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KINETIC MODELS FOR PREDICTION OF COD EFFLUENT FROM UPFLOW ANAEROBIC SLUDGE BLANKET (UASB) REACTOR FOR CANNERY SEAFOOD WASTEWATER TREATMENT

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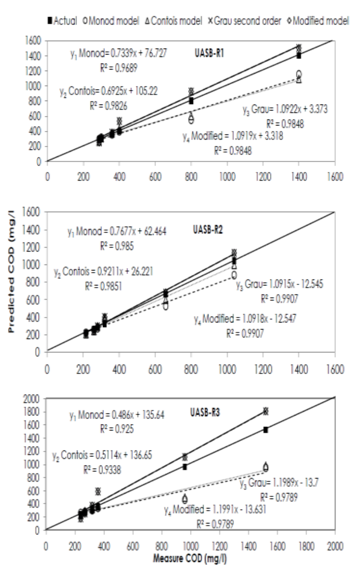
Graphical abstract



Abstract

The three identical lab-scale upflow anaerobic sludge blanket (UASB) reactors were operated continuously for treating cannery seafood wastewater at seven hydraulic retention times (HRTs) of 5, 4, 3, 2, 1, 0.5 and 0.25 days. The different of granule sizes from three sources: a cassava factory (CS), a seafood factory (SS), and a palm oil mill (PS), average sizes in the range 1.5-1.7, 0.7-1.0 and 0.1-0.2 mm respectively were used as inocula for anaerobic digestion. The UASB-R1 used only granules from seafood factory (R1-SS), the UASB-R2 used mixed granules from seafood with cassava factory (R2-SS+CS) and the UASB-R3 used mixed granules from seafood factory with palm oil mill (R3-SS+PS). In this study selected mathematical models including Monod, Contois, Grau second-order and modified Stover-Kicannon kinetic models were applied to determine the substrate removal kinetics of UASB reactor. Kinetic parameters were determined through linear regression using experimental data obtained from the steady-state experiment and subsequently used to predict effluent COD. The results showed that Grau second-order and modified Stover-Kicannon kinetic models were more suitable than that of others for predicting the effluent COD, with high the correlation coefficient (R^2). In addition, the UASB-R2 from mixed granules with cassava factory (SS+CS) gave the best performance and highest coefficient value.

Keywords: UASB reactor, cannery seafood wastewater, kinetic model

1.0 INTRODUCTION

Currently, the world is facing environmental crisis and global warming. Agro-industries are major contributors to worldwide industrial pollution. Effluents from many agro-industries are hazardous to the environment and require appropriate and comprehensive management approach. The anaerobic digestion is an environmentally friendly green biotechnology to treat agro-industrial wastewater. It is widely used not only to treat wastewater reduce but also to generating biogas, a clean and renewable energy which can substitute energy from fossil sources partly as targeted by current Thai energy policy [1].

In Thailand, the canned seafood industry represents one of the significant parts of economic resources for exporting, with an average annual income of 320 million US dollars together with approximate 10% growth rate each year. Most seafood factories are located in Southern Thailand [2]. Canned seafood processing requires large amounts of water. The processing operations produce wastewater, which contains organic contaminants insoluble, colloidal and particulate form. Depending on the particular operation, the degree of contamination may be small (e.g., washing operations), mild (e.g., fish filleting), or heavy (e.g., blood water drained from fish storage tanks) [3].

Many researchers found that high-strength wastewater from cannery seafood factory was suitable for anaerobic biological treatment such as upflow anaerobic sludge blanket (UASB) reactor, anaerobic filter (AF) and anaerobic fluidized bed (AFB) [3]. In the UASB reactor wastewater was supplied from the bottom of the reactor and the organic matter is digested as the wastewater moves upward. During digestion, methane gas bubbles are produced and carry the sludges upwards, resulting in the formation of dense sludge flocs (granules) that readily settle [4, 5]. The successful treatment in UASB reactor is principally attributed to the formation of anaerobic granules in sludge bed. The granule size is an important parameter directly influences the performance of reactor [6]. The scope of this research is to study the effect of granule sizes on the performance of UASB reactors for cannery seafood wastewater treatment in term of organic removal and biogas potential from different sizes of inocula/granules using kinetic models include, Monod, Contois, Grau second-order and modified Stover-Kicannon models. The preliminary results in this work could be valuable for design and operation in continuous biogas plants.

2.0 EXPERIMENTAL

2.1 Seed and Wastewater

The wastewater sample was collected from a cannery seafood factory. Characteristics of wastewater are shown in Table 1. It was kept at 0-4 °C until used in the experiments. The granular sludges were collected from the methanogenic fermentation stage of the UASB reactors from three sources: cassava factory (CS), seafood factory (SS) and palm oil mill (PS), having the average size range of 1.5-1.7, 0.7-1.0, and 0.1-0.2 mm respectively.

2.2 Reactor and Operating Condition

The three identical laboratory-scale UASB reactors were used in this study. They have the cylindrical shape with 100 cm high, 5.4 cm internal diameter and 2.06 L working volumes. The feed was pumped by peristaltic pump (Longer pump, Model BT 100-1F, DG-4 channel pump head) at the rate defined by HRT. Three reactors were operated continuously at seven hydraulic retention times (HRTs) of 5, 4, 3, 2, 1, 0.5, and 0.25 days. The corresponding organic loading rates (OLR) were 0.84, 1.05, 1.4, 2.1, 4.2, 8.4, and 16.8 kg COD/$m^{-3}d^{-1}$ respectively. Table 1 below shows the basic parameters of cannery seafood wastewater.

Table 1 Basic parameters of cannery seafood wastewater

Be the difference	Value
pH	6.3
COD (g/l)	4.2
TKN (mg/l)	343
TP (mg/l)	42
TS (g/l)	3.5
VS (g/l)	2.6
SS (mg/l)	256.7
VSS (mg/l)	172.2
Alkalinity (mg/l as$CaCO_3$)	1,400
VFA (mg/l as$CaCO_3$)	740

2.3 Analytical Procedures

Chemical oxygen demand (COD), Total Kjeldahl Nitrogen (TKN), Total Phosphorus (TP), Total Solids (TS), Volatile Solids (VS), Suspended Solids (SS), Volatile Suspended Solids (VSS), Alkalinity, Volatile Fatty Acids (VFA) and pH were analyzed. All analytical procedures were performed in accordance with standard methods for the examination of water and wastewater APHA [7]. Gas production was measured daily by using water displacement method [8]. The methane content was measured using Gas Chromatograph (GC-8A Shimadzu).

3.0 RESULTS AND DISCUSSION

3.1 Reactor Performance

The steady state COD removal efficiency decreased from 93.14 to 38.33 %, 94.86 to 51.67 % and 94.29 to 28.33% for UASB-R1, R2 and R3 respectively, with decreasing hydraulic retention times from 5 days to 0.25 days. This was the result of shorter residence time, thus lowered the efficiency. It also showed that the size of granule had a strong effect on the process performance and substrate removal in the UASB reactors. The UASB reactor R2 which used granules from its own sources mixed with granules from cassava factory gave the highest substrate removal and biogas production.

For the UASB reactors R1 and R3 COD removal efficiency became less than 50% at 0.25 day HRT with OLR of 16.8 KgCOD/m^3d^{-1}, because of the disintegration and wash away of biomass or granules along with the effluent due to high mixing intensities [9, 10]. Moreover, as the HRTs decreased the pH and alkalinity in all three reactors decreased. However pH and the alkalinity were in the normal operating range (in all three UASB reactors (6.5-7.5). In contrary, the volatile fatty acid (VFA) and oxidation reduction potential (ORP) increased with decreasing HRTs for R1, R2 and R3 (VFA increased from 87.5 to 575, 62.5 to 487.5 and 75 to 512.5 mg/lasCaCO3 respectively), and (ORP increased from -357.70 to -244.40, -356.40 to -263.10 and -365.20 to -257.10 mv respectively), which was in the normal range suitable for anaerobic microorganism in anaerobic digestion [11].

3.2 Kinetic Models

3.2.1 Monod Kinetic Model

In a UASB reactor without biomass recycles, the rate of change in biomass and substrate concentration in the system can be expressed as Equation 1, 2 [12-14].

$$\frac{dX}{dt} = \frac{QX_0}{V} - \frac{QX_e}{V} + \mu X - K_d X \tag{1}$$

$$-\frac{dS}{dt} = \frac{QS_0}{V} - \frac{QS}{V} + \frac{\mu X}{Y} \tag{2}$$

The ratio of the total biomass in the reactor to the biomass washed in a given time period represents the average time that microorganism spends in the reactor. This parameter is called mean cell-residence time (θ_c) and is calculated from Equation 3 for UASB reactor.

$$\theta_c = \frac{VX}{QX_e} \tag{3}$$

Assuming that the concentration of biomass in the influent can be ignored, at steady-state $dX/dt = 0$, and the HRT (θ_H) is defined as the volume of the reactor divided by the flow rate of the influent. The relationship between the specific growth rate and the rate limiting substrate concentration can be expressed by Monod kinetics as shown in Equation 4

$$\mu = \frac{\mu_{max} S}{K_s + S} \tag{4}$$

Thus Equation 1 reduces to

$$\frac{QX_e}{V} = X(\mu - K_d) \tag{5}$$

$$\mu = \frac{1}{\theta_c} + K_d \tag{6}$$

$$\frac{\mu_{max} S}{K_s + S} = \frac{1}{\theta_c} + K_d \tag{7}$$

Under steady-state conditions, the rate of change in substrate concentration (dS/dt) is negligible and, Equation 2 can be reduced to Equation 8 by substituting Equation 6

$$\frac{S_0 - S}{\theta_H} = \frac{X}{Y}\left(\frac{1}{\theta_c} + K_d\right) \tag{8}$$

The kinetic parameters Y and K_d can be obtained by rearranging Equation 8 as shown below:

$$\frac{S_0 - S}{\theta_H X} = \frac{1}{Y\theta_c} + \frac{K_d}{Y} \tag{9}$$

By plotting Equation 9, the values of Y and K_d can be calculated from the slope and intercept of the best-fit line. The value of μ_{max} and K_s could be determined by plotting Equation 10, which was derived by rearranging Equation 7. Finally, by arranging Equation 7, Equation 11 is obtained that is used to predict effluent substrate concentration in the reactor.

$$\frac{\theta_c}{1 + \theta_c K_d} = \frac{K_S}{\mu_{max}}\frac{1}{S} + \frac{1}{\mu_{max}} \tag{10}$$

$$S = \frac{K_S(1 + K_d\theta_c)}{\mu_{max}\theta_c - K_d\theta_c - 1} \tag{11}$$

3.2.2 Contois Model

Similar to Monod model, in Contois model, the relationship between the specific growth rate and the rate limiting substrate concentration can be expressed by the following relation.

$$\mu = \frac{\mu_{max} S}{\beta X + S} \tag{12}$$

Again the kinetic parameters Y and K_d can be calculated from the slope and intercept of the best-fit line Equation 9. The value of μ_{max} and β could be determined by plotting Equation 14. By substituting Equation 12 into Equation 9 and rearranging, we obtain Equation 13 and 14. Finally, we can predict the effluent substrate concentration of the reactor using Equation 15.

$$\frac{\mu_{max} S}{\beta X + S} = \frac{1}{\theta_c} + K_d \tag{13}$$

$$\frac{\theta_c}{1 + \theta_c K_d} = \frac{\beta}{\mu_{max}}\frac{X}{S} + \frac{1}{\mu_{max}} \tag{14}$$

$$S = \frac{\beta X(1 + K_d\theta_c)}{\mu_{max}\theta_c - K_d\theta_c - 1} \tag{15}$$

3.2.3 Grau Second-order Multicomponent Substrate Removal Model

The general equation of a second-order Grau model is illustrated in Equation 16 [12-15]

$$-\frac{dS}{dt} = K_s X\left(\frac{S}{S_0}\right)^2 \tag{16}$$

Integrating Equation 16 and then linearizing it, Equation 17 is obtained.

$$\frac{S_0\theta_H}{S_0 - S} = \theta_H + \frac{S_0}{k_s X} \quad (17)$$

$$\frac{S_0\theta_H}{S_0 - S} = a + b\theta_H \quad (18)$$

$$S = S_0\left(1 - \frac{\theta_H}{a + b\theta_H}\right) \quad (19)$$

3.2.4 The Modified Stover-Kicannon Model

In this model the substrate utilization rate is expressed as a function of the organic loading rate using monomolecular kinetics. A special feature of the modified Stover-Kicannon model is it uses the total organic loading rate as the major parameter to describe the kinetics of an anaerobic reactor in terms of organic matter removal and methane production [13, 14]. The rate of change in substrate concentration in modified Stover-Kicannon model is shown in Equation. 20.

$$\frac{dS}{dt} = \frac{R_{max}\left(QS_0/V\right)}{K_B + \left(QS_0/V\right)} \quad (20)$$

Where dS/dt is defined as

$$\frac{dS}{dt} = \frac{Q}{V}\left(S_0 - S\right) \quad (21)$$

$$\frac{V}{Q\left(S_0 - S_e\right)} = \frac{K_B}{R_{max}}\left(\frac{V}{QS_0}\right) + \frac{1}{R_{max}} \quad (22)$$

$$S = S_0 - \frac{R_{max}S_0}{K_B + QS_0/V} \quad (23)$$

All kinetic parameters for Monod, Contois, Grau second-order and modified Stover-Kicannon models were obtained by fitting steady-state experimental data to the model equations (Equation 9, 10, 13, 14, 17, 18 and 22) are shown in Table 2.

The results showed that UASB-R3 gave higher biomass yield in term of Y (gVSS/gCOD) than that of UASB-R1 and R2 (R3>R1>R2). This can mislead to conclude for UASB-R2 (mix-granules with cassava factory) that there was insignificant new cell generation here since methane production is strong growth associated. The better explanation is that, in our cases, the cell density is so high (large granules size) such that the limiting substrate could not be supplied throughout the granule mass, causing partial cell starvation, death, and lysis which almost balance with new cell generate.

Table 2 Kinetic parameters of the UASB reactors treating cannery seafood wastewater

Seed sources	Kinetic models	Kinetic parameters	Values	Regression coefficient (R^2)
Seafood factory (UASB-R1)	Monod	Y (gVSS $gCOD^{-1}$)	0.0463	0.869
		K_d (d^{-1})	0.0056	
		μ_{max} (d^{-1})	0.027	0.934
		K_s (g/l)	1.079	
		K_{max} (μ_{max} Y^{-1}) (d^{-1})	0.58	
	Contois	Y (mgVSS $mgCOD^{-1}$)	0.0463	0.869
		K_d (d^{-1})	0.0056	
		μ_{max} (d^{-1})	0.029	0.944
		β (gCOD $gVSS^{-1}$)	0.096	
	Grau second order	a (d^{-1})	0.27	0.998
		b (dimentionless)	1.009	
		K_s (d^{-1})	1.30	
	modified Stover-Kincannon	K_B (gCOD $l^{-1}d^{-1}$)	15.47	0.998
		R_{max}(gCOD $l^{-1}d^{-1}$)	15.34	
Seafood + Cassava factory (UASB-R2)	Monod	Y (gVSS $gCOD^{-1}$)	0.0236	0.970
		K_d (d^{-1})	0.0032	
		μ_{max} (d^{-1})	0.032	0.971
		K_s (g/l)	1.875	
		K_{max} (μ_{max} Y^{-1}) (d^{-1})	1.35	
	Contois	Y (mgVSS $mgCOD^{-1}$)	0.0236	0.970
		K_d (d^{-1})	0.0032	
		μ_{max} (d^{-1})	0.074	0.958
		β (gCOD $gVSS^{-1}$)	0.544	
	Grau second order	a (d^{-1})	0.18	0.999
		b (dimentionless)	1.017	
		K_s (d^{-1})	2.68	
	modified Stover-Kincannon	K_B (gCOD $l^{-1}d^{-1}$)	24.27	0.999
		R_{max}(gCOD $l^{-1}d^{-1}$)	23.87	

Seed sources	Kinetic models	Kinetic parameters	Values	Regression coefficient (R^2)
Seafood+ Palm oil factory (UASB-R3)	Monod	Y (gVSS $gCOD^{-1}$)	0.0685	0.735
		K_d (d^{-1})	0.0099	
		μ_{max} (d^{-1})	0.024	0.808
		K_s (g/l)	0.370	
		K_{max} (μ_{max} Y^{-1}) (d^{-1})	0.35	
	Contois	Y (mgVSS $mgCOD^{-1}$)	0.0685	0.735
		K_d (d^{-1})	0.0099	
		μ_{max} (d^{-1})	0.025	0.838
		β (gCOD $gVSS^{-1}$)	0.036	
	Grau second order	a (d^{-1})	0.39	0.995
		b (dimentionless)	0.966	
		K_s (d^{-1})	0.98	
	modified Stover-Kincannon	K_B (gCOD $l^{-1}d^{-1}$)	10.28	0.995
		R_{max}(gCOD $l^{-1}d^{-1}$)	10.64	

The kinetic parameters of the UASB reactors treating cannery seafood wastewater. Moreover, it was found that UASB-R3 which contained mix-inocula from palm oil (smallest average size in the range 0.1-0.2 mm.) gave the highest biomass yield in term of Y(gVSS/gCOD) and highest death rate constant value (K_d). Other interesting results were the saturated constant (K_s) in Monod model and (β) in Contois models. Whereas high (β) in UASB-R2 reflected the strong negative effect of granule size on the substrate accessibility of microbial cells, K_s in Monod model indirectly showed a similar trend albeit with a different interpretation. Highest K_s values in UASB-R2 were a combined effect of high cell density (thus high substrate demand) and diffusion-limiting in-granule substrate transport; both were a result of mix-granule with the biggest granule size.

The apparent high K_s value again does not explain high half-substrate consumption rate according to Monod model formulation. So there is no surprise that both Monod and Contois models could not represent the experimental results so well since their basis in model formulation do not directly include diffusion-limiting step into consideration. Consequently, Monod and Contois are fundamentally unsuitable for modeling UASB with granules and some diffusion-limited consideration must be included in the formulation.

3.2.5 Model Evaluation

The kinetic values can be used to explain the performance of UASB reactors and to predict the effluent COD from UASB reactors. From four kinetic models (Monod, Contois, Grau-second order, and modified Stover-Kicannon models), when compared with data from experiments, Grau-second order and modified Stover-Kicannon models were more suitable for predicting COD effluent as indicated by higher regression coefficients (higher than 0.98) for all reactors (UASB-R1, R2 and R3) as shown in Figure 1.

4.0 CONCLUSION

The results of this study showed that the model predictions (COD effluent) were in good agreement with the observed data in Grau second-order and modified Stover-Kicannon models. Thus these models are recommended for describing the kinetics kinetics of UASB for this type of wastewater. Although both Monod and Contois models predicted correct trends for COD degradation, they showed significantly lower R2. This can be explained as follows. Both models not only ignore the effect of in-granules substrate diffusion in their derivations but also assume well-mixed reactor configuration. When this is a significant deviation from these assumption,they give poor prediction.On the othe hand, Grau second order and modified Stover-Kicannon models are more empirical yet fit well to our set data and others.These two models has further advantage as they predict that the effluent COD depends on HRT and initial COD, thus they are easily verified by experimental data.

In addition, the UASB-R2 used mixed granules with cassava factory (SS+CS) gave the best performance in term COD removal efficiencies and biogas production, which highest coefficient value (R^2). In conclusion, the sizes of granules highly affected the reactor performance and biogas production in UASB reactors. The production decreased with decreasing HRTs or inversely increasing organic loading rate (OLR).

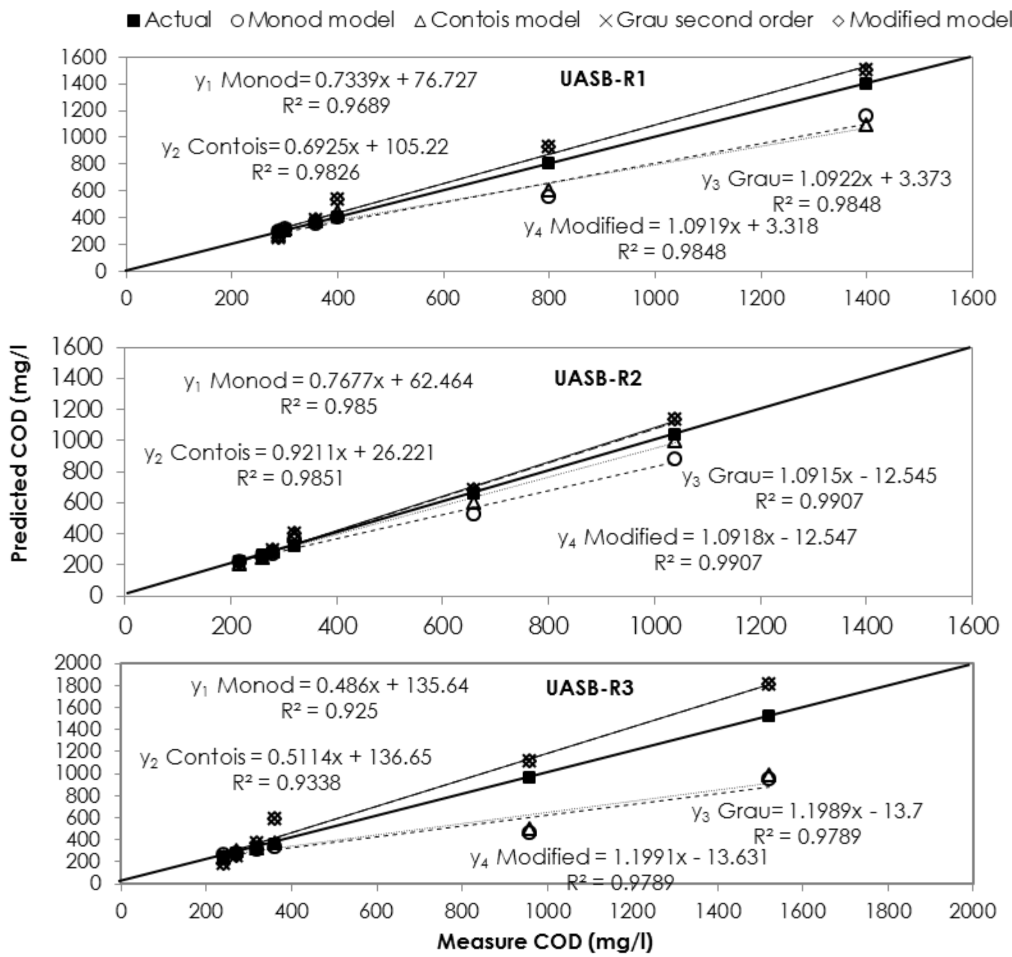


Figure 1 Comparison of the predicted and measure COD value from lab scale UASB reactors

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