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Research Article

Kinetics of Ethylene Glycol Biodegradation in a Sequencing Moving Bed Biofilm Reactor

Abstract

Treatment of waste water containing ethylene glycol (EG) by implementing a sequence of two Moving Bed Biofilm Reactors (MBBR) were studied. Reactors were operated at different hydraulic retention times (HRT) of 48, 24, 18, and10 hours while EG concentration was in the range of 10 mg/l to 1,150 mg/l. Throughout the experiments the ratio of EG Chemical Oxygen Demand (COD) to total COD was changed from 0.0 to1.0. The maximum removal efficiency of EG was achieved at HRT of 18 hours during the tests and COD removal efficiency varied from 71.7% to 96.7%.

To describe the kinetics of biodegradation in biofilm processes, models based on Monod's equations as well as models suggested by other researchers including Grau and Stover- Kincannon were used. As an outcome of this study, both Grau and Kincannon-Stover models were determined to be the most appropriate models for this reactor. These models gave high correlation coefficients and appeared to be able to predict the reactor performance under different conditions. The kinetic studies showed that biofilm diffusion is the most important parameter in controlling the mass transfer phenomena compared to hydraulic factors in the system.

Introduction

The moving bed bioreactor (MBBR) has emerged as a compact treatment alternative to conventional activated sludge reactors for the treatment of municipal and industrial wastewater [1]. In an MBBR system the biomass is grown as a thin layer on small plastic carrier elements which move around in the reactor and forms a large quantity of biomass. The accumulation of biomass eliminates the need for sludge recycling. The biofilm reactor was completely mixed and operated continuously. The carrier elements were slightly less dense than water and circulated with a water stream. In an aerobic reactor aeration can cause water circulation. An advantage of this system is that the volume of carrier fill in the reactor can be varied to requirements. The standard carrier fill is 70% of the volume and results in total specific area of 465m^2/m^3 and an effective specific area of 335m^2/m^3 [2].

This process was first introduced by Kaldnessin the 1990's. It was then used successfully to treat many industrial waste sites. There are presently more than 400 large-scale wastewater treatment plants in 22 different countries throughout the world based on this process in operation in [3]. During the past decade it has been successfully used for the treatment of many industrial effluents including pulp and paper industry waste [4], poultry processing wastewater [5], cheese factory wastes [6], refinery and slaughter house waste [7], phenolic wastewater [8], dairy wastewater [9], and municipal wastewater [10-17]. Another important application of this system was to upgrade existing treatment plants where activated sludge plants can be readily converted to MBBR plants at little cost.

Because MBBR is efficient in treating high strength waste, has a low foot print, and is operational simplicity, it is fast becoming a preferred means for on-site treatment of industrial effluents. Some petrochemical plants, specifically "Olefin" production plants, have to treat large quantities of wastewater containing ethylene glycol where low space and treated effluent standards are important objectives.

Modelling and simulation of reactors is an important tool for design and operation of MBBR plants [18]. In contrast to activated sludge plants, which have been widely modelled using the ASM model family [19], the modelling of MBBR systems remains very challenging to process engineers. Mathematical models for biological reactors have found little use in engineering practice because the applications are too complex to model easily. Although many studies regarding the performance and application of MBBR have been published so far, very little attempt has been made to describe the kinetics and modelling of this reactor type.

In this research, the organic removal rate in a new MBBR system (using Kaldnes type suspended media) was studied and different mathematical models, which could describe the behaviour of the reactor, were tested. The objective was to find a model which could closely follow the experimental results and could describe the kinetics of the system.

Mathematical models describing the biofilm processes, especially biological filters and Rotating Biological Contactors (RBC), have been proposed in the past [20-26]. Kincannon and Stover [25] proposed a design concept for RBC's based on total organic loading rate and established a kinetic model for such a reactor. Experiments and research carried out on moving bed biofilm reactors indicate that models based on Monod kinetics developed by Stover-Kincannon could be useful models to describe the process and accurately predict results.

The primary difference between the two models is that in the Kincannon-Stover model, the substrate utilization rate is expressed as a function of the organic loading rate, which is considered to be the most important parameter influencing the behaviour of the reactor.

Monod model

In a complete midex system the substrate concentration rate of change in, assuming that first order kinetics prevail, can be expressed as follows:

$$\frac{dS}{dt} = \frac{U_{max}(\frac{QS_0}{A})}{K_B + (\frac{QS_0}{A})} \quad (1)$$

Under steady state conditions, the rate of change in substrate concentration is negligible and Equation 1 can be rearranged and reduced to:

$$\frac{S_0 - S}{\theta_H} = k_1 S \quad (2)$$

The slope k1 can be obtained by plotting

$$\frac{S_0 - S}{\theta_H}$$

versus S in Equation (2), 1.2 Stover-Kincannon model. In the Stover-Kincannon model the substrate utilization rate is expressed as a function of the organic loading rate by the monomolecular kinetic for biofilm reactors including rotating biological contactors and biological filters. However, due to the difficulties in measuring the active surface area which supports the biofilm growth, the effective volume of the reactor is used in the version of the Stover-Kincannon model originally suggested by Borghei and Hosseyni [27] for Moving Bed Biofilm Reactor:

$$\frac{dS}{dt} = \frac{U_{max}(\frac{QS_0}{A})}{K_B + (\frac{QS_0}{A})} \quad (3)$$

Where dS/dt, the rate of substrate utilization is defined in Equation4:

$$\frac{dS}{dt} = \frac{Q}{V}(S_0 - S) \quad (4)$$

Eq. (5) is obtained from linearizing Eq. (4) as follows:

$$\frac{V}{Q(S_0 - S)} = \frac{K_B}{U_{max}}(\frac{V}{QS_0}) + \frac{1}{U_{max}} \quad (5)$$

Grau model

The general equation of a second-order kinetic model used by Optaken [28], Grau et al. [29] is illustrated in Eq. (6)

$$-\frac{dS}{dt} = k_S \times X \times \left(\frac{S}{S_0}\right)^2 \quad (6)$$

If Eq. (6) is integrated and then linearized, Eq. (7) will be obtained:

$$\frac{S_0 \times \theta_H}{S_0 - S} = \theta_H - \frac{S_0}{k_S \times X} \quad (7)$$

If the second term of the right part of Eq. (7) is accepted as a constant, Eq. (8) will be obtained:

$$\frac{S_0 \times \theta_H}{S_0 - S} = n \times \theta_H + m \quad (8)$$

(S0-S)/S0 expresses the substrate removal efficiency and is symbolized as E. Therefore, the last equation can be written as follows:

$$\frac{\theta_H}{E} = m + n \times \theta_H \quad (9)$$

Materials and Methods

The pilot scale plant

The pilot scale plant incorporated one reactor which had a volume of 30m^3 and one secondary settling tank of 4 m^3. The reactor was filled with Kaldnes carrier elements (K_1). The Kaldnes carrier elements are made of polyethylene (density 0.95 g/cm^3) and shaped like small cylinders (about 10mm in diameter) with a cross inside (Figure 1). The effective specific growth area is about 500m^2/m^3 at 100% filling grade [1]. The reactor filling grade was 40% which provide 200m^2/m^3. The reactor was aerated using membrane diffusers. In order to retain the carrier in the reactor, a sieve with 6 mm opening was placed at the reactor outlet. Effluent from the secondary settling tank was recycled to the reactor every one to two days depending on HRT.

The reactor flow rate was calculated based on the desired HRT. An air pump aerated the solution such that dissolved oxygen (DO) was maintained at 2.0-2.5 mg/l. Mixed liquor suspended solids (MLSS) varied from 3000 mg/l to 5000mg/l, depending on the stage of bioflim formation. Biofilm formation on the carrier was cyclical, meaning the biofilm grew from a micro thin layer to 5 millimeters, completely clogging the carrier openings, Figure 1, and then detached from oxygen and food starvation, and then the micro thin layer reformed thereby restarting the cycle.

Feed and microorganisms

Synthetic wastewater comprising sugar beet molasses and ethylene glycol, plus phosphate hydrogen dipotassium and alkalinity

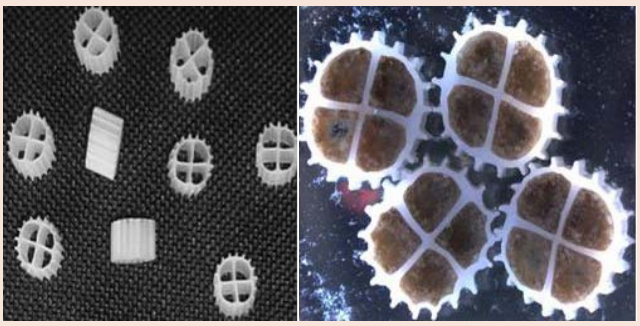

Figure 1: Carrier elements and biofilm formation in the reactor.

was used to feed the reactor according to C: N: P (100:5:1). Ethylene glycol was added incrementally to the wastewater. Each milligram per liter of EG is equivalent to aCOD concentration of 1200 mg/l.

Characteristics of the prepared wastewater used as the feedstock are shown in Table 1. The EG COD ratio to the total COD concentration of wastewater ranged from 0.0 to 1.0 (COD EG/COD tot). In order to achieve conditions conducive for the growth of microorganisms, the wastewater was enriched by adding the following (in mg/l): (NH4)2SO4:500 mg/l; KH2PO4:200 mg/l; MgCl2:30 mg/l; NaCl:30 mg/l; CaCl2 :20 mg/l; and FeCl3 :7 mg/l as recommended [26,28]. The inoculum was the activated sludge taken from the lab scale biological treatment of herbicide unit.

Analysis

All analyses were performed according to Standards methods for the examination of water and wastewater, 1998.The filtered chemical oxygen demand (FCOD) samples were first filtered through a Whatman GF/C microfiber filter. Total suspended solids (SS) and mixed liquor volatile suspended solids (MLVSS) were determined according to Standard Methods [30]. The biofilm solids (BS) were determined using 50 carrier elements that were sampled from the MBBR. The carrier elements were separated from the water and dried overnight until constant weight in an oven at 105 °C. The dried samples were weighed in order to determine the total mass (*M* tot) composed of carrier element mass (*M*carrier) and the fixed biomass. The biomass was then washed, the clean carriers weighed, and the amount of biofilm solids attached to the 50 carrier elements (BS50) was calculated (Eq. (1)):

$$BS50 = Mtot - Mcarrier \quad (1)$$

The amount of biomass in the reactor could then be determined because the filling grades and the number of carrier elements at 100% filling grade (FG) are known (Eq. (2)). The filling grades were set by the pilot plant operator to 50% and 65% and the number of carrier elements at 100%. The filling grade is known to be 1.024×106 m−3 [26]:

$$BS = BS50\ 1.024 \times 106\ m{-}3\ FG\ /50 \quad (2)$$

Laboratory experiments were conducted at room temperature (22±5°C) and under controlled conditions of dissolved oxygen (DO) concentration between 2-5 mg/l. ThepH was adjusted to 7 by using sodium carbonate. The synthetic wastewater was fed by using peristaltic pump with flow controlling mechanism from feed tank to the first reactor. The DO was measured by a membrane covered amperometric electrode.

Table 1: Water quality parameters of synthetic wastewater.

Parameter	Quantity
Temperature °c	25±5
pH	7/5±0/5
COD mg/l	1000
Urea mg/l	50
Phosphate mg/l	10

Batch experiments

The reactor was started by addition of sludge to form biomass on the carriers while operating in batch mode. Aeration was provided by aquarium aerators. In the start-up phase, the system was fed by synthetic waste water containing 1000mg/l COD. The reactor was run for a period of 60 days for biomass acclimatisation before starting the experiments. The reactor was fed at an organic loading rate (OLR) of 0.51 kgCOD/m^3 day which gradually increased to 0.68 kgCOD/m^3 day at the end of 60th day. After the start-up period the EG COD concentration was increased from 357.5mg/l to 1500mg/l while molasses COD was decreased from 1000mg/l to 0mg/l, at hydraulic retention times of 48, 24, 18, and 10 hours.

Results and Discussion

The performance of MBBR reactor under different COD and HRT condition is shown in Figures 2, 3. It can be seen that the COD removal was increased when the EG increased at all HRT times except in 24hr. This is may be due to a sharp rise in OLR.

As illustrated in Figure 3 the COD removal rate decreased as a result of reduction in hydraulic retention time. Also, the maximum COD removal occurred at HRT 18hr. COD removal in conventional activated sludge could be in range of 40% to 85%, depending on the water organic content type, HRT, and operational temperature. Unfortunately, ethylene glycol removal via conventional activated sludge systems has not been studied well, therefore a comparison to conventional systems was not possible. Results indicate that high efficiencies of organic removal in terms of COD is achieved at high loading rates which are several times that of conventional activated sludge plants.

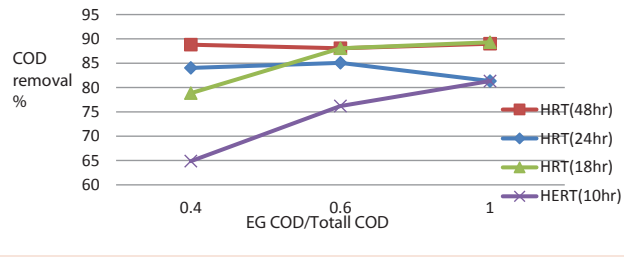

Figure 2: COD removal rates for the MBBR system at different HRT.

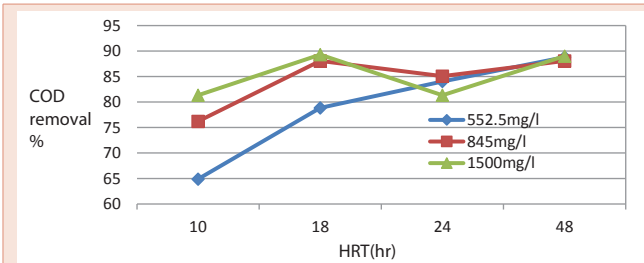

Figure 3: COD removal rate at different HRT at different COD loads of ethylene glycol.

Many methods have been used to describe the overall organic removal kinetics in biological and biofilm reactors. The most important models include of: Monod model, Stover-Kincannon model, and second-order substrate removal (Grau model) are selected for considering COD removal in MBBR reactor.

Monod model

The value of k_1 was obtained from slope of the line drawing ($S_\circ$-S)/HRT versus S in Eq. (4). The k1 value obtained from Figure 4 can be estimated as 3.463 per day with a correlation coefficient of 0.41 / day. The low value of the coefficient (R^2) indicates that first order kinetics cannot be applied with good precision.

Stover-Kincannon model

Figure 4 shows the reciprocal of total organic loading removal rate, $V/(Q(S_0-S))$ plotted against the reciprocal of total organic loading rate, $V/(Q.S_0)$. Since the plot of $[V/(Q(S_0-S))]$ versus $[V/(Q.S_0)]$ was linear, a least squares linear regressions was applied. The saturation value constant (K_B) and maximum utilization rate (U_{max}) were obtained graphically from Figure 5 as 12.32 g (l per day) and 11.74 g (l per day). The saturation value indicates the substrate removed by microorganisms and the maximum utilization rate shows the maximum substrate removed by aerobic organisms versus time.

Grau model - Second Order model

In order to determine the kinetic coefficients (m, n and k_s), Eq. (11) was plotted in Figures 5, 6. The values of m and n were determined graphically from the intercept and slopes. The value of m and b were found to be 0.1084 and 0.9547 with high correlation coefficient (R^2) of 0.99. The substrate removal rate k_s was then calculated from equation $m=S0/(ksX)$ per day indicating substrate removal for each unit of microorganism depending on second-order substrate removal rate constant(k_s).

Evaluation of kinetic models

The calculated kinetic data from the models showed that Stover-Kincannon and Grau second-order substrate removal kinetics were more appropriate than the first order model for predicting the performance of the lab-scale MBBR reactor when the regression coefficients and kinetic coefficients were compared. A summary of the constants determined from the applicable models in previous studies and compares with coefficients is shown in Table 2. In this study, the saturation constant (K_B) and maximum utilization (U_{max}) values are larger than those obtained by Yu et al. [23] and Borghei and Hosseiny [27] in a Stover-Kincannon model. The difference may be due to higher rates of substrate utilization in a submerged aerated filter using carbohydrate based synthetic wastewater (molasses).

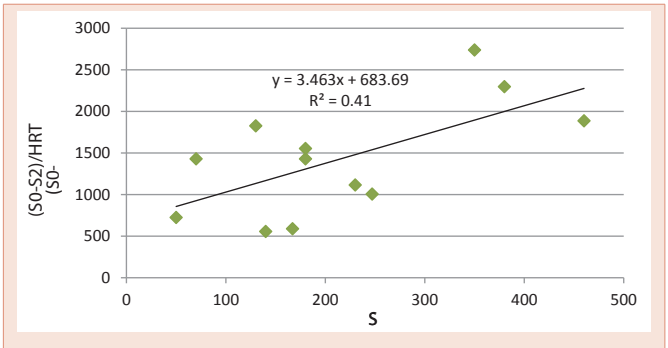

Figure 4: Correlation between Monod model and experimental pilot.

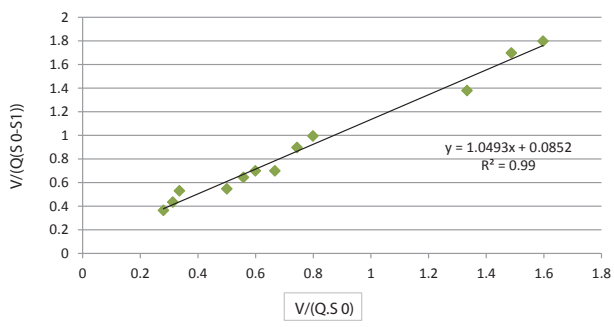

Figure 5 Correlation between Stover-Kincannon model and experimental pilot.

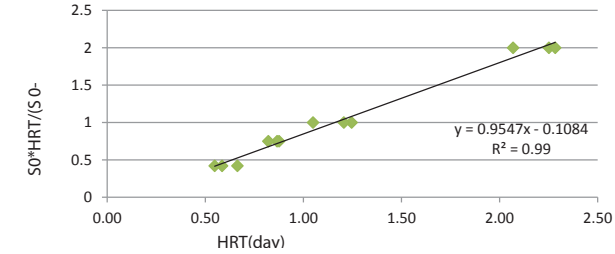

Figure 6 Correlation between Grau second-order substrate removal and experimental pilot.

According to the Grau model, the multi component substrate removal rate constant (k_s) value obtained from this study was between the k_s value determined in other studies. The ks values will be increased as the substrate removal rate increased depending to initial substrate (S_0) and microorganism concentrations (X) in the reactor. In conclusionit appears that kinetic coefficients obtained from the aerobic treatment of simulated sugar-manufacturing wastewater, agree with the Stover-Kincannon and Grau second order substrate kinetic models.

Conclusion

A laboratory scale study was conducted to evaluate the phenol removal efficiency by means of a moving bed biofilm reactor. It proved flexible, reliable, and easy-to-operate with no clogging problems. The primary conclusion of these experiments is that the Kincannon-Stover model can be implemented to predict the kinetic characteristics of MBBR system in order to have successful treatment process.

- Based on the experimental results obtained from the laboratory study, the following conclusions were madeAs the COD_{EG}/COD_{tot} was increased, the COD removal rate increases.

Table 2: Comparison of kinetic constants of the pilot study and models reported in the literature.

Models	substrate	S0(mg/l)	HRT(day)	Kinetic parameters			References
				Umax	KB		
Stover-Kincannon	Soybean wastewater	7250-11450	1-1.45	83.3	85.5		Yu et al (1998)
Stover-Kincannon	Simulated waste water	750-4500	1	8.3	9.45		Borghei and Hosseyni (2002)
Stover-Kincannon	Simulated waste water	750-2250	0.5-1	101	106.8		Borghei et al. (2007)
Stover-Kincannon	Simulated waste water	1252.5-1500	0.42-2	11.74	12.32		This study
Grau second order	Municipal wastewater	230-445	0.25-1	Ks	m	n	Grau et al.(1975)
				0.217	0.002	1.346	
Grau second order	Molasses	2000-15000	0.5-2	10.81	0.033	1.192	Optakan (1982)
Grau second order	Simulated waste water	750-4500	1	0.337	0.562	1.095	Borghei and Hosseyni (2002)
Grau second order	Simulated waste water	750-2250	0.5-1	3.582	0.047	1.007	Borghei et al.(2007)
Grau second order	Simulated waste water	1252.5-1500	0.42-2	13.3	.1084	.9547	This study

- With decreasing the HRT the efficiency the maximum COD removal rate occurred at HRT 18hr.
- Kincannon-Stover model is a good mathematical model for the substrate removal rate in moving bed biofilm reactors.
- The reactor volume and effluent substrate concentration can be determined from the Kincannon-Stover model if the model constants are available.
- In the present study, Kincannon-Stover model constants U_{max} and K_B were found to be 12.32 and 11.74 g(l per day), respectively.

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