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Research article

Kinetics of biogas production and chemical oxygen demand removal from compost leachate in an anaerobic migrating blanket reactor

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ABSTRACT

In this study, laboratory anaerobic migrating blanket reactor (AMBR) with four units was used to reduce and remove COD leachate of composting process; it was also used to determine the kinetic coefficients of COD removal and biogas and methane gas production in several different OLRs. The maximum concentration of organic matter entering the reactor was 100,000 mg/L and the reactor was under operation for 319 days. The results showed that the COD removal efficiency of AMBR in all concentrations of substrate entering the reactor was above 80%. First-order model and Stover-Kincannon were used to investigate the kinetics of COD removal via AMBR biological process; in addition, the two models of Modified Stover-Kincannon and Van der Meer and Heertjes were used to check the kinetic constants of biogas and methane gas production. The results obtained from the models showed that the experimental data on COD removal were more consistent with the results obtained from Stover-Kincannon model ($R^2 = 0.999$) rather than with the First-order model ($R^2 = 0.926$). Kinetic constants calculated via Stover-Kincannon model were as follows: saturation value constant (KB) and maximum utilization rate constants (U_{max}), respectively, were 208,600 mg/L d and 172,400 mg/L d. We investigated the linear relationship between the experimental data and the values predicted by the models; as compared with the values predicted by the First-order model, the values predicted by Stover-Kincannon model were closer to the values measured via experiments. Based on the results of the evaluation of kinetic coefficients of Stover-Kincannon model, with the migration of the leachate flow from unit 1 to unit 4, U_{max} value has fallen significantly. The values of maximum specific biogas production rate (G_{max}) and proportionality constant (GB) obtained from the Stover-Kincannon model, respectively, were 35,714 ml/L d and 42.85 (dimensionless) and value of kinetic constant of Van der Meer and Heertjes (ksg) was 0.0473 ml CH_4/mg COD.

1. Introduction

The amount of waste produced globally has increased in the past decade, as the amount of waste a decade earlier was 0.68 billion tons and it already has reached about 1.3 billion tons. In addition, it is estimated that the amount of waste will have reached 2.2 billion tons by 2025 (Pellera et al., 2016). Apart from the increase in population, there are some other reasons for the increased production of waste, such as changes in lifestyle, rapid

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economic growth, industrialization, and increased rate of urbanization in many developing countries (Luo et al., 2014; Pellera et al., 2016). Increased solid waste quantities require improving and expanding the solid waste management options such as landfilling and composting. This increase in waste quantities and their management practices affect various environmental issues, posing numerous threats and creating major potential problems (El-Gohary and Kamel, 2016; Pellera et al., 2016). Composting is the microbial degradation of organic solid material that involves aerobic respiration and passes through a thermophilic stage (Finstein and Morris, 1975). The compost leachate is the liquid that leached from the bottom of the compost reactor (Zhang et al., 2007). Leachates are heavily polluted wastewaters with a complex composition containing four groups of pollutants: Dissolved organic matter, inorganic macro-components, heavy metals, and xenobiotic organic compounds with a foul odor. If the leachate enters the environment without treatment, it will have very unfavorable and irreparable effects on the environment (Amin et al., 2014b; Chen et al., 2008; Luo et al., 2014; Pellera et al., 2016). Nowadays, a lot of research is conducted to find suitable methods for the treatment of leachate (Chen et al., 2008) such as biological processes, chemical oxidation processes, coagulation, flocculation, chemical precipitation, and membrane procedures (Hashemi et al., 2016; Renou et al., 2008). To date, several anaerobic and aerobic processes and tools have been used for leachate treatment such as the followings: up-flow anaerobic sludge blanket reactor, anaerobic filter, hybrid bed reactor, and anaerobic sequencing batch reactor or aerobic processes such as aerated lagoons, conventional activated sludge processes, and sequencing batch reactors (Chen et al., 2008). Anaerobic treatment methods are very suitable for the treatment of concentrated leachate and usually have several advantages such as high organic load, low operating costs, and their capability of biogas production. However, inability to remove nitrogen and long retention time are among the disadvantages of these methods. Aerobic biological systems are suitable for the treatment of quickly biodegradable organic materials with low concentrations, but their need for aeration systems and the production of high levels of sludge are among the disadvantages of this method (Almasi et al., 2014; Amin et al., 2014a, b; Kuscu and Sponza, 2007). Anaerobic migrating blanket reactor (AMBR) system is one of the derivatives of up-flow anaerobic sludge blanket (UASB) system. This anaerobic system which has a high load capacity has several specific characteristics, for instance, it is multi-part, has a continuous flow, short hydraulic retention time, and simple design, does not require a gas-liquid separation system and multiple distribution systems, and does not have wastewater return (Angenent and Sung, 2001; Eslami et al., 2017; Kuşçu and Sponza, 2011). This system was used by the researchers for the treatment of p-nitrophenol (Kuscu and Sponza, 2007), glucose-chemical oxygen demand (Kuşçu and Sponza, 2009b), and nitrobenzene (Kuşçu and Sponza, 2009a).

Nowadays, process modeling methods are widely used to control and predict the performance of anaerobic treatment systems (Abtahi et al., 2013; Alavi et al., 2011). Being familiar with biokinetics is necessary for the design and optimization of biological treatment systems (Hamza et al., 2009). In the present study, AMBR system was used for the treatment of leachate of composting; in addition, to evaluate the kinetics of COD removal by AMBR biological process we used First-order model and Stover-Kincannon model. Moreover, in order to check the kinetic constants of biogas and methane gas production, we used two models including Modified Stover-Kincannon model and Van der Meer and Heertjes model.

2. Materials and methods

2.1. Experimental set-up and seed

A powered Plexiglas AMBR reactor was used to conduct the experiments. The inflow sample entering the AMBR was real compost leachate with different concentrations. Table 1 presents the characteristics of the examined leachate. We used a rectangular AMBR reactor with internal length, width, and height of 43, 10, and 23.5 cm, respectively, with an efficient capacity of 10 L. Using three vertical Plexiglas plates attached to the bottom of the reactor, the AMBR was divided into four equal units. Keeping a centimeter away from the plates, three Plexiglas plates were hung, so that the hung baffles were 8 inches away from the floor of the reactor; it helped to create a rising and falling flow in various parts of the reactor. In order to mix the materials in the reactor, four mixers (LANDA) equipped with adjustable timer with a rotation of 80 rpm, with a functioning time of 10 s, and a 15-min time-off were used. The mixer installed in the end chamber was off so that to prevent the exit of biomass flocs. The reactor was fed through taking leachate from the reservoir using a peristaltic pump (ETATRON, Italy) with a flow of 1 L within 24 h. Using a tube installed at the top of the reactor, the gas produced from biological interactions was moved outside and was connected to a gas meter to quantitatively analyze the biogas. We used a wet gas meter (Elster, AMCO, Germany).

In order to seed the AMBR reactor, we used anaerobic digester sludge collected from an urban wastewater treatment plant and produced at a temperature of 35 °C. First, using a 2 mm sieve, rubbish and large seeds were separated and then the leachate was injected into the reactor. The amount of TSS and VSS of the sludge were 35,500 mg/L and 26,650 mg/L, respectively.

2.2. Reactor start-up

As the organic loading of the leachate was high, first it was diluted extent, and then over time, the amount of dilution was reduced. The maximum level of dilution was performed during the launch of the reactor. The AMBR reactor launch was performed over a period of 40 days and in the first 20 days the mean loading was 500 mg COD/L d while in the second 20 days it was 750 mg COD/L d. At the end of the desired period of time, COD removal efficiency reached 75%.

2.3. Operation condition

After launching the reactor and achieving an appropriate COD removal efficiency, the reactor was operated with a load of 1000 mg COD/L d. The flow rate injected into the reactor was 1 L per 24 h. The dilution was decreased over the time and during the 9th round of operation the leachate samples were injected into the reactor without dilution. In the 10th and 11th rounds the input flow was increased to 2 L and the reactor performance was evaluated. Table 2

Table 1
Leachate characterization that was collected from compost manufacturer.

Raw leachate	Range	Average	SD
BOD_5 (g/l)	49–69.5	55.2	22.76
COD (g/l)	80–110	95.5	37.2
TSS (g/l)	14–17	15.5	6.3
TDS (g/l)	28–31.5	29.6	11.48
TP (g/l)	0.25–0.35	0.28	0.01
TKN (g/l)	1.8–2.8	2.3	0.07
pH	3.5–5.5	4.4	0.33
EC (ms/cm)	30–37.5	33.5	13.52

Table 2
Operation condition of the AMBR reactor.

Time (d)	Run	HRT (d)	OLR (g COD/L d)	COD (mg/L)
1–37	1	10	1.04	10.43 ± 0.92
38–46	2	10	1.34	13.38 ± 0.89
47–59	3	10	1.79	17,890
60–74	4	10	2.02	20,190
75–98	5	10	3.79	37,870
99–128	6	10	4.34	43,430
129–159	7	10	5.84	58,380
160–189	8	10	7.71	77,090
190–248	9	10	10.08	100,770
249–263	10	5	18.52	92,610
264–279	11	5	19.65	98,260
Min	5	1.04	10,430	
Max	10	19.65	100,770	

presents the operation condition of the AMBR reactor.

2.4. Analytical methods

The majority of the parameters were measured based on the instructions presented in a book entitled “Standard methods for water and wastewater experiments” (Rice et al., 2012). To measure the biogas produced in the reactor, the biogas-collector pipes were connected to the gas meter (Elster, AMCO, Germany). The biogas entering the gas meter moved its needle; after a round of needle movement within its graded plate, the device counter started counting the gas volume. The gas meter measured a range from -0.2 m^3/hr to 0.002 m^3/hr. A gas chromatograph device was used to determine the amount of methane in the biogas. Measurements were performed using Auto System Perkin Elmer, USA equipped with a column (Perkin Elmer, 6' × 1.8″OD, 80/100, Mesh, USA) and a TCD detector (Thermal Conductivity Detector) (Perkin Elmer, USA). The injection temperature was 150 °C and nitrogen was used as a carrier gas with an injection flow of 20 ml/min at 75 °C (Pagés-Díaz et al., 2014).

3. Kinetic models

3.1. Substrate removal kinetics

In order to investigate the kinetic constants of substrate removal entering the AMBR reactor, we used two models including First-order substrate removal model and Stover-Kincannon model.

3.1.1. First-order substrate removal model

The removal of organic matters from anaerobic biological systems is expressed in Equation (1) that represents the First-order kinetics (Abbas et al., 2015; Khosravi et al., 2013).

$$-\frac{ds}{dt}=\frac{QSi}{V}-\frac{Qse}{V}-K_1Se \tag{1}$$

In a pseudo-steady-state condition, there is a small change in substrate concentration (-ds/dt), thus it can be eliminated from Equation (1), and Equation (2) can be introduced.

$$\frac{Si-Se}{HRT}=K_1Se \tag{2}$$

where Si and Se, respectively, are the concentrations of input and output COD (mg/L), HRT is hydraulic retention time (d), K_1 is the speed constant of First-order model for the removal of organic matter (1/d), Q is the inflow (L/d), and V is the volume of the reactor (L).

The constant of organic matter removal rate (K_1) can be obtained through plotting the slope of the Si-Se/HRT line against Se, as presented in Equation (2).

3.1.2. Stover-Kincannon model

Stover-Kincannon model is one of the models most widely used for anaerobic systems, including UASB, AMBR (Kuşçu and Sponza, 2009b), and internal-loop airlift bio-particle (Abbas et al., 2015). However, we did not find any study on the use of this model for determining the kinetic constants of leachate treatment using AMBR reactor.

The equations of Stover-Kincannon model are as follows:

$$\frac{ds}{dt}=\frac{Q}{V}(Si-Se) \tag{3}$$

$$\frac{ds}{dt}=\frac{U_{max}\left(\frac{QSi}{V}\right)}{K_B+\left(\frac{QSi}{V}\right)} \tag{4}$$

$$\frac{V}{Q(Si-Se)}=\frac{K_B}{U_{max}}\times\frac{V}{QSi}+\frac{1}{U_{max}} \tag{5}$$

where (ds/dt) is the COD removal rate (mg/L d), U_{max} is the constant of maximum consumption (Utilization) (mg/L d), and KB is the constant of Saturation Value (mg/L d). V/Q (Si-Se) is the reverse of loading removal rate plotted against the total loading rate (V/QSi) which results in a straight line with ($1/U_{max}$) intercept and KB/U_{max} slope.

3.2. Biogas and methane production kinetics

To determine the accuracy rates of specific total gas and methane production, we used two models including Modified Stover-Kincannon and Van der Meer and Heertjes.

3.2.1. Modified Stover-Kincannon model

Similar to COD removal, biogas and methane gas production rates can also be mathematically modeled. The quantity and quality of biogas and methane production depends on COD removal and loading. The model developed by Stover (Eq. (6) and (7)) can be used to determine the total gas and methane production rates (Kuşçu and Sponza, 2009b).

$$\frac{1}{G}=\frac{G_B}{G_{max}}\times\frac{1}{OLR}+\frac{1}{G_{max}} \tag{6}$$

$$\frac{1}{M}=\frac{M_B}{M_{max}}\times\frac{1}{OLR}+\frac{1}{M_{max}} \tag{7}$$

where G is the specific biogas production rate (ml/L d) and Gmax is the maximum specific biogas production rate (ml/L d). G_B in the ratio constant (ml/L d) of biogas production.

3.2.2. Van der Meer and Heertjes model

The model developed by Van der Meer and Heertjes (Eq. (8)) is used to determine methane production rate (10). In this model methane production is associated with the kinetics constant of Van der Meer and Heertjes (k_{sg}), the AMBR inflow, and COD removal efficiency.

$$V_M=k_{sg}Q(Si-Se) \tag{8}$$

where V_M is methane production (ml/d), Q is wastewater flow rate

(L/d), Si and Se, respectively, are influent and effluent COD concentrations (mg/L), and k_{sg} is kinetic constant of Van der Meer and Heertjes (ml CH_4/mg COD).

4. Results and discussion

4.1. Reactor performance

4.1.1. COD removal performance

AMBR operation was started in a COD concentration of 10,430 mg/L with a hydraulic loading of 10,430 mg COD/L d. According to the results presented in Fig. 1, with raising the OLR system by up to about 10,000 mg COD/L d, COD removal efficiency had a relatively constant increasing trend which was more than 80%. In such a condition, when the hydraulic retention time was 10 days, the COD concentration injected into the system was 100,000 mg/L; in this condition, the leachate was injected into the system without dilution and an efficiency of about 80% was obtained. In order to evaluate the AMBR removal efficiency in higher OLR, the hydraulic retention time was reduced from 10 days to 5 days and an input OLR of about 20,000 mg COD/Ld was reached. In that condition, the efficiency of the process had a decreasing trend, as presented in Fig. 1a. However, considering the amount of input and output COD, it was found that at the highest OLR, organic load was reduced by about 75,000 mg/L. With an excessive increase in OLR, the COD removal efficiency decreased which might be attributed to the extra concentration of volatile fatty acids in a reactor, thus, it passed the limit required to inhibit the hydrogen producing bacteria. This condition, not only reduced the COD removal efficiency, but also decreased the concentration of bacteria (Intanoo et al., 2016).

In general, as the results indicated, the AMBR process was able to tolerate high organic loads such as waste leachate; it not only tolerated such a load of COD but also resulted in very high removal efficiency. In this study, the optimal OLR was set between 1000 and 10,000 mg COD/L d with an efficiency of about 80%. Compared with the results of other studies, the results of this study indicate the higher efficiency of the AMBR process (Angenent et al., 2001; Kuscu and Sponza, 2007; Kuşçu and Sponza, 2011). Fig. 1b represents the COD removal efficiency in different units of AMBR; clearly, when using most of the loadings, the efficiency was higher in units 1 and 3, as compared with the other two units; moreover, in most cases the lowest efficiency was observed in unit 2 of the reactor. Accordingly, the highest efficiency was observed in unit 1 which was equal to 48%, while the lowest efficiency in the units of OLR was about 20,000 mg COD/L d i.e. equal to 34%. However, the highest efficiency in unit 2 of the reactor in OLR was about 1790 mg COD/L d i.e. equal to 29%. The highest efficiency of unit 2 was about 5% lower than the lowest efficiency in unit 1. This shows that unit 1 of the reactor played a prominent role in reducing the organic load inflow into the reactor. With removing the organic matters, there was an increase in the production of volatile fatty acids; as a result, the concentration of volatile fatty acids entering the second unit of the reactor reached an amount that prevented the growth of methane-producing bacteria. On the other hand, as a large amount of biodegradable materials are eliminated in unit 1, the BOD/COD ratio also declines and there would be an increase in the ratio of slowly biodegradable materials (Intanoo et al., 2016; Kuscu and Sponza, 2007; Kuşçu and Sponza, 2009a). In addition, with increasing the amount of OLR inflow into the reactor, there would be an increase in the amount of produced VFA which in turn increases the ratio of VFA/Alkalinty in the system. On the other hand, with increasing the activity of the bacteria, the amount of CO_2 production increases too which in turn increases the alkalinity, thus requiring acidity to neutralize it (Kuscu and Sponza, 2007). As a result, in the next units of the reactor, there was a remarkable decline in efficiency, as compared with the first unit; it continues, until the time when the amount of VFA accumulated in the system decreased and the system pH increased.

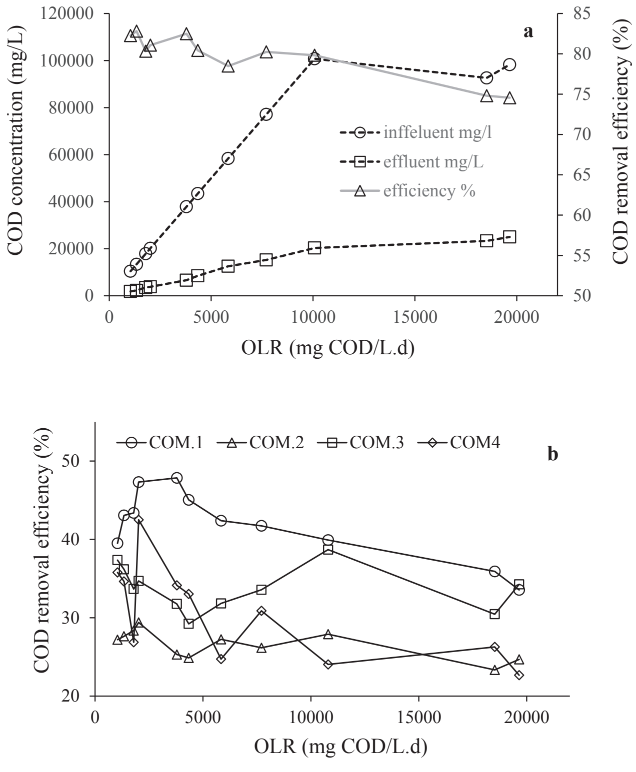


Fig. 1. COD removal efficiency at different loading rates in AMBR (a) and in compartments of AMBR (b).

4.1.2. Biogas and methane gas production

Fig. 2 presents the changes in biogas and methane gas production and their relationship with changes in OLR; it shows that with increasing OLR, the amount of produced gas significantly increased too. The results indicate that in an OLR of about 1040 mg COD/L d, the amount of biogas and methane gas, respectively, were 0.77 and 0.42 L. With increasing OLR to about 18,500 mg COD/L d, the amount of biogas and methane gas, respectively, changed to 10.47 and 6.18 L d. However, with increasing OLR to 19,650 mg COD/L d, the amount of gas production had a decreasing trend. To justify this observation, it can be said that the growth of methane-producing

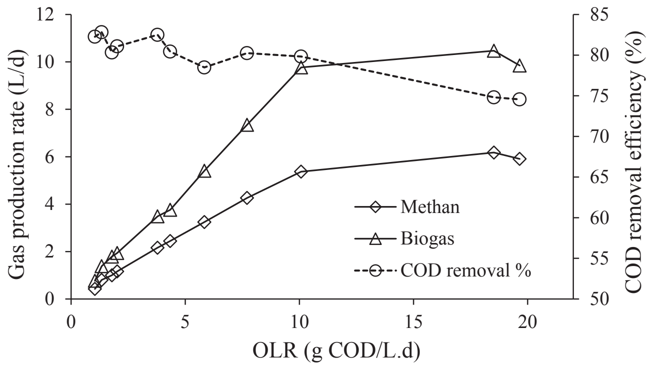


Fig. 2. Effect of increasing loading rates on Biogas and Methane production.

bacteria depends on the presence of organic acids and hydrogen produced by acid-producers and acetate-producers. On the other hand, the inhibitory limit of accumulated organic acids for methane-producers (400 mg/L) is much lower than that for hydrogen-producers (10,000 mg/L) (Intanoo et al., 2016). Overall, Fig. 2 shows that with increasing the amount of COD removal, the amount of gas produced in the system increases as well.

4.2. Determination of kinetic coefficients for substrate removal models

In this study the kinetic coefficients of first-order models, Stover-Kincannon, and Michaelis-Menton were used for determining COD removal. Then, using the obtained coefficients and putting them in the relevant models, we evaluated the models and predicted COD removal rates. Kinetic coefficients of models were calculated for all the four units of AMBR reactor and also for the overall AMBR reactor and the results are presented in Table 3. However, among the figures plotted by the models, we only presented the figure of the overall AMBR reactor.

4.2.1. First-order substrate removal model

As shown in Fig. 3a, the data obtained from operating the reactor in a steady-state with various concentrations of input substrate were used to determine the kinetic coefficients of the first-order model. We plotted Si-Se/HRT against Se, and a linear equation was achieved based on which the kinetic constant of K_1 was calculated as 0.54. The correlation coefficient of R^2 was equal to 0.926.

4.2.2. Stover-Kincannon model

Considering the linear plot of V/Q (Si-Se) against V/QSi, we used Equation (5) and calculated the intercept and the slope of the straight line which, respectively, were $1/U_{max}$ and KB/U_{max} (Fig. 3b). Taking into account the intercept and the slope of the plotted line, the maximum utilization rate (U_{max}) and saturation value constant (KB) for the COD removal in the overall AMBR reactor, respectively, were 172,400 and 208,600 mg COD/L d and there was a high correlation ($R^2 = 0.999$). In a study by Kusca et al., the maximum speed of substrate consumption (U_{max}) for COD removal by AMBR reactor was 29,490 mg COD/L d (Kuşçu and Sponza, 2009b). In Pandian et al.'s study (2011) the amount of pharmaceutical wastewater treatment in an anaerobic hybrid reactor was 1,086,900, the amount of simulated wastewater treatment in up-flow anaerobic sludge blanket reactor (UASB) was 7500 mg COD/L d, and the amount of soybean wastewater treatment in anaerobic filter reactor (AF) was 83.3 (Pandian et al., 2011). Moreover, in Sponza and Uluköy's study (2008) the amount of U_{max} in COD removal using UASB reactor was very low i.e 7.5 mg COD/L d (Sponza and Uluköy, 2008). Considering the results of the mentioned studies, it can be concluded that our study achieved a much higher maximum substrate utilization rate for the removal of COD by AMBR reactor. Table 3 presents the U_{max} and KB values for different units of the reactor. U_{max} value was 169,400 mg COD/L d in unit 1 and 76,300 mg COD/L d in unit 2, which shows that the maximum speed of COD consumption in the first unit was more than twice as much as that in the second unit 1. The results indicate that a very large percentage of COD entering the reactor is consumed by unit of AMBR reactor. Moreover, the U_{max} values for the third and fourth units, respectively, were 27,200 and 11,200 mg COD/L d. The results indicate that the maximum speed of COD consumption gradually decreases from the beginning to the end of AMBR reactor; it indicated different trend of COD removal efficiency in different parts of AMBR reactor. The difference might be attributed to the very high COD concentration in unit 1 of the reactor, where a lot of biodegradable food ingredients are provided for microorganisms and thus the speed of the consumption of food materials is increased. However, the removal efficiency is calculated based on the Si-Se/Si, thus it is affected by the concentration of materials entering the reactor. The concentration of materials entering unit 2 is more than the concentrations entering units 3 and 4 of the reactor. As a result, the COD removal efficiency in unit 2 of the reactor is lower than in units 3 and 4 where the speed of COD consumption is higher.

4.2.3. Model testing

Kinetic constants of both models of first-order and Stover-Kincannon are presented in Table 3. These two models were used to determine the output COD exiting the AMBR reactor and compares it with the input concentration entering the reactor. Fig. 3a and b, respectively, represent the first-order model and Stover-Kincannon model. Comparing these two models, R^2 coefficient of determination in Fig. 3b is clearly higher than that in Fig. 3a. Thus, it can be stated that the output values observed in the reactor are more consistent with Stover-Kincannon model than with the first-order model. In order to test the validity of the models, the results obtained from the analysis of experiments (observed COD) were compared with the results obtained from the models (predicted COD). To this end, the constants obtained were pasted within the relevant equations and the output substrate (effluent COD) was calculated. Table 4 presents the measured values as well as the values predicted by the models. As shown, the results predicted by Stover-Kincannon model are much closer to the values measured in the experiments (observed values), while the results predicted by the first-order model are very different from the actual values

Table 3
Comparison of the kinetic constants according to First-order and StoverKincannon models for total AMBR and its compartments.

Kinetic model	Reactor compartment	Kinetic parameter	Value	Determination coefficient R^2
First-order	COM.$_1$	K_1 (1/d)	0.37	0.899
	COM.$_2$	K_1 (1/d)	0.23	0.883
	COM.$_3$	K_1 (1/d)	0.37	0.875
	COM.$_4$	K_1 (1/d)	0.22	0.838
	Total AMBR	K_1 (1/d)	0.54	0.926
Stover−Kincannon	COM.$_1$	K_B (g/L d)	409.7	0.991
		U_{max} (g/L d)	169.4	
	COM.$_2$	K_B (g/L d)	276	0.996
		U_{max} (g/L d)	76.3	
	COM.$_3$	K_B (g/L d)	74.9	0.993
		U_{max} (g/L d)	27.2	
	COM.$_4$	K_B (g/L d)	31.8	0.958
		U_{max} (g/L d)	11.2	
	Total AMBR	K_B (g/L d)	208.6	0.999
		U_{max} (g/L d)	172.4	

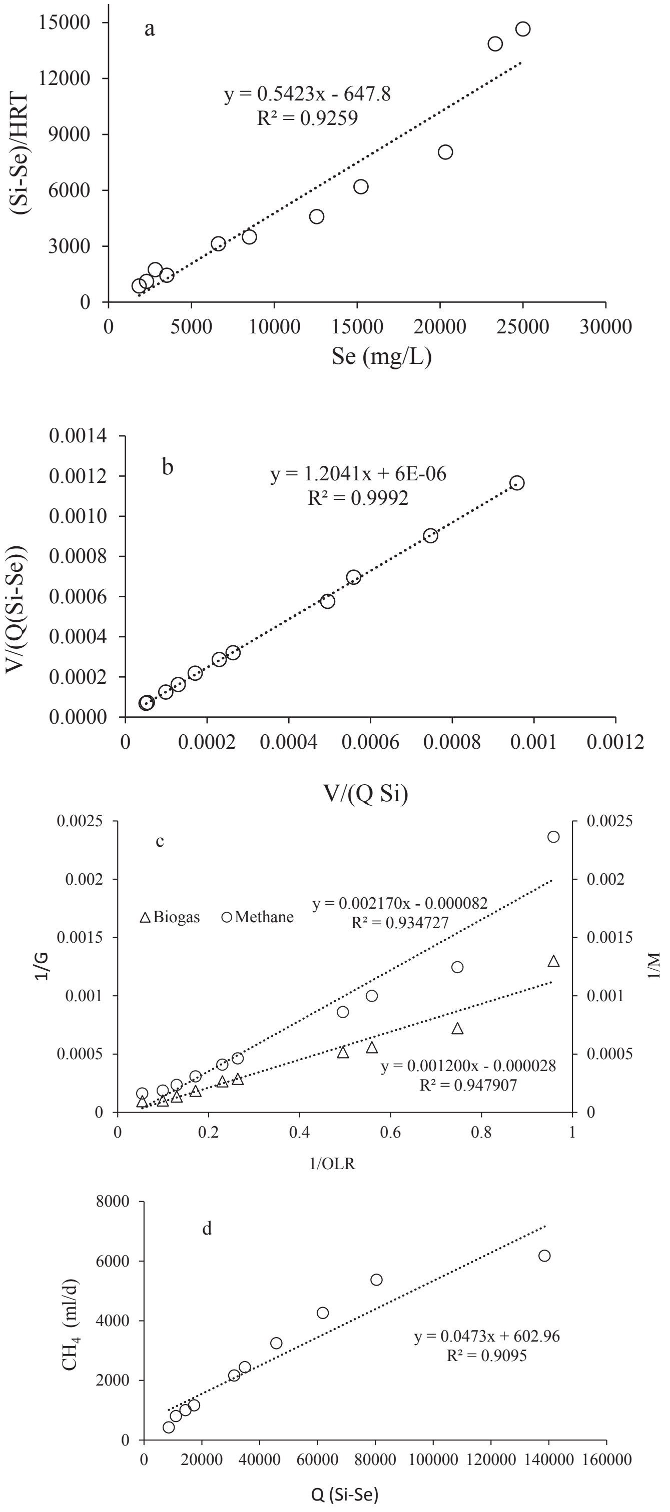


Fig. 3. Determination of Kinetic constant for First-order model (a), Determination of Kinetic constant for modified Stover-Kincannon model (b), Biogas and methane gas production kinetic constants by modified Stover-Kincannon model (c), and methane gas production kinetic constant by Van der Meer and Heertjes model (d).

(observed COD). Fig. 4a presents the output COD values predicted by the models and compares them with the output COD values observed in the analysis of experiments. Considering all loadings in Stover-Kincannon model, there was a very significant relationship between the observed and predicted values with high regression coefficients ($R^2 = 0.99$). Considering the first-order model, the regression coefficient between predicted values and observed values was 0.92 which indicated a low validation parameter, as compared with Stover-Kincannon model. The comparison of the standard deviations and the means of predicted data from the models with the observed data also confirms that the prediction of Stover-Kincannon model is more realistic.

4.3. *Biogas production kinetics*

The kinetic constants of biogas and methane gas production in the AMBR reactor were evaluated by the two models.

4.3.1. *Modified Stover-Kincannon model*

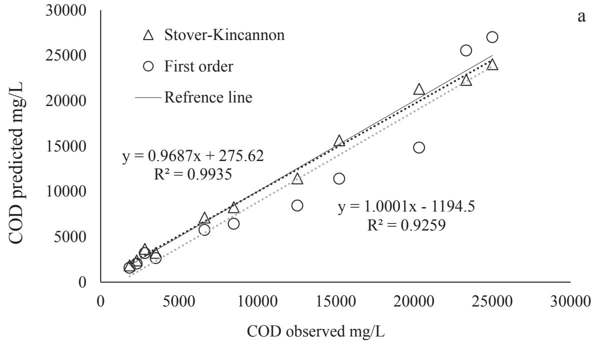
To determine the kinetic coefficients (G_{max} and M_{max}), Equations (6) and (7) were used for measuring biogas and methane produced in the AMBR reactor. To determine the constants of produced biogas, we used a linear graph which plotted the reversed specific gas production (1/G) against the reversed COD loading (1/OLR). In addition, to determine the constants of produced methane we used a linear graph plotting the reciprocal of specific methane production (1/M) against the reversed COD loading (1/OLR). The slope and intercept of the best line represent $1/G_{max}$ and GB/G_{max} for biogas and $1/M_{max}$ and MB/M_{max} for methane. The coefficient of determination of Modified Stover-Kincannon model for produced biogas and methane, respectively, were 0.947 and 0.934. Considering the results of the equation used in Fig. 3c, the maximum specific total gas production rate (G_{max}) and the constant of proportionality (GB), respectively, were 35,714 mL/L d and 42.85 (dimensionless). The maximum methane gas production rate (M_{max}) and the constant of proportionality (MB), respectively, were 12,195 mL/L d and 26.46 (dimensionless). These values are much higher than the values observed in Ozlem et al.'s study (Kuşçu and Sponza, 2009b) which reported a Gmax of 1666.7 mL/L d and a Mmax of 476.2 mL/L d. The observed difference might be attributed to the fact that in our study the concentration of input COD entering the AMBR reactor was very high, thus the treatment of every liter of input leachate had the potential to produce a large amount of gas.

4.3.2. *Van der Meer and Heertjes model*

Equation (8) was used to determine the kinetic constants (ksg) in Van der Meer and Heertjes model. Kinetics constant (ksg) was experimentally calculated via considering the slope of the line plotted between Q (Si-Se) and methane (CH_4) gas. As shown in Fig. 3d, the R^2 coefficient of determination was 0.909. In this study, the kinetics constant of methane gas production (ksg) was equal to 0.0473 ml CH_4/mg COD. In Ozlem et al.'s study (Kuşçu and Sponza, 2009b), Ksg was 0.0947 which shows that the constant of methane production, as compared with the COD removal in Ozlem et al.'s study, was about two times more than the amount of methane gas produced in this study. The mentioned study used kinetic wastewater which mainly contained glucose; it only used 40 mg/L of p-nitrophenol. In the present study we used real leachate which contained various different materials (Table 1); because of this difference, in proportion to the amount of removed COD, a lower amount of methane was produced in our study. In addition, the results of testing the model showed that the amount of kinetic constant was less than the real amount of produced methane. As a result, because of the low R^2 value, it cannot be generalized to this study. To determine the kinetic constant of Van der Meer and Heertjes model, we used the concentration of produced methane, the input flow entering the reactor, and the concentration of input and output COD in AMBR reactor.

Table 4
Comparison of predicted and experimental (observed) results for First-order and modified Stover-Kincannon kinetic model.

OLR (g COD/L.d)	Effluent (observed) COD (mg/L)	Predicted COD (mg/L)	
		First-order	Stover-Kincannon
1.04	1850	1582	1852
1.34	2300	2043	2391
1.79	3520	2649	3229
2.02	2820	3203	3662
3.79	6630	5760	7127
4.34	8500	6441	8266
5.84	12,560	8449	11,441
7.71	15,230	11,406	15,644
10.08	20,330	14,833	21,320
18.52	23,330	25,550	22,308
19.65	25,000	27,018	24,038
Mean (SD)	11,188 (8644)	9903 (9078)	11,025 (8489)



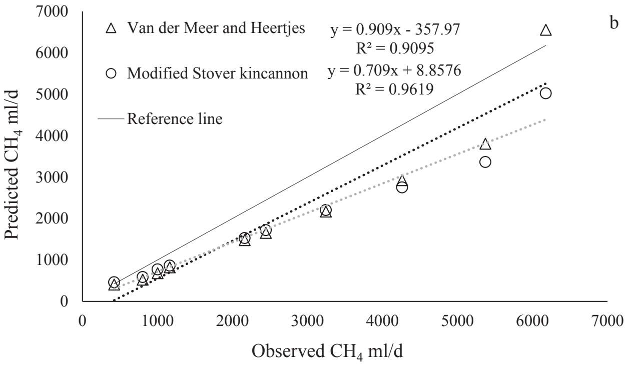


Fig. 4. The observed effluent COD concentration and predicted effluent COD in First-order and Stover-Kincannon kinetic models (a), and The observed and predicted daily methane gas productions for modified Stover-Kincannon and Van der Meer and Heertjes models (b).

4.3.3. Model testing

The amount of methane and biogas produced in this experiment were measured using the two models of Modified Stover-Kincannon and Van der Meer and Heertjes. The regression coefficients of Modified Stover-Kincannon model and Van der Meer and Heertjes model for the produced methane gas, respectively, were 0.93 and 0.9. It indicates that the regression coefficient of Modified Stover-Kincannon model was higher than that of the other model. Thus, it shows that the experimental data were more consistent with the results of Modified Stover -Kincannon model. Therefore, the kinetic constants of gas production and the constant of proportionality derived from this model for maximum biogas and methane gas produced by the AMBR process were significant (Kuşçu and Sponza, 2009b). Table 5 presents the amount of produced methane measured at different OLRs, and the predicted amounts of methane estimated by the two models of Modified Stover-Kincannon and Van der Meer and Heertjes. Based on the data presented in Table 5, the amount of methane predicted by Van der Meer and Heertjes model is closest to the amount of produced methane measured at different experiments with different loadings. We also investigated the relationship between produced methane and the amount of gas predicted by Modified Stover-Kincannon model and Van der Meer and Heertjes model. Fig. 4b presents the relationship between produced methane and the amount of gas predicted by Modified Stover-Kincannon model and Van der Meer and Heertjes model. Regarding Fig. 4b it is shown that the R^2 of Modified Stover-Kincannon model is higher (0.96) than the R^2 of Van der Meer and Heertjes model (0.9). As a result, we can say that Modified Stover-Kincannon model fits the points better than Van der Meer and Heertjes model. But the closeness of the mean and standard deviation (SD) of predicted values from Van der Meer and Heertjes model than the Modified Stover-Kincannon model to the SD and the mean of experimental data (Table 5) suggests that the predicted values of Van der Meer and Heertjes model will be more realistic. Therefore, since the difference between the R^2 of two models is not high and both are in the acceptable range, Van der Meer and Heertjes model is more suitable for more accurate estimation.

4.4. Conclusion

The results of this study showed that the AMBR reactor was capable of reaching a COD removal of above 80% for all loadings entering the system with a hydraulic retention time of 10 days. The results also showed that different units of the reactor played a different role in the removal of organic matters. As compared with the other units of the reactor, unit 1 of AMBR had the highest level of COD removal efficiency (48%). The results showed that with an OLR of 1040 mg COD/L d, the amounts of produced biogas and methane gas, respectively, were 0.77 and 0.42 L/d. With increasing the OLR to about 18,500 mg COD/L d, the amount of biogas and methane gas produced, respectively, reached 10.47 and 6.18 L/d.

The results also showed that Stover Kincannon model with a very high regression coefficient (0.999) was appropriate for the removal of COD via the AMBR process. The COD values predicted by the Stover Kincannon model were properly consistent with the COD removal efficiency observed in the experiments. U_{max} obtained from the Stover Kincannon model was 172,400 mg/L d which indicates the significant amount of substrate consumed by the AMBR. Comparing the Gas models of Modified Stover-Kincannon and Van der Meer and Heertjes, it was found that the kinetic constants of biogas production and methane gas production were similar and the regression coefficient of Modified Stover-Kincannon model was higher than that of Van der Meer and Heertjes model. But the comparison of mean and SD of predicted data by models show that Van der Meer and Heertjes model estimates more realistic data than Modified Stover-Kincannon model. Therefore, Van der Meer and Heertjes model, given the acceptable coefficient, can be a better model to predict the amounts of methane gas produced from leachate treatment using the AMBR reactor. Overall, the results of this study showed that the AMBR reactor with a hydraulic retention time of 10 days changed the COD concentration from 100,000 mg/L to about 20,000 mg/L; it showed that, in such a short period of time, the reactor removed about 80,000 mg/L of organic matters in the leachate. In addition, the results of evaluation of Stover-Kincannon model and Van der Meer and Heertjes model showed that these models, respectively, were suitable for predicting the removal of

Table 5
Comparison of predicted and experimental (observed) results for total biogas and methane gas production in modified Stover-Kincannon kinetic and Van der Meer and Heertjes models.

OLR (g COD/L.d)	Observed values (mL/d)		Predicted values (mL/d)		
	Biogas	Methane	Modified Stover-Kincannon model		Van der Meer and Heertjes model
			Biogas	Methane	Methane
1.04	769	423	848	462	405
1.34	1384	803	1081	587	524
1.79	1788	1001	1431	772	679
2.02	1938	1163	1606	864	821
3.79	3487	2162	2899	1526	1477
4.34	3762	2445	3286	1719	1652
5.84	5408	3245	4281	2204	2167
7.71	7347	4261	5444	2751	2925
10.08	9767	5372	6798	3363	3804
18.52	10,470	6177	10,777	5021	6553
Mean (SD)	4613 (3517)	2705 (2010)	3845 (3130)	1928 (1453)	2101 (1915)

the substrate and the production of gas via leachate treatment using the AMBR reactor.

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