 150 gm⁻³. The specific surface area of Kaldnes carriers is 500 m² m⁻³.

About 50% of MBBR reactor volume was filled with Kaldnes carriers K1. Laboratory experiments were con-

Table 1
Composition of sugar-manufacturing synthetic wastewater (100 ppm)

Chemical parameter	Parameter value
pH	7.2
Electrical conductivity, mS/m	1.57
TOC, mg/L	29
Color, U	2.6
T-N, mg/L	1.19
NH ₄ -N, mg/L	0.19
NO ₂ -N, mg/L	1.00
PO ₄ -P, mg/L	1.41
Ammonia-nitrogen, mg/L	13.2
F ⁻ , mg/L	0.12
Cl ⁻ , mg/L	3.75
SO ₄ ²⁻ , mg/L	3.53
Na ⁺ , mg/L	1.95
K ⁺ , mg/L	5.82
Mg ²⁺ , mg/L	0.33
Ca ²⁺ , mg/L	0.64
COD, mg/L	978

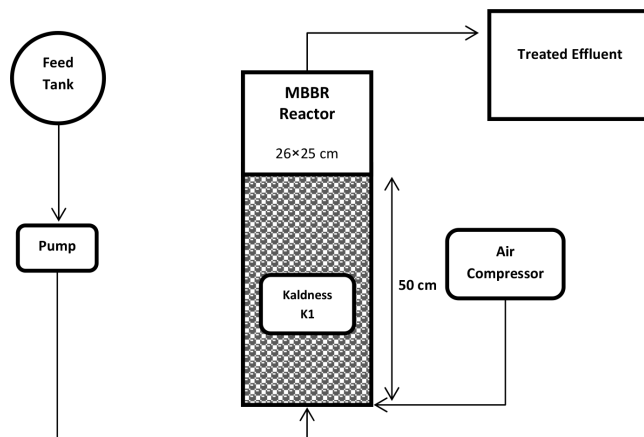


Fig. 1. Schematic view of MBBR Reactor.



Fig. 2. Schematic view of K1 Kaldnes carriers.

ducted at room temperature ($22 \pm 2^\circ\text{C}$) and under controlled condition of dissolved oxygen (DO) concentration above $3.0 \text{ mg O}_2/\text{L}$. For removing the excessive biomass which might cause clogging in the system, the reactor was washed once a week by excess air flow for 5 min.

This reactor operated in upward mode by using a peristaltic pump with a flow rate of 70 L h^{-1} to feed waste water from the bottom. An air compressor in liquid phase over the bed provides dissolved oxygen to biomass through continuous recycle at 60 L h^{-1} . The reactor was kept in a controlled temperature chamber of 24°C . During the period of test operation, COD, pH and DO were measured at the influent and effluent from the MBBR system. Analytical procedures followed in this research for COD, pH and DO, determinations were from those outlined in standard methods for examination of water and waste water [30]. It should be noted that the influence of pH was investigated for COD removal from waste water. Results have shown that the best performance was achieved with increasing of $\text{pH} > 8$ [31].

2.4. Theoretical development

In order to determine the performance behavior of the biological reactors, following simplified models, containing a smaller number of variables were investigated:

2.4.1. First-order substrate removal model

The rate of change of substrate concentration in the complete mixed system can be illustrated using the following first order equation:

$$\frac{-dS}{dt} = \frac{QS_i}{V} - \frac{QS_e}{V} - k_1 S_e \quad (1)$$

Since the rate of change of substrate concentration ($-dS/dt$) is negligible under pseudo-steady-state conditions, the equation can be derived as:

$$\frac{(S_i - S_e)}{\theta_H} = k_1 S_e \quad (2)$$

where V is the reactor volume (L), θ_H is hydraulic retention time (d), S_i and S_e are substrate concentration in the feed and effluent (mg COD L^{-1}), Q is inflow rate (L/d), and finally k_1 is first order kinetic constant (per day).

2.4.2. Grau second-order substrate removal model

The general equation of a second-order model is illustrated as below:

$$-\frac{dS}{dt} = k_2 X \left(\frac{S_e}{S_i} \right)^2 \quad (3)$$

The above equation can be expressed as follow via integration and linearization steps [32]:

$$\frac{(S_i \theta_H)}{(S_i - S_e)} = \theta_H + \frac{S_i}{(k_2 X)} \quad (4)$$

If $S_i/(k_2 X)$ is considered as a constant (a) and $(S_i - S_e)/S_i$ can be replaced by the substrate removal efficiency (E), and therefore, Eq. (4) can be modified as [33]:

$$\frac{\theta_H}{E} = a + b\theta_H \quad (5)$$

where k_2 is second order kinetic constant (per day).

2.4.3. Stover–Kincannon model

The Stover–Kincannon model is described by the following equation [34]:

$$\frac{dS}{dt} = \frac{Q(S_i - S_e)}{V} \quad (6)$$

The dS/dt is the substrate removal rate ($\text{kg m}^{-3} \text{d}^{-1}$) and can be defined as:

$$\frac{dS}{dt} = \frac{U_{\max} \left(\frac{QS_i}{V} \right)}{k_B + \left(\frac{QS_i}{V} \right)} \quad (7)$$

So Eq. (6) can be illustrated as:

$$\left(\frac{dS}{dt} \right)^{-1} = \frac{V}{Q(S_i - S_e)} = \frac{k_B}{U_{\max}} \times \frac{V}{QS_i} + \frac{1}{U_{\max}} \quad (8)$$

where $U_{\max}$ is maximum substrate removal rate (mg COD (L/d)), and k_B is saturation value constant (g (L/d)).

3. Kaldnes results and discussion

3.1. Start-up period

A sludge sample from the aeration tank of a conventional domestic sewage treatment plant was used for inoculation and a combination of milk (40%) and glucose (60%) was used to provide the carbon source. At the first step, the amount of COD was adjusted to 250 mg/L . After reaching high efficiency (above than 97%), the amount of COD increased gradually to 350 mg L^{-1} . After 8 d, the system was switched from batch to continuous state. 15 d after the change of regime to continuous system, the MBBR system was ready to work properly by formation of biofilm on the Kaldnes carriers' plastic particles [22]. The COD concentration in MBBR feed gradually increased during 80 d from 350 to 1000 mg L^{-1} [35]. After this time, with established efficiency of 80%, the COD concentration was increased from 978 to 2615 mg L^{-1} at a hydraulic retention time of 10 h in 5 stages [6,22,36,37].

3.2. First order substrate removal model evaluation

The value of k_1 was obtained from the slope of the line by plotting $(S_i - S_e)/\text{HRT}$ vs. S in Eq. (2). Fig. 3 shows the plot between $(S_i - S_e)/\text{HRT}$ and S , was calculated as $7.4/\text{d}$ with a correlation coefficient of 0.8382. The low value of this coefficient (R^2) clearly indicates that first order kinetics may not be used without good degree of precision.

Table 2

Experimental data obtained under steady state conditions at operation period 0 to 300 days (values for standard deviation are given in brackets)

Parameter	HRT (h)									
	10	10	8	8	6	6	5	5	4	4
Operation period (days)	0–30	31–60	61–90	91–120	121–150	151–180	181–210	211–240	241–270	271–300
Influent COD (mg/L)	1021.7 (±218)	2615.8 (±557)	1196.4 (±255)	2609.1 (±556)	1123.7 (±239)	2430 (±517)	1046.1 (±223)	2542 (±541)	978.3 (±208)	2496.7 (±532)
Effluent COD (mg/L)	95.38 (±13)	46.2 (±6)	89.6 (±12)	39.7 (±5)	82.5 (±11)	34.0 (±5)	78.8 (±11)	29.9 (±4)	74.9 (±10)	25.7 (±3)
Removal efficiency (%)	90.67 (±2)	98.47 (±0)	92.51 (±1)	98.47 (±0)	92.65 (±1)	98.60 (±0)	92.46 (±1)	98.82 (±0)	92.34 (±1)	98.97 (±0)
MLVSS (mg/L)	1454 (±310)	704 (±150)	1228.5 (±262)	679 (±145)	1100 (±234)	557.7 (±119)	803.5 (±171)	371 (±79)	788 (±168)	249 (±53)
OLR (kg-COD/m ³ ·d)	2.45 (±1)	6.28 (±1)	3.59 (±1)	7.83 (±2)	4.49 (±1)	9.72 (±2)	5.02 (±1)	12.2 (±3)	5.87 (±1)	14.98 (±3)
SLR (g-COD/m ² ·d)	9.81 (±2)	25.11 (±5)	14.36 (±3)	31.31 (±7)	17.98 (±4)	38.88 (±8)	20.09 (±4)	48.81 (±10)	23.48 (±5)	59.92 (±13)

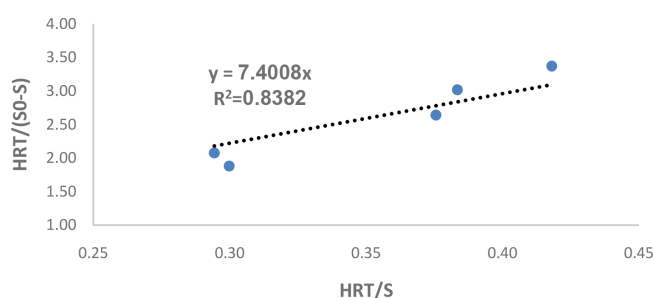


Fig. 3. The model plot of first order COD removal.

3.3. Stover Kincannon model evaluation

Fig. 4 shows the graph plotted as a reciprocal of the total organic loading removal rate, $[V/(Q(S_i - S_o))]$, vs. the reciprocal of total organic loading rate, $V/(Q \times S_o)$. Since the plot of $[V/(Q(S_i - S_o))]$ vs. $V/(Q \times S_o)$ was linear, linear regressions (least squares method) were used to determine

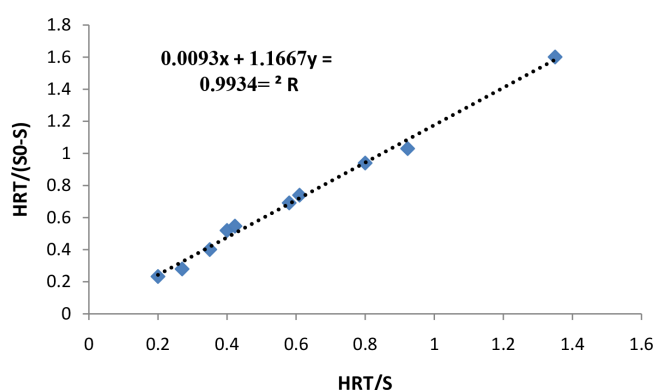


Fig. 4. Stover Kincannon model plot.

a related intercept. The saturation value constant (K_b) and maximum utilization rate (U_{max}) were calculated from the line plotted on the graph as 125.45 g L/d and 107.5 g L/d, indicating the substrate removal by microorganisms and the maximum substrate removal by the aerobic organisms vs. time, respectively. The correlation coefficient (R^2) was calculated to be 0.9934. The high value of this coefficient clearly indicates that Stover Kincannon can be used with a good degree of precision.

3.4. Grau second-order substrate removal model evaluation

In order to determine the kinetic coefficients (a , b and k_2), as indicated in Grau Second-order model, Eq. (4) is plotted in Fig. 5. The values of a and b were calculated from the intercept and slope of the straight line on the graph. They were found to be 1.022 and 1.133, respectively, with high correlation coefficients (R^2) of 0.9985. The substrate removal rate constant (k_2) was then calculated from the equation $a = S_o/(k_2 X)$ as 5.1, indicating substrate removal for each unit of microorganism depending on second-order substrate removal rate constant (k_2). The high value of the correlation coefficient clearly indicates that the Grau model can be used

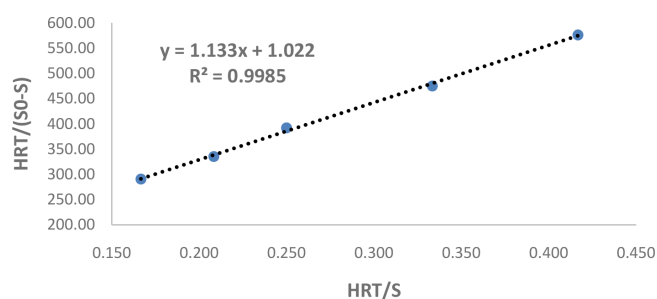


Fig. 5. Grau second-order substrate COD removal model plot.

Table 3

Comparison of kinetic constants in the Stover–Kincannon and Grau second-order models cited in the literature with the present results

Models	Substrate	S_0 (mg L ⁻¹)	HRT (h)	Kinetic parameters			Reference
				k_s	m	n	
Grau second order	Simulated wastewater	4214	4–100	0.337	0.562	1.095	Mustafa ISik and Delia Teresa Sponza [32]
Grau second order	Municipal wastewater	230–445	4–24	0.217	0.002	1.346	Grau et al. [28]
Grau second order	Molasses	2000–15000	8–48	10.81	0.033	1.192	Optaken [29]
Grau second order	Simulated wastewater	750–4500	24	0.337	0.562	1.095	Borghei and Hosseiny [34]
Grau second order	Simulated wastewater	750–2250	12–24	3.582	0.047	1.007	Borghei and sharbatmaleki [22]
Grau second order	Simulated wastewater	978–2615	4–10	5.1	0.122	1.133	This study
				U_{max}	K_B		

with an acceptable degree of precision, even higher than the Stover Kincannon model.

3.5. Comparing different kinetics models

Table 3 summarizes the constants determined from the applicable models in previous studies and compares them with coefficients obtained here. As shown in this table, the kinetic data evaluation showed that the Grau second order substrate removal model was more appropriate than the Stover Kincannon and first order substrate removal models for predicting the performance of the MBBR treatment system.

Table 3 summarizes the constants determined from the applicable models in previous studies [32,38,39]. As shown in this table, the saturation constant (K_B) and maximum utilization rate (U_{max}) values of the present work are larger than those obtained by Yu et al. [38], Mustafa ISik and Delia Teresa Sponza [32] and Borghei and Sharbatmaleki [39] in Stover-Kincannon model.

In addition, in according with the Grau second order kinetic models, the multicomponent substrate removal rate constant (k_s) value obtained in this study was in the range of k_s values determined in other studies [22,28,29,32,34]. The k_s value is increased as the substrate removal rate increase, depending on the initial substrate (S_0) and microorganism concentrations (X) in the reactor.

4. Conclusion

In this study, it was investigated that simulated sugar manufacturing wastewater could be treated effectively by MBBR system at different HRTs, varying between 4 and 10 h. After steady-state conditions were prevailed, the unit was tested under organic loading rates of 978–2615 g COD m³/d and hydraulic retention times of 0.16–0.41 d, stepwise. The results indicated that the MBBR system was capable to bio-

degrade the organic matter up to 98.97% at loading rates several times that of conventional aerobic bioreactors.

In this study, the kinetics of the MBBR system treating synthetic wastewater were investigated using different models such as the first order substrate removal, the Grau second order, and the Stover-Kincannon kinetic models. The Grau second order substrate removal model and the Stover-Kincannon kinetic models with correlation coefficients of 0.9985 and 0.9934 respectively, were found to be more suitable than the first order substrate removal model. The results of kinetic studies obtained from the lab scale MBBR system can be used to predict the treatment performance of a full-scale MBBR system if the sugar wastewater was treated at similar loading conditions and wastewater composition.

The best regime for removal of COD by MBBR achieved at HRT = 10, operation period 31–60 d with efficiency 98.47%.

It was demonstrated that the MBBR system has convenient operating conditions, produces acceptable results under high loadings, and delivers sludge with very good settling characteristics.

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