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Estimation of Bio-Kinetic Coefficients for Treatment of Brewery Wastewater

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Abstract**—**Anaerobic modeling is a useful tool to describe and simulate the condition and behaviour of anaerobic treatment units for better effluent quality and biogas generation. The present investigation deals with the anaerobic treatment of brewery wastewater with varying organic loads. The chemical oxygen demand (COD) and total suspended solids (TSS) of the influent and effluent of the bioreactor were determined at various retention times to generate data for kinetic coefficients. The bio-kinetic coefficients in the modified Stover–Kincannon kinetic and methane generation models were determined to study the performance of anaerobic digestion process. At steady-state, the determination of the kinetic coefficient (K), the endogenous decay coefficient (K_d), the maximum growth rate of microorganisms (μ_{max}), the growth yield coefficient (Y), ultimate methane yield (B_o), maximum utilization rate constant U_{max} and the saturation constant (K_B) in the model were calculated to be 0.046 g/g COD, 0.083 (d^{-1}), 0.117 (d^{-1}), 0.357 g/g, 0.516 (L CH_4/$gCOD_{added}$), 18.51 (g/L/day) and 13.64 (g/L/day) respectively. The outcome of this study will help in simulation of anaerobic model to predict usable methane and good effluent quality during the treatment of industrial wastewater. Thus, this will protect the environment, conserve natural resources, saves time and reduce cost incur by the industries for the discharge of untreated or partially treated wastewater. It will also contribute to a sustainable long-term clean development mechanism for the optimization of the methane produced from anaerobic degradation of waste in a close system.

Keywords**—**Brewery wastewater, methane generation model, environment, anaerobic modeling.

I. INTRODUCTION

RECOVERY of bioenergy from spent biomass, industrial wastewaters and other types of wastes is commonly achieved with the conventional anaerobic digestion (AD) process [1]. Anaerobic digestion technology, such as upflow anaerobic sludge blanket (UASB) reactor technology is becoming important for energy needs through the treatment of different types of wastewater [2], [3]. Bioconversion of organic substances to biogas can be slow, with a long hydraulic retention time (HRT) [4] and sometimes may fail or encounter serious problems, depending on characteristic of wastewater, pH, temperature, loading rates, and carbon and nitrogen ratio of the source material. These factors affect the microorganisms that are responsible for the degradation of organic matter in the bioreactors [5]. Thus, it is important to improve the efficiency of the UASB digestion process in the production of biogas, in particular, methane content to offset non-renewable energy use by the industry.

A simple mathematical model that describes some of the parameters that define the anaerobic treatment process will be useful for giving information on the state of the reactor process and any impending failure [6], [7]. Kinetic modelling is a generally accepted approach in defining the specific parameters of system performance. The results of such modelling can be used to estimate treatment efficiencies and characteristics of full–scale reactors operating under similar conditions.

The design and operation of an anaerobic digestion system are based on fundamental knowledge of kinetics and stoichiometry of biological reactions [7]. Prediction of industrial–scale anaerobic reactor performance based on UASB technology in treating brewery wastewater depends on the estimated value of model parameters [8], [9]. Thus, the determination of model coefficients (K, B_o, μ_{max}, K_d, Y, K_B, and U_{max}) is important for the validation of the model, to predict and optimize not only the volumetric methane production rate of any UASB reactor treating brewery wastewater but other different wastewater sources. Hence, the objective of the study is to determine bio-kinetic parameters of a newly developed modified methane and Stover–Kincannon kinetic models to predict both volumetric methane production rate and final effluent quality respectively, during anaerobic digestion of brewery wastewater.

II. MATERIALS AND METHODS

A. Description of the UASB Reactor System Used and Wastewater Sampling

Full-scale UASB reactor treatment brewery wastewater was used as described by [7]. A series of pre-screened brewery wastewater (reactor effluent) and the full–scale UASB reactor effluent ready to be discharged into the municipal sewer system were collected in one–liter sterile glass bottles and transported to the laboratory at 4°C and analyzed for performance evaluation. Physico-chemical analyses were conducted within 48 hours of collection with the necessary preservation techniques adapted from the Standard methods [10]. Biogas was collected in a Tedlar bag (Sigma-Aldrich) for analysis.

B. Wastewater Characterization

Brewery wastewater samples were analyzed for parameters such as temperature, pH, alkalinity, total chemical oxygen

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demand (TCOD), biological oxygen demand (BOD_5), ortho-phosphorous (PO_4) and total oxidized nitrogen (TON) and TSS, which were thought to be significant according to Standard Methods for Examination of Water and Wastewater [10]. Samples were analyzed using appropriate conventional and instrumental methods [10]. The pH and temperature were measured using a pH meter (Beckman pH 211 Microprocessor, USA). The pH was an indicator of the process stability while the conductivity was an indicator of production of total dissolved solids. The BOD_5 measurement was done using the respirometric method for five days (OxiTop TS 606/2-i system). The COD concentration in the wastewater was determined by close refluxing according to the standard method 5220D [10], microwave digestion (Milestone Start D, Sorisole, Italy) was first used to digest the samples at 150°C for 1 h in COD vials containing the Digestion Solution (0–15,000 mg COD/L). Then, COD concentration was measured using Aquakem Gallery discrete autoanalyser (Thermo Scientific, UK). Alkalinity was measured by potentiometric titration using 0.02N H_2SO_4 to an endpoint pH value of 4.5. The aim of measuring alkalinity was to evaluate the buffering capacity of the UASB reactor treating brewery wastewater and the effect on the granular sludge [10]. The TSS was determined gravimetrically by drying well homogenized samples, respectively at 103-105°C for 24h [10]. The composition of biogas produced was analyzed using a gas chromatograph equipped with a thermal conductivity detector (TCD). The column used was a Porapak Q 1.8m × 2.10mm with the column oven, injector and detector temperatures set at 40°C, 100°C and 100°C, respectively. Helium gas was used as the carrier at 20 ml/min.

C. Analytical Quality Assurance and Statistical Analysis

Both reagent and sample blanks were used for all the methods that required the use of the Spectrophotometer and Aquakem Gallery discrete autoanalyser. Standard solutions were prepared for the analysis of COD, PO_4 and TON. Instruments were first calibrated before use using standard solutions. The sample bottles were cleaned thoroughly using a detergent, 1:1 HCl, triple rinsed with distilled water and a final triple rinse was done with the sample as suggested by Fatoki and Mathabatha [11]. All tests were carried out in triplicate and statistical analysis was performed. The data obtained was used to calculate mean, ranges and standard deviations. Graphs and data analysis were carried out using GraphPad Prism v 5.0, software package.

III. RESULTS AND DISCUSSION

Removal efficiencies for both BOD_5 and COD of 80% and 78% indicates the conversion of organic matter in the industrial wastewater to usable biogas with 65.9% of methane and good effluent composition (Table I). Ortho-phosphorous (PO_4) and TON tests were measured in the settled brewery wastewater collected to determine the level of these nutrients for efficient biological treatment. The COD:N:P for the wastewater was found to be C:N:P = 250:0.07:2.66 as against the recommended value of 100:5:1 [12]. This indicated low concentration of nitrogen in the influent wastewater into the reactor and this could hinder a satisfactory biological treatment. Therefore, urea was added as a supplementary nitrogen source in the influent wastewater to meet the required amount for anaerobic treatment [13].

Prediction of industrial–scale anaerobic reactor performance based on UASB technology in treating brewery wastewater depends on the estimated value of parameters. Kinetic coefficients of interest for the design of anaerobic treatment processes are K, μ_{max}, K_d, Y, B_o, U_{max} and K_B. The value of K, according to the Monod equation, may be associated with the ability of microorganisms to degrade the substrate present in the waste to produce methane. A high K value is an indication that the microorganisms present in the reactor have greater difficulty in converting the organic matter to methane [14]. Studies have shown that B_o depends on the organic loading rate (OLR), sludge or hydraulic retention time used during the treatment of brewery wastewater [4], [14]. Ultimate methane yield coefficient, B_o is directly proportional to the biodegradable COD loading rate [15]. The value of B_o depends on the type of waste that is being treated, environmental conditions such as operating temperature of treatment plant or reactor, as well as the hydraulic retention time of the wastewater used in the reactor [4], [14]. Endogenous decay coefficient, K_d is used to find out the net amount of sludge to be handled. Growth yield coefficient, Y is used to estimate the total amount of sludge produced as a result of wastewater treatment. The experimental data used to determine model values are obtained from the full-scale reactor. The mean values of S_i, S_e, X and methane yield corresponding to each are presented in Table II.

The following linearized equation was used to find the saturation constant (K_B) and the maximum utilization rate constant (U_{max}) (1) [7].

$$\left(\frac{dS}{dt}\right)^{-1} = \frac{V_r}{(Q(S_i - S_e))} = \frac{K_B V_r}{U_{max}(QS_i)} + \frac{1}{U_{max}} \qquad (1)$$

TABLE I
INFLUENT AND EFFLUENT COMPOSITION OF THE FULL–SCALE UASB TREATING BREWERY WASTEWATER AND THE BIOGAS COMPOSITION [7]

	Wastewater concentrations	
Parameters	Digester inflow⁺	Digester outflow⁺
Temperature (°C)	29.21	29.46
pH	6.90	6.93
COD	2005.73	421.80
BOD_5	1877.09	370.46
TSS	2449.40	3268.97
Alkalinity(mg $CaCO_3$/ L)	3172.78	2462.42
Methane, CH_4 (%)		65.9%

⁺All the concentrations are mean and in mg/L except otherwise stated.

TABLE II
DATA (AVERAGE) OBTAINED FROM THE FULL-SCALE UASB REACTOR TREATING BREWERY WASTEWATER

θ_h (h)	COD loading rate (g/L)	S_i (g/L)	S_e (g/L)	X_e (g/L)	Methane yield (L/g COD $_{added}$)
8	171.43	1.03	0.51	0	0.18
9	167.24	0.93	0.23	2.19	0.27
9	929.53	3.10	1.01	4.40	0.24
11	520.05	2.89	0.43	1.00	0.30
12	248.66	1.00	0.23	6.11	0.27
12.1	170.16	1.10	0.11	4.00	0.32
13	900.62	3.00	0.23	1.73	0.32

The inverse of loading rate $V_r/Q\ (S_i - S_e)$ is plotted against the total loading rate of the reactor $V_r/Q\ (S_i)$. A straight line result is obtained; the slope and intercept of the line are K_B/U_{max} and $1/U_{max}$ respectively. From equation (1), K_B and U_{max} in the model were estimated as 13.64 and 18.51 (g/L/day) respectively (Fig. 1).

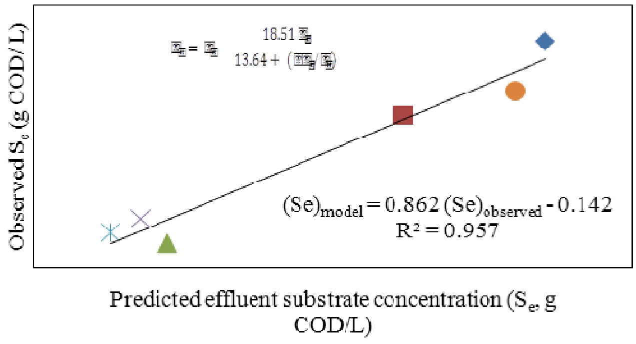

Fig. 1 Determination of the kinetic constants K_B and U_{max} using the data obtained from the full-scale reactor

According to Bhunia and Ghangrekar [16], (2) can be used to obtain the values of K_d by plotting a linear regression of $1/\theta_h$ against $(S_i - S_e)/(X_e\theta_h)$. The intercept is equal to K_d and Y is the slope of the straight line that passes through the plotted points.

$$\frac{1}{\theta_h} = \frac{Y.Q(S_i - S_e)}{V_b.X_e.\theta_h} - K_d \tag{2}$$

The estimated endogenous decay coefficient, K_d value of 0.083 $d^{-1}$is represented by the intercept of the graph, while the slope Y, correspond to 0.357 g/g. The ultimate methane yield (B_o) was determined using a least–squares method through nonlinear regression of $1/\theta_h$ versus methane yield. The B_o is equal to the intercept of the graph. Fig. 2 shows the graph of methane yield against $1/\theta_h$ with the intercept; B_o corresponds to 0.516 L CH_4/g COD_{added}.

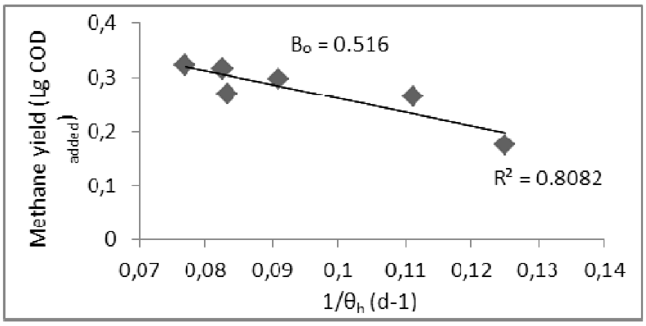

Fig. 2 Determination of ultimate methane yield (B_o)

Then, the first–order kinetic constant coefficients K and μ_{max} can be determined by plotting θ_h against S using (3):

$$\theta_h = \frac{1}{\mu_{max}} + \frac{k}{\mu_{max}} \frac{S_i - S_e}{S_e} \tag{3}$$

The first-order kinetic coefficients K and μ_{max} as determined by plotting θ_h against S produced a straight line with μ_{max} given by 1/intercept and K as slope/intercept. The values of μ_{max} and K derived in this study were 0.117 d^{-1} and 0.046 g/g, respectively. The estimated model coefficients from the data obtained from full-scale UASB reactor treating brewery wastewater are presented in Table III.

TABLE III
ESTIMATED MODEL COEFFICIENTS OBTAINED FROM A FULL-SCALE UASB REACTOR TREATING BREWERY WASTEWATER DATA

Parameter	Estimated value	Units
μ_{max}	0.117	d^{-1}
K	0.046	g/g
K_d	0.083	d^{-1}
B_o	0.516	L CH_4/g COD $_{added}$
Y	0.357	g/g
K_B	13.64	g/L/day
U_{max}	18.51	(g/L/day)

The estimated model coefficients are within the range of values reported in the literature for mesophilic anaerobic digestion for waste types that include, banana stem and peel waste, palm oil mill wastewater, dairy manure and the organic fraction of municipal solid waste from anaerobic treatment plants [6], [14], [15], and [17].

The comparison studies exploring the modified Stover-Kincannon model for anaerobic treatment of different types of wastewater under different experimental conditions are shown in Table IV. From Table IV, the maximum utilization constant (U_{max}) values (11.83 and 1.996 g/L/day) reported by Yetilmezsoy [18] is lower than the value obtained in this study, however, lower than the estimated value obtained for synthetic-based wastewater [19]. The high U_{max} in the synthetic wastewater could be attributed to the presence of readily biodegradable substrates that are easily accessible to microorganisms [19].

The value of μ_{max} obtained for our UASB reactor treating of brewery wastewater was higher than the value reported by Zainol, [15] and lower than 0.135 d^{-1} reported by Fdez-Guelfo et al. [14]. Furthermore, our value of B_o is very similar to those reported in the literature [6], [14], [15] and [16]. Hence, the values of coefficients K, B_o, μ_{max}, K_d, K_B and U_{max} so determined will be used to validate the model and to predict treatment efficiency and predict volumetric methane productivity of any UASB reactor treating brewery wastewater.

IV. CONCLUSION

Estimation of kinetic parameters in the models using the mean values of influent and effluent COD, VSS and methane yield obtained at steady-state conditions of the actual full–scale UASB reactor treating industrial wastewater indicated that the composition of the wastewater strongly affects the kinetics of the digestion process. The determination of these model coefficients is important for the validation of the model (methane generation model), to predict and optimize volumetric methane production rate and substrate concentration of the final effluent of anaerobic reactor treating brewery wastewater.

TABLE IV
COMPARISON OF DIFFERENT TYPES OF ANAEROBIC WASTEWATER TREATMENT PROCESSES USING MODIFIED STOVER-KINCANNON MODEL [7]

Digester type	Type of substrate	Operating temperature (°C)	Modified Stover- Kincannon model kinetic and estimated coefficients			
			K_B (g/L/day)	U_{max}(g/L/day)	R^2	References
UASB	Brewery wastewater	28-32	13.64	18.51	0.978	Present study
UASB	Poultry manure wastewater	30-34.5	13.02	11.83	0.991	[18]
Anaerobic biphasic fixed film reactor	Distillery wastewater	37	1.69(kg/m^3/d)	2 (kg/m^3/d)	0.992	[6]
UASB	Municipal wastewater	17.1-21	1.536	1.996	0.972	[20]
UASB	Synthetic wastewater (2,4-dichlorophenol)	-	0.0098 (mg/L/day)	0.01 (mg/L /day)	0.992	[21]
Anaerobic filter	Synthetic wastewater (saline)	37	5.3	7.05	0.910	[22]
Mesophilic anaerobic filter	Synthetic wastewater (starch)	35	50.6	49.8	0.998	[19]
Mesophilic anaerobic filter	Paper pulp liquor	35	6.14	6.71	0.998	[19]

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