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Biogas production kinetics in an anaerobic multiphase hybrid reactor treating antibiotic industry wastewater

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ABSTRACT

Experiments were performed in an anaerobic multiphase hybrid reactor at the mesophilic temperature (30°C–35°C) for simultaneous bioenergy recovery and antibiotic wastewater treatment. The reactor was operated for 245 d. Acclimatization was done at 24 h hydraulic retention time for 41 d. From day 42 to 113, the reactor was operated at six different organic loadings (COD/L) at same hydraulic retention time (HRT) and found that the initial substrate concentration of 4,000 mg COD/L is the best suited to achieve greater reactor performance. Between 114 and 245 d, by varying the HRT from 30 to 3 h, the biogas production rate increased with decrease in HRT. In this study, the mathematical models viz., modified Stover-Kincannon and Van der Meer and Heertjes models were applied to determine the gas production kinetics.

Keywords: Anaerobic treatment; Antibiotic wastewater; Modified Stover-Kincannon model

1. Introduction

Energy is the basic need for economic development of a country. India is the fourth largest producer of electricity. Energy consumption per capita is directly linked to living standard of a country. Energy supply, energy security, pollution reduction and prevention of global warming by decreasing CO_2 emissions are compelling arguments for reducing our dependence on fossil fuels [1]. In 2002, 5.8 metric tons of CO_2 was emitted in the United States of America, 98% of which was emitted as a result of combustion of fossil fuels. Further, worldwide direct combustion of fuel for transportation and heating accounts for over half of greenhouse gas emission [1]. In the aftermath of the energy crisis of 1973, the major focus of India was to reduce its dependence on conventional energy resources. India was among the first few countries to recognize the potential of renewable energy for meeting the energy demands in different sectors of the economy. Both developing and developed countries have prompted to utilize the waste and wastewater for energy production through biomethanation processes [2,3]. Biomethanation is a multistage process in which organic matter is decomposed to biogas, water and ammonia [4]. A cubic metre of biogas is said to be equivalent to half a kilogram of liquefied petroleum gas or 6 kWh of thermal energy. Among the wide range of biomethanation processes developed for the treatment of high strength wastewater, anaerobic multiphase hybrid reactor (AMHR) has emerged with more successful applications [5–9]. The AMHR, a conglomeration of upflow anaerobic sludge blanket reactor and anaerobic filter, has many advantages, such as better resilience to hydraulic and organic shock loads, longer biomass retention times and lower sludge yields [10–12]. Furthermore, it is simple and economical. Because of

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these potential advantages, the AMHR was selected for this research work. The main disadvantage of the bioreactor is subject to failure during the start-up process, especially when biodegradable substrates are applied.

An extensive range of products such as human and animal medications are produced from the pharmaceutical manufacturing industry. Generally, main processes of pharmaceutical manufacturing are fermentation, extraction, chemical synthesis, formulation and packaging. The wastewater streams from all five processes have the potential to contain high organic load and characterized by high COD concentration, some can have COD as high as 40,000 mg/L stated in the synthesis and fermentation based drug industry, produce larger volumes of effluent [13,14]. The standard effluent discharge of pharmaceutical industry wastewater in India is pH – 6.0 to 8.5; COD – 250 mg/L; BOD – 30 mg/L; TSS – 100 mg/L [15,16].

In this research work, the treatment of fermentation-based antibiotic industry wastewater was investigated. The wastewater contains significant levels of aliphatic organic solvents and includes spent mycelia, extracted broth, wash waters, residual organic solvent and wastewaters from demineralization plant, boilers, generators, chillers and air compressors [14]. Fig. 1 presents the source of wastewater from various units of the fermentation-based antibiotic industry. The high content of organic pollutant besides imparts objectionable odour, depletes the oxygen content of water bodies and subsequently causes ill effects on their biota [17]. The antibiotic wastewater, therefore, needs treatment prior to disposal either on land or into water bodies.

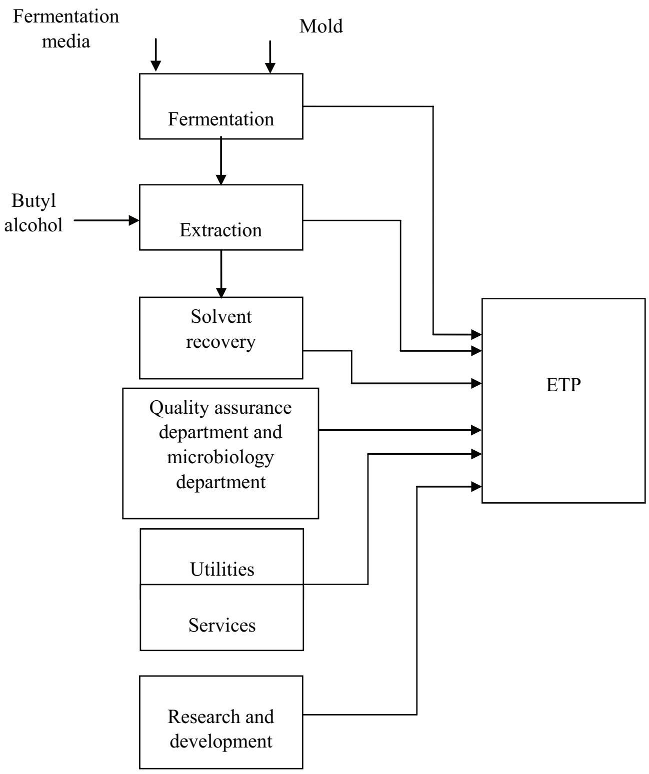

Fig. 1. Sources of wastewater from an antibiotic manufacturing industry.

Researchers have studied the pharmaceutical wastewater treatment in the most successful anaerobic reactors include the anaerobic suspended film contact reactor [18], anaerobic batch reactor [19], anaerobic fixed film reactor [20], expanded granular sludge bed anaerobic reactor [21], upflow anaerobic stage reactor [22], continuous stirred tank acidogenic reactor [23], sequential upflow anaerobic sludge blanket (UASB) reactor [24], hybrid upflow anaerobic sludge blanket (HUASB) reactor [5], anaerobic packed bed reactor [25], anaerobic sequencing batch reactor [26], anaerobic upflow packed bed reactor [27], anaerobic membrane bioreactor [28] and UASB reactor [29]. From the available literature, it is also known that hitherto scant attention has been given to treat antibiotic wastewater, especially penicillin-G wastewater in the AMHR. Moreover, no attempt has been made to determine the gas production kinetics of AMHR using antibiotic wastewater.

Kinetic models are important tool for explaining and predicting the performance of anaerobic treatment systems [19,30]. These models are normally divided into two classes: structured and unstructured one. The metabolic pathways are taken into consideration in structured models and are complicated models. On the other hand, the unstructured kinetic models are much simpler than the structured ones [1,31]. Of the several kinetic models available in the literature, kinetic models, such as modified Stover-Kincannon and Van der Meer and Heertjes models [32] were applied to determine the gas production kinetics of AMHR using antibiotic wastewater and verified the validity of the models by comparing the experimental and predicted data at decreasing hydraulic retention times (HRTs).

2. Materials and methods

2.1. Substrate

The effluent collected from an antibiotic industry, Tamil Nadu State, India, was used as a substrate. The physicochemical characteristics of the wastewater are given in Table 1.

2.2. Anaerobic multiphase hybrid reactor

A laboratory scale AMHR used in this study was made of perspex tube (Lark Innovative Fine Teknowledge, Chennai, India) (Fig. 2). With an internal diameter of 10.4 cm and overall height of 60 cm, the total capacity of the AMHR was 5 L. The packing section of the reactor (10 cm) contained 260 polypropylene spherical beads of 1.5 cm diameter each. An inlet was fixed at the lower part of the reactor. An outlet for the effluent was made above the packing section. A gas flow meter used to measure the volume of biogas was connected to the outlet fixed at the topmost part of the reactor.

2.3. Inoculum and start-up process

The inoculum was prepared using sewage sludge collected from the pumping station and cow dung slurry (700 mg/L of suspended solids and grey in colour) in varying ratios and fed into the reactor for 10 weeks at 24 h HRT. Then, acclimatization medium consisting (mg/L) of glucose – 1,000,

Table 1
Physicochemical characteristics of antibiotic wastewater

Parameters	Concentration
pH	5.5–6.5
Colour	Yellowish
Odour	Fruity smell
BOD (mg/L)	5,100–9,020
COD (mg/L)	15,000–25,000
Acidity as acetic acid (mg/L)	300–500
Alkalinity as $CaCO_3$ (mg/L)	1,000–2,000
Total solids (mg/L)	1,000–3,000
Temperature (°C)	30–45

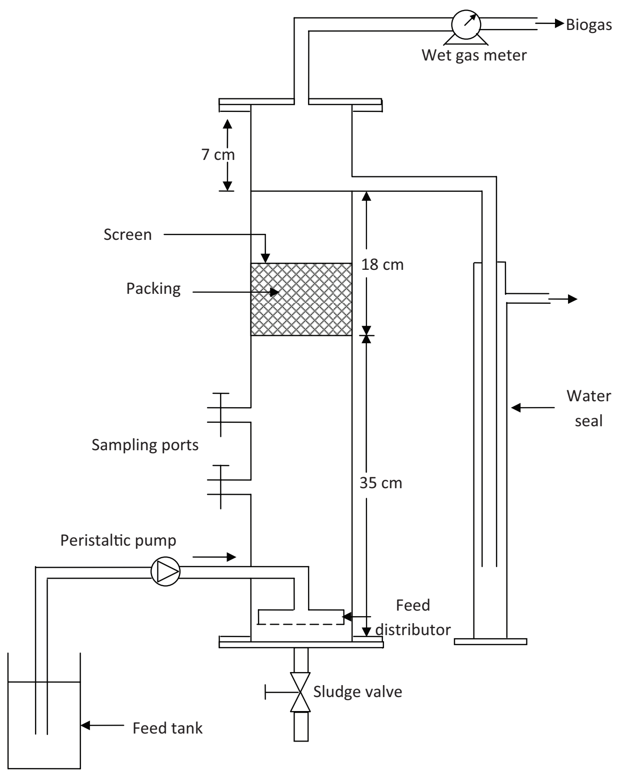

Fig. 2. Schematic diagram of AMHR reactor.

urea – 227, magnesium sulphate – 100, ferric chloride – 0.5, calcium chloride – 0.7, di-potassium hydrogen orthophosphate –1,070, potassium dihydrogen orthophosphate – 527 was fed into the reactor for 22 d. The biogas production was noticed at the far end of this period. When the methane content of the obtained biogas exceeded 60%, it was considered as zeroth day [33]. Thereafter, the evaluation experiments were started. In these experiments, when the COD of the effluent and biogas production rates were found to remain constant (within ± 3%) for three consecutive days, the steady-state conditions were expected to have set-in. Variations in the treatments were made only after "stable state" conditions continued.

2.4. Sampling and analysis

Analyses of volatile suspended solids (VSS), chemical oxygen demand (COD), acidity, alkalinity, volatile fatty acid (VFA) and pH of influent and effluent samples were carried out by following the Standard Methods [34]. Biogas produced in the reactor was measured by the gas flow meter (Toshniwal, India). The biogas content was analyzed using a gas chromatograph (Shimadzu, 221-70026-34, Japan) equipped with a thermal conductivity detector and the column was packed with a dual packed column. The operating temperatures of the column, detector and injector were 40°C, 80°C, 50°C, respectively. The microbial community present in the sludge granules was found out using scanning electron microscope (JEOL – JSM 5300, Japan).

3. Results and discussion

3.1. Reactor operation

The AMHR was operated continuously for 245 d in three different phases.

3.2. Phase I: acclimatization phase

At constant 24 h HRT, different proportions of antibiotic wastewater and acclimatization medium were loaded into the reactor for 41 d. The proportion of antibiotic wastewater was gradually increased and the quantum of the acclimatization medium was decreased till the end of acclimatization phase. As antibiotic wastewater banded granular formation, acclimatization medium was added to hasten the degradation process. The role of glucose as the promoter in colonizing the microbes in treating pharmaceutical wastewater is demonstrated [23]. The COD removal efficiency was found to increase with the increase of organic loading rate (OLR) (Table 2). In their work on distillery wastewater treatment, Fernandez et al. [35] enunciated a similar trend. In this phase, for the five different OLRs, viz., 1.680, 2.245, 2.324, 2.532 and 2.686 kg COD/m^3 d, the obtained steady-state values of biogas production were 830, 900, 924, 930 and 985 mL/d, respectively. The record of the minimum amount of biogas (200 mL/d) during the first day of this phase (Fig. 3) could be due to meagre growth of biomass. When the days started progressing, granulation getting developed and henceforth a slow rise in biogas production could be noticed. The biomass concentration ranged between 28.8 and 34.7 g/VSS L during 0–41 d. At the commencement of each OLR, the biogas production rate was very low and it could be due to the stress produced on the biomass by the supply of increased substrate concentration as pronounced by Senturk et al. [36]. The volumetric biogas production rate was shoot-up from 0.1628 m^3/m^3 d at 1.680 kg COD/m^3 d to 0.1932 m^3/m^3 d at 2.686 kg COD/m^3 d. The methane content of the biogas ranged from 65% to 68% (Table 2). The VFA was detected in the wastewater and the concentration of VFA during this phase ranged between 283 and 660 mg acetic acid/L in the effluent. When the reactor was operated at the lowest OLR of 1.680 kg COD/m^3 d, the concentration of effluent pH at the beginning was 6.8 and the corresponding effluent VFA concentration was 660 mg acetic acid/L. Pervasiveness of such a low pH was an indication of the occurrence of acidogenesis which hindered

Table 2
Operational parameters and steady-state results

Time (d)	HRT (h)	OLR (kg COD/m³ d)	COD removal efficiency (%)	VFA (mg acetic acid/L)	pH	Biogas production rate (mL/d)	CH_4 (%)
Phase I							
0–7	24	1.68	54.6	335	7.1	830	65
8–14	24	2.245	73.54	348	7.2	900	66
15–22	24	2.324	84.77	342	7.2	924	66
23–30	24	2.532	86.15	315	7.3	930	67
31–41	24	2.686	92.34	299	7.4	985	68
Phase II							
42–52	24	0.949	77.96	359	7.4	200	65
53–64	24	1.560	83.95	381	7.5	528	68
65–76	24	2.106	88.60	334	7.6	1,030	69
77–89	24	3.084	91.025	318	7.6	1,120	70
90–101	24	4.000	95.00	281	7.7	1,990	71
102–113	24	5.000	75.51	489	7.5	2,775	66
Phase III							
114–134	30	3.200	91.25	319	7.7	1,200	70
135–155	18	5.320	89.90	307	7.8	2,581	71
156–175	12	8.040	88.50	303	7.8	4,450	69
176–197	8	11.988	86.54	281	7.9	5,775	68
198–217	6	16.048	84.50	290	7.9	8,780	68
218–228	3	32.256	68.00	598	7.4	7,890	63
229–245	6	16.016	82.50	436	7.5	8,695	67

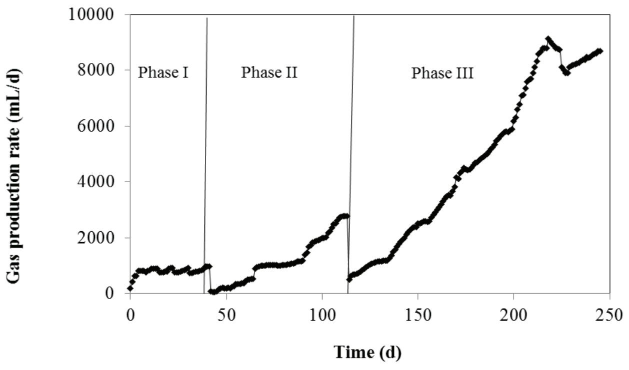

Fig. 3. Variation of biogas production for 245 d.

methanogenesis [24]. However, at the end of the acclimatization phase, on 41st d, the steady-state concentration values of VFA and pH obtained were 299 mg acetic acid/L and 7.4, respectively, indicated a healthy anaerobic environment [37].

3.3. Phase II: effect of organic loading

In this phase, the reactor was run from 42nd to 113th d. The addition of acclimatization medium was stopped and the raw wastewater at different proportion was used from 42nd d onwards. At constant HRT of 24 h, the OLR was steadily increased by increasing the organic loading (OL) in the order of 949; 1,560; 2,106; 3,084; 4,000 and 5,000 mg COD/L (Table 2) and the obtained COD removal efficiency were 77.96%, 83.95%, 88.6%, 91.025%, 95.0% and 75.51%, respectively. When the OL of antibiotic wastewater was enhanced to 4,000 mg COD/L from 949 mg COD/L, the COD removal efficiency raised to 95.0% from 77.96% (Table 2). Further escalation of OL to 5,000 mg COD/L decreased the COD removal efficiency to 75.51% and increased the effluent VFA concentration to 898 mg acetic acid/L (Table 2). The reactor performance was said to be deteriorated and the reason could be adduced to higher initial substrate concentration of 5,000 mg COD/L. Results similar to that of the present work were also documented [38–40]. According to the results, the OL of 4,000 mg COD/L is optimum for achieving a better AMHR performance. The production of biogas ranged from 54 to 27 mL/d (Fig. 3) and the methane content varied between 65% and 71% (Table 2). The steady-state values of biogas production for the six mentioned OLRs were 200; 528; 1,030; 1,120; 1,990 and 2,775 mL/d, respectively. Among all the OLs, at 5,000 mg COD/L, that is, 5.0 kg COD/m³ d, the biogas production rate was the highest and increased from 2,030 to 2,775 mL/d between 102 and 113 d (Fig. 3). In this period, the total biogas production per gram of COD reduction improved with the increase in OL but the methane content reduced. During this phase, relatively higher ranges in biomass concentration of 36–45 g VSS/L were recorded. Gangagni Rao et al. [20] in their study stated that the pH concentration of 7.5 was optimum for methane production and in this phase, pH concentration ranged between 7.2 and 7.7.

3.4. Phase III: effect of hydraulic retention time

In this phase (114–245 d), the OLR was increased from 3.2 to 32.256 kg COD/m^3 d, by decreasing the HRT and keeping the substrate concentration constant at around 4,000 mg COD/L. The steady-state values of the COD removal efficiency and biogas production rate for the seven OLRs (3.20, 5.32, 8.04, 11.988, 16.048, 32.256, 16.016 kg COD/m^3 d) were 91.25%; 89.9%; 88.5%; 86.54%; 84.5%; 68.0%; 82.50%; and 1,200; 2,581; 4,450; 5,775; 8,780; 7,890; 8,695 mL/d, respectively. The resulted minimum COD removal efficiency of 68.0%, at low HRT of 3 h (at 32.256 kg COD/m^3 d) might be due to the high proportion of spent fermentation broth with the complex organic content of antibiotic wastewater need longer HRT to degrade.The methane content ranged from 63% to 71% (Table 2). With the decrease in HRT from 30 h (3.2 kg COD/m^3 d) to 6 h (16.048 kg COD/m^3 d), the biogas production rate increased and reached 9,120 mL/d on 218th d (Fig. 3). This might be attributed to the growth in biomass concentration and it ranged between 46 and 50.1 g/VSS L. When the HRT was further decreased to 3 h, the concentration of biomass declined to 49.1 g VSS/L; the biogas production rate decreased and reached 7,890 mL/d and the VFA concentration abruptly shot up to 1,372 mg acetic acid/L. The VFA increased with the decreasing HRT. The findings of the present investigation compare well with the work of Jijai et al. [41]. The decrease in the value of biomass concentration could be ascribed to washing out of the methanogenic sludge and resulted in the souring of the reactor [8,42]. Subsequently, the raise in the concentration of VFA increased the growth of acidogenic bacteria. After observing the performance of the reactor for 11 d (218–228 d), the HRT was once again increased and maintained at 6 h. As such additional 17 d were required to reinstate to the earlier performance. When the HRT was returned to 6 h, the VSS concentration slightly improved to 49.2 g VSS/L. As a result, the COD removal efficiency resumed to 82.5% and the biogas production rate to 8,695 mL/d and the concentration of VFA also reached to 436 mg acetic acid/L on 245th d. At short HRT and high OLR, there was a transient inhibitory effect. This finding corroborates well with the results on pharmaceutical wastewater [5,42].

3.5. Biogas production kinetics

The kinetic constants were evaluated for biogas production in AMHR using modified Stover-Kincannon, and Van der Meer and Heertjes models

3.5.1. Modified Stover-Kincannon model

The biogas production rate modelling by modified Stover-Kincannon model is dependent on the substrate removal and OLR [43]. This model can be given by Eq. (1) [44] as follows:

$$\frac{1}{G} = \frac{G_B}{G_{\max}} \times \frac{1}{\text{OLR}} + \frac{1}{G_{\max}} \tag{1}$$

where G is the specific biogas production rate (m^3/m^3 d) and $G_{\max}$ is defined as the maximum specific biogas production rate (m^3/m^3 d). G_B is the proportionality constant for biogas production. The maximum specific biogas production rate ($G_{\max}$) and saturation value constant (G_B) were calculated from Fig. 4 as 3.83 m^3/m^3 d and 29.99 with high R^2 value (0.876) (Fig. 4). The values were indicating that the maximum substrate removed by the anaerobic organisms vs. time and the substrate removed by microorganisms during time, respectively. The value of the saturation constant (G_B) could represent the substrate affinity, which means a higher COD removal efficiency when higher GB values are obtained [45].

3.5.2. Van der Meer and Heertjes model

The model developed by Van der Meer and Heertjes [32]. Eq. (2) was applied to determine biogas production. In this model, the biogas production is related to Van der Meer and Heertjes kinetic constant (G) (m^3/kg), with flow rate applied and removal efficiency of the substrate.

$$Q_{\text{gas}} = GQ\,(S_o - S) \tag{2}$$

where Q is antibiotic wastewater flow rate (m^3/d); S_O and S are explained as the influent and effluent substrate concentrations (kg/m^3), respectively. The kinetic constant G was evaluated from Fig. 5 as 0.118 m^3/kg. The Van der Meer and Heertjes type model with a correlation coefficient of 0.977 was found to be suitable for stating the biogas production kinetics of the AMHR (Fig. 5).

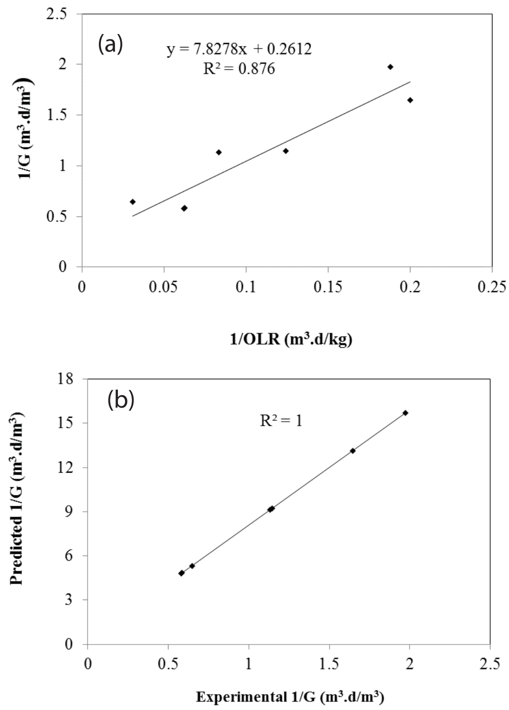

Fig. 4. (a) Determination of the maximum specific biogas production rate and proportionality constant in modified Stover-Kincannon model, and (b) comparison between experimental 1/G values and theoretical 1/G values predicted from Eq. (1).

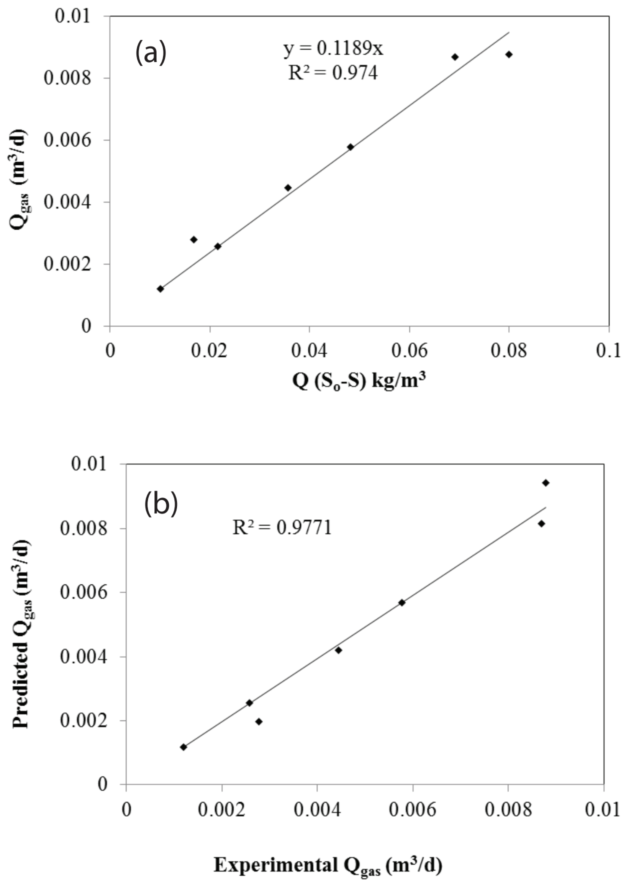

Fig. 5. (a) Determination of kinetic constant in Van der Meer and Heertjes model, and (b) comparison between experimental Q gas values and theoretical Q gas values predicted from Van der Meer and Heertjes model.

A good linear relationship was observed between the experimental and predicted biogas production values calculated in Stover-Kincannon model (Fig. 4) and Van der Meer and Heertjes model (Fig. 5) at different HRTs. Similar to that of the present investigation in the research work of Kuscu and Sponza [43] on para-nitro phenol removal from synthetic wastewater in the anaerobic migrating blanket reactor, these biogas kinetic models have been used and they enunciated the same trend.

3.5.3. *Error functions*

The R^2 value alone is not a factor to select the best model [46]. In addition to this, four different types of error analysis were applied for this study, to check the better data fitness among the experimental and predicted values (Table 3). All the error functions confirmed the similarity between the experimental and predicted values, by the positive, lowest and zero nearer values. It means that the values from the model and experiment were expected to be equal. The values of the error functions indicated the deviation between these two. Findings akin to this error analysis were discussed by Vishali and Mullai [46].

Table 3
Error functions

Error functions	Modified Stover-Kincannon model	Van der Meer and Heertjes model
Chi-square test $(\chi^2) = \sum_{i=1}^{n}\left[\frac{\left(q_{\text{exp}} - q_{\text{pre}}\right)^2}{q_{\text{pre}}}\right]$	0.290	0.0003
Sum of the squares of the error (ERRSQ) $\sum_{n=1}^{n}(q_{\text{exp}} - q_{\text{pre}})_n^2$	0.403	0.000001
Sum of the absolute errors (EABS) $\sum_{n=1}^{n}\left|q_{\text{exp}} - q_{\text{pre}}\right|_n$	0.25924	0.00049
Residual root mean square error (RMSE) $= \sqrt{\frac{1}{n-1}\sum_{n=1}^{n}\left(q_{\text{exp}} - q_{\text{pre}}\right)_n^2}$	1.492	0.001

4. Conclusions

The AMHR is one of the viable options for the anaerobic treatment of antibiotic industry wastewater at OL rates up to 16.016 kg COD/m^3 d. The optimum biogas production rate of 8,780 mL/d was recorded at 16.048 kg COD/m^3 d and 6 h HRT. The kinetic parameters of modified Stover-Kincannon and Van der Meer and Heertjes models determined through linear regression using the experimental data could be used to predict the biogas production rate of full-scale AMHR if the antibiotic wastewater is used with similar wastewater composition and loading conditions.

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