Chemical Engineering Journal 102 (2004) 193–201

Chemical Engineering Journal

www.elsevier.com/locate/cej

Studies on biomethanation of distillery wastes and its mathematical analysis

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Accepted 3 May 2004

Abstract

Distillery wastes from alcohol manufacturing units such as breweries etc. are highly polluted with organic substances. It is necessary to decrease the pollution load to have eco-friendly environment and simultaneously to recover energy from the distillery slop which possesses enormous energy potential. In view of these experimental studies on biomethanation of distillery wastes have been carried out in a semi-batch digester having different BOD loading of 1.54, 2.12, 2.74, 3.28 and 4.45 kg/Cu m at different digestion temperatures in the range of 35–55 °C for hydraulic retention time of 14 days under controlled pH in the range of 6.8–7.2. Generated biogas has been collected at different retention days, and analysis of the gas has been made accordingly. It has been observed that biogas yield as well as methane yield have increased gradually giving maximum yield on 7th day after which biogas generation has gradually decreased.

The present study deals with the mathematical analysis of the experimental data on biomethanation and suggests model equations relating maximum specific growth rate and kinetic parameter with digestion temperatures and BOD loading.

Keywords: Anaerobic processes; Biodegradation; Biogas; Biomethanation; Bioreactors; Waste treatment

1. Introduction

Anaerobic digestion is a biological process in which organic material is decomposed by bacteria in the absence of air to yield methane and carbon dioxide. The general technology of anaerobic digestion of complex organic matter is well known and has been applied for over 60 years as part of domestic sewage treatment to stabilize organic wastes. Carty [1] points out that the anaerobic process is more advantageous than the aerobic process in organic waste treatment because of the high degree of waste stabilization, low production of excess biological sludge, low nutrient requirement and high production of methane gas as a useful byproduct. Several studies have been done for evaluating kinetic parameter and model equations on anaerobic digestion by Andrews [2], Graef and Andrews [3], Lee and Donaldson [4], Bolle et al. [5], Moletta et al. [6], Yang and Okos [7], Attal et al. [8], Fakuzaki et al. [9] and Moravai et al. [10] which are all based on monod kinetic model [11] and also on revised kinetic model developed by Chen et al. [12] and Hashimoto et al. [13]. Only a few studies have been reported on continuous anaerobic digestion of distillery wastes by Sanchez et al. [14], Sweeney and Graetz [15] and Boopathi et al. [16]. Goyal et al. [17], Harada et al. [18], Garcia-Calderon et al. [19], Blonskaja et al. [20], but no work has been reported on semi-batch digestion system of distillery wastes.

In the microbiology of methanogenic process four different bacterial groups are identified as being responsible for carrying out the anaerobic digestion of complex organic matter [12,13]. The first group of bacteria is hydrolytic bacteria which catabolizes carbohydrate, protein, lipid and other minor components of organic matter to fatty acids, H_2 and CO_2. The second group of bacteria is hydrogen producing acetogenic bacteria which catabolizes certain fatty acids and neutral end products to acetate, CO_2 and H_2. The third group of bacteria is homo acetogenic which synthesizes acetate using H_2, CO_2 and formate, and hydrolyzes multicarbon compound to acetic acid. Finally, the fourth group of bacteria i.e. methanogenic bacteria utilizes acetate, carbon dioxide and hydrogen to produce methane. The concerted action of these four bacterial groups ensures process stability during anaerobic digestion of the complex organic matter.

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doi:10.1016/j.cej.2004.05.006

Nomenclature

B_u	ultimate methane yield (Cu m/Cu m DW)
B_0	methane yield (Cu m/Cu m DW)
DW	distillery wastes
k	kinetic parameter
S	BOD loading (kg/Cu m)
T	digestion temperature (°C)

Greek symbol

μ_m	maximum specific growth rate (day^{-1})
Ø	retention time (days)

The reactions involved in these steps are given below [21]:

- Phase-I. Solubilization of carbohydrate

$$[C_6H_{10}O_5]n + nH_2O = nC_6H_{12}O_6 \tag{1}$$

- Phase-II. Acidogenesis fermentation of glucose

$$C_6H_{12}O_6 + 2H_2O = 2CH_3COOH + 4H_2 + 2CO_2 \tag{2}$$

- Phase-III. Methanogenic reaction

$$CH_3COOH = CH_4 + CO_2 \tag{3}$$

$$4H_2 + CO_2 = CH_4 + 2H_2O \tag{4}$$

2. Materials and methods

A semi-batch digester has been designed and fabricated to carry out the experimental work. This is a cylindrical equipment made of mild steel of capacity 10 l with the provision of feed inlet opening, gas outlet nozzle and pressure measurement nozzle. There is an opening at the bottom through which the effluent can be discarded after experiment. The digester is surrounded by water jacket to maintain constant temperature of the slurry inside the digester. One limb of the U-tube manometer is connected to the pressure measurement nozzle and the other opening of the U-tube is kept open to the atmosphere. The digester contains two thermometer wells through which thermometers are introduced to measure the temperature of the feed slurry and that of the water in the jacket. The manometer measures the pressure of the produced gas. The digester also fitted with stirrer and motor with a speed-controlling regulator so as to keep the slurry at constant agitation at controlled stirrer speed. A schematic diagram of the digester set-up is given in Fig. 1. The anaerobic digestion process has been carried out using distillery wastes having characteristics as given in Table 1.

In order to carry out the biomethanation process 5 l of distillery wastes slurry of known substrate concentration in terms of BOD loading have been fed into the digester in which 1% mixed culture as inoculum has been added, which has been prepared using cow dung dissolved in distilled water maintaining pH within the range of 6.8–7.2 being incubated at 35 °C for 7 days under anaerobic condition and preserved in the incubator at 0 °C.

Experiments have been carried out at varying digestion temperatures in the range of 35–55 °C for retention time of 14 days using BOD loading of 1.54, 2.12, 2.74, 3.28 and 4.45 kg/Cu m. Biogas generated at different retention days has been collected and measured, and the same has been analyzed in a gas analyzer [22] to ascertain contents of methane and carbon dioxide in the biogas produced, as it has been found that there is no other component present in the biogas.

3. Results and discussion

The results of experimentation have been represented graphically in Figs. 2A, 2B, 3A, 3B, 4A, 4B, 5A, 5B, 6A,

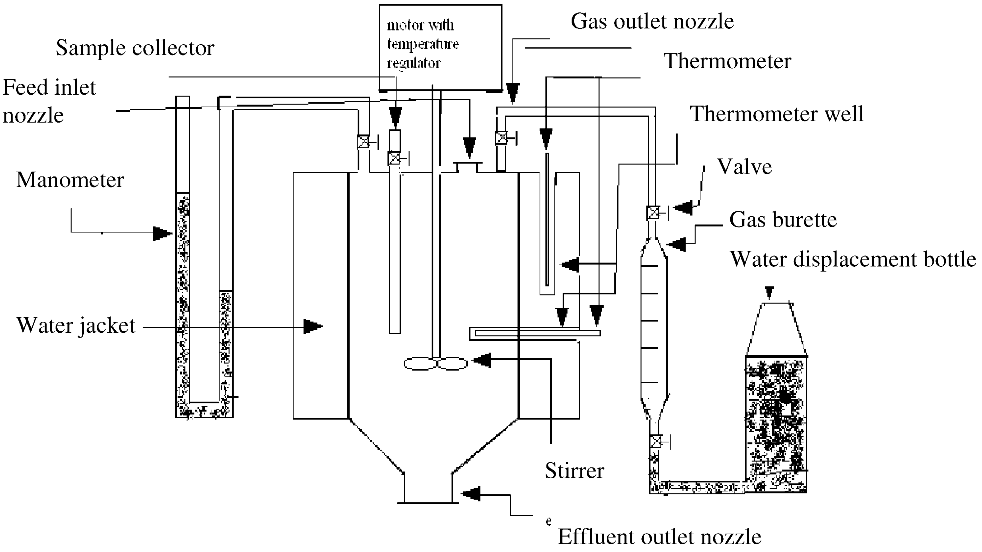

Fig. 1. A schematic diagram of digester set-up.

Table 1
Characteristics of distillery wastes

Parameters	Results	Parameters	Results (%)	Parameters	Results (%)
BOD of the raw slop	51.74933 kg/Cu m	Proximate analysis (by weight)		Non-volatile solid (by weight)	7.5
COD of the raw slop	71.54458 kg/Cu m	Ash	1.8	CHN analysis (by weight)	
pH of the slop	5.5	Moisture	82.4	Total carbon	5.77
Specific gravity	1.162	Volatile matter	10.1	Hydrogen	7.34
Boiling Range	96.5–105.9 °C	Fixed carbon	5.7	Nitrogen	0.34

6B, 7, 8, 9, 10 and 11 and the results based on data analysis have been tabulated in Tables 2–5.

Fig. 2A shows the variation of cumulative methane yield in Cu m/Cu m DW against inverse retention time in day^{-1} at digestion temperature 35 °C for BOD loading of 1.54, 2.12, 2.74, 3.28 and 4.45 kg/Cu m and Figs. 3A, 4A, 5A and 6A show the variation of cumulative methane yield in Cu m/Cu m DW against inverse retention time (Ø) in day^{-1} at digestion temperatures 40, 45, 50 and 55 °C respectively for BOD loading of 2.74 and 3.28 kg/Cu m.

Fig. 2B shows the plot of log $[B_0/(B_u - B_0)]$ against log [retention time] at digestion temperature 35 °C for different BOD loading, and Figs. 3B, 4B, 5B and 6B show the plot of log $[(B_0/(B_u - B_0)]$ against log (retention time) at digestion temperatures 40,45,50 and 55 °C respectively for BOD loading of 2.74 and 3.28 kg/Cu m.

It appear from the Figs. 2A, 3A, 4A, 5A and 6A that cumulative methane yield in Cu m/Cu m DW shows non-linear relationship with inverse retention time in day^{-1} within the range of parameters experimented with, from which ulti-

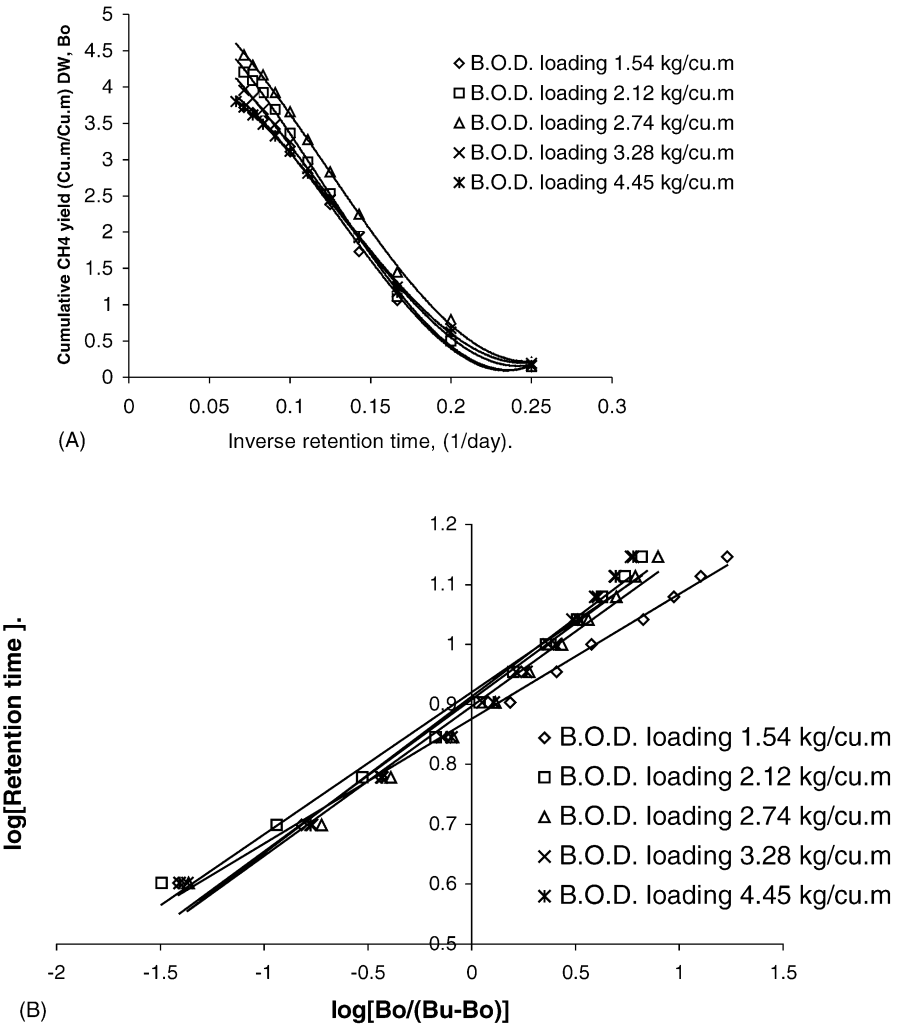

Fig. 2. (A) Plot of cumulative methane yield against inverse retention time at digestion temperature 35 °C for different BOD loading. (B) Plot of $\log(B_0/(B_u - B_0))$ against log (retention time) at digestion temperature 35 °C for different BOD loading.

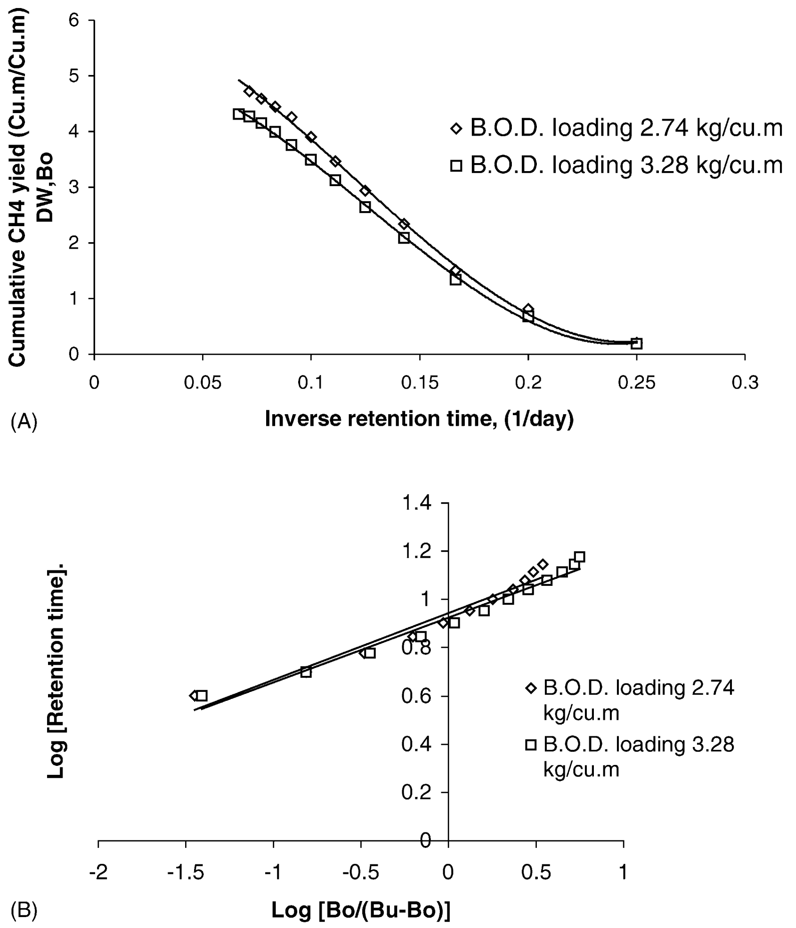

Fig. 3. (A) Plot of cumulative methane yield against inverse retention time at digestion temperature 40 °C for different BOD loading. (B) Plot of $\log(B_0/(B_u - B_0))$ against log (retention time) at digestion temperature 40 °C for different BOD loading.

mate methane yield (B_u) has been evaluated at inverse retention time = 0 and values have been tabulated in Tables 3–5.

It has been found that the graphical analysis is more significant to reduce the approximation error as made by Chen and Hashimoto [23,24], who assumed a linear relationship between cumulative methane yield in Cu m/Cu m DW and inverse retention time in day^{-1}. It has been observed that the ultimate methane yield is maximum for BOD loading of 2.74 kg/Cu m at 35 °C.

It has been further observed from Fig. 2B that log $[(B_0/(B_u - B_0)]$ shows linear relationship with log (retention time) at digestion temperature 35 °C for different BOD loading ranging from 1.54 to 4.45 kg/Cu m, and similar relationships have been found also at digestion temperatures 40, 45, 50 and 55 °C respectively for BOD loading of 2.74 and 3.28 kg/Cu m as shown in Figs. 3B, 4B, 5B and 6B which, however, do not corroborate with the previous workers [23,24]. The equation which fits such curves may be represented by a generalized correlation given as

$$Ø = A\left[\frac{B_0}{B_u - B_0}\right]^n \quad (5)$$

where coefficient A and exponent n depend on digestion temperature, BOD loading, cell mass concentration and process kinetics. Values of A and n of Eq. (5) for different BOD loading and digestion temperature are tabulated in Table 2.

Table 2
Values of A and n of Eq. (5) for different BOD loading and digestion temperature

	Digestion temperature (°C)				
	35	40	45	50	55
BOD loading (kg/Cu m)					
2.74					
A	7.88	8.455	8.16	7.958	8.234
n	0.2497	0.2665	0.2626	0.2568	0.2548
3.28					
A	7.81	8.06	7.875	7.61	7.88
n	0.2608	0.25	0.2405	0.2337	0.2456
BOD loading (kg/Cu m)					
A	8.429	8.051	7.881	7.81	8.167
n	0.2082	0.2373	0.2497	0.2608	0.2611
	Digestion temperature (35 °C)				
	1.54	2.12	2.74	3.28	4.45

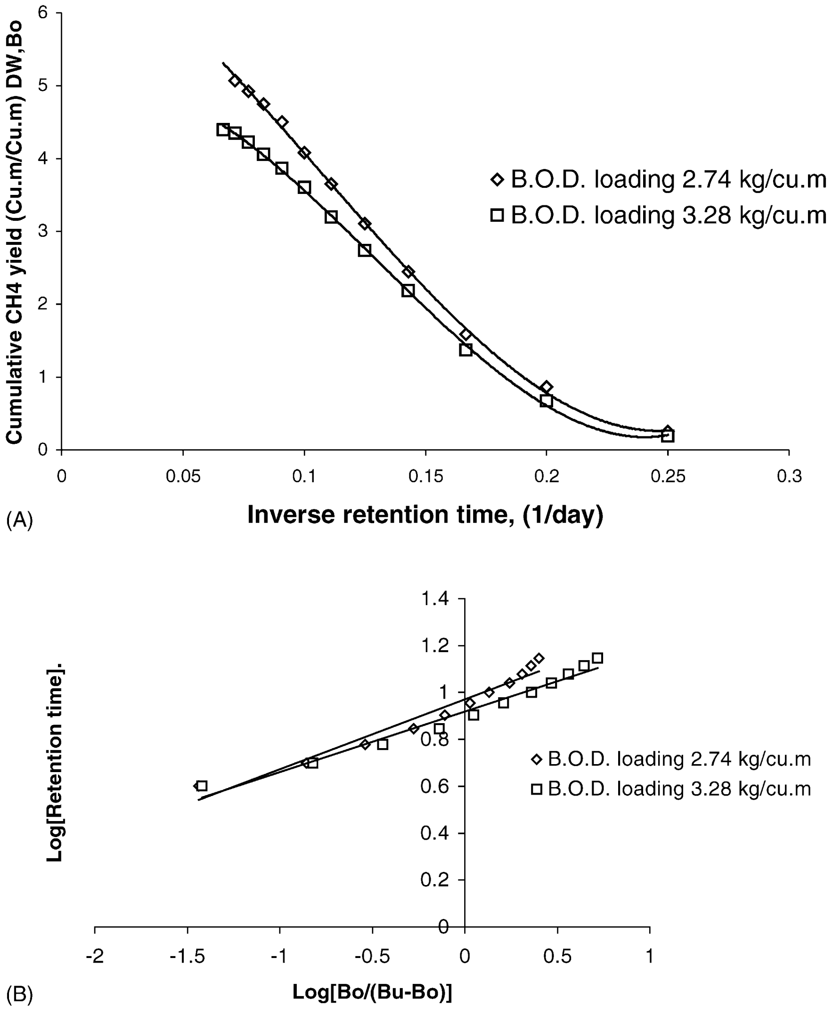

Fig. 4. (A) Plot of cumulative methane yield against inverse retention time at digestion temperature 45 °C for different BOD loading. (B) Plot of log $(B_0/(B_u - B_0))$ against log (retention time) at digestion temperature 45 °C for different BOD loading.

It has, therefore, been found that Chen and Hashimoto kinetic model equation given as

$$Ø = \frac{1}{\mu_m} + \frac{k}{\mu_m}\frac{B_0}{B_u - B_0} \quad (6)$$

is not valid for semi-batch digestion of distillery wastes. However, comparing with the model equation of Chen and Hashimoto [23] intercepts and slopes of the graphs of Figs. 2B, 3B, 4B, 5B and 6B represent the terms $1/\mu_m$ and k/μ_m respectively, from which maximum specific growth rate (μ_m) and kinetic parameter (k) have been determined and tabulated in Tables 3–5.

Fig. 7 shows the variation of ultimate methane yield in Cu m/Cu m DW with digestion temperatures for BOD loading of 2.74 and 3.28 kg/Cu m. It has been observed that ultimate methane yield has gradually increased as the digestion temperature increases up to 50 °C for BOD loading of 2.74 and 3.28 kg/Cu m, after which ultimate methane yield has

Table 3
Results of experimental parameters for different BOD loading at 35 °C digestion temperature and for retention time of 14 days

BOD loading (kg/Cu m)	Total volume of biogas produced (m^3/m^3 at STP)	Total volume of CH_4 produced (m^3/m^3 at STP)	Total volume of CO_2 produced (m^3/m^3 at STP)	% CH_4 (average)	% CO_2 (average)	Residual BOD (kg/Cu m)	Percent reduction of BOD	Ultimate methane yield (Cu m/Cu m DW) [Bu]	μ_m	k
1.54	4.998	3.7133	1.2846	74.29	25.71	0.445	71.1	3.9325	1.0094	0.2308
2.12	5.77	4.201	1.5687	72.82	27.18	0.4	81.13	4.841	1.0343	0.2684
2.74	6.15	4.438	1.715	72.17	27.83	0.425	84.49	5.0009	1.069	0.2954
3.28	5.473	3.955	1.5176	72.28	27.72	0.55	83.23	4.6296	1.093	0.2881
4.45	5.208	3.7965	1.411	72.89	27.11	0.76	82.92	4.3419	1.0254	0.2412

Table 4
Results of experimental parameters for different digestion temperatures at BOD loading of 2.74 kg/Cu m and for retention time of 14 days

Digestion temperature (°C)	Total volume of biogas produced (m^3/m^3 at STP)	Total volume of CH_4 produced (m^3/m^3 at STP)	Total volume of CO_2 produced (m^3/m^3 at STP)	% CH_4 (average)	% CO_2 (average)	Residual BOD (kg/Cu m)	Percent reduction of BOD	Ultimate methane yield (Cu m/ Cu m DW) [Bu]	μ_m	k
35	6.15	4.438	1.712	72.17	27.83	0.425	84.49	5.0009	1.009	0.2954
40	6.422	4.718	1.703	73.48	26.52	0.34	87.59	6.0832	1.078	0.287
45	6.79	5.0727	1.717	74.71	25.29	0.29	87.67	7.087	1.116	0.285
50	7.03	5.11	1.911	72.81	27.18	0.27	85.37	7.1455	1.2461	0.2828
55	7.381	5.395	1.986	73.09	26.91	0.27	90.15	6.3204	1.092	0.278

gradually decreased. However, the maximum value of ultimate methane yield has been found at 50 °C for BOD loading of 2.74 kg/Cu m. Eqs. (7) and (8) fit the curves well of Fig. 7 for BOD loading of 2.74 and 3.28 kg/Cu m respectively.

$$B_u = -0.0136T^2 + 0.2936T - 23.757 \tag{7}$$

$$B_u = -0.0045T^2 + 0.4144T - 4.4062 \tag{8}$$

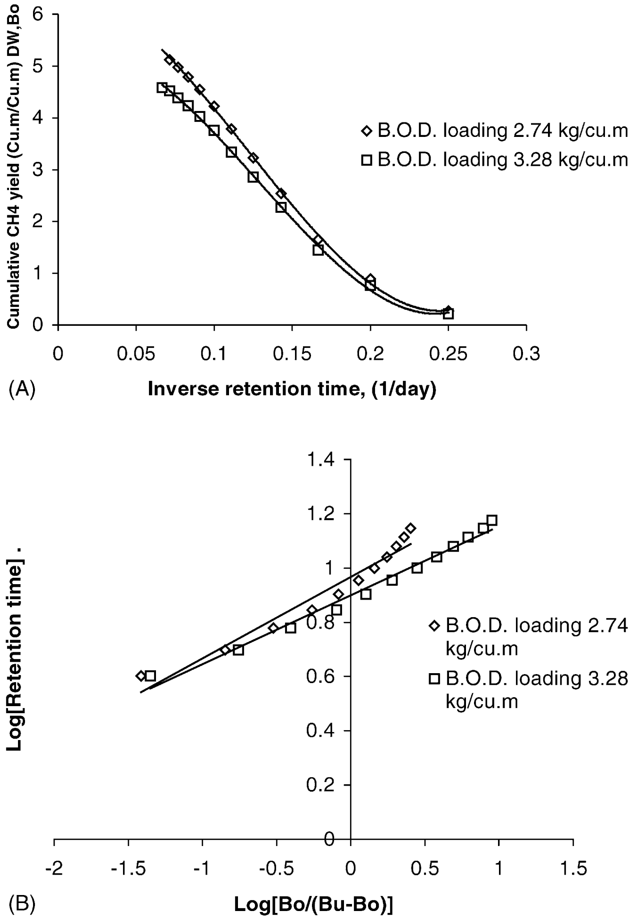

Fig. 5. (A) Plot of cumulative methane yield against inverse retention time at digestion temperature 50 °C for different BOD loading. (B) Plot of log $(B_0/(B_u - B_0))$ against log (retention time) at digestion temperature 50 °C for different BOD loading.

Figs. 8 and 9 show the variation of μ_m and k with change in BOD loadings at digestion temperature of 35 °C respectively, and Figs. 10 and 11 show the variation of μ_m and k with change in digestion temperatures for BOD loading of 2.74 and 3.28 kg/Cu m respectively. It has been observed from Fig. 8 that the maximum specific growth rate (μ_m) depends on BOD loading at 35 °C and shows non-linear relationship with BOD loading. It also reveals that the BOD loading for which μ_m is maximum is 3.15 kg/Cu m. The equation which fits the curve is,

$$\mu_m = -0.03S^2 + 0.189S + 0.7814 \tag{9}$$

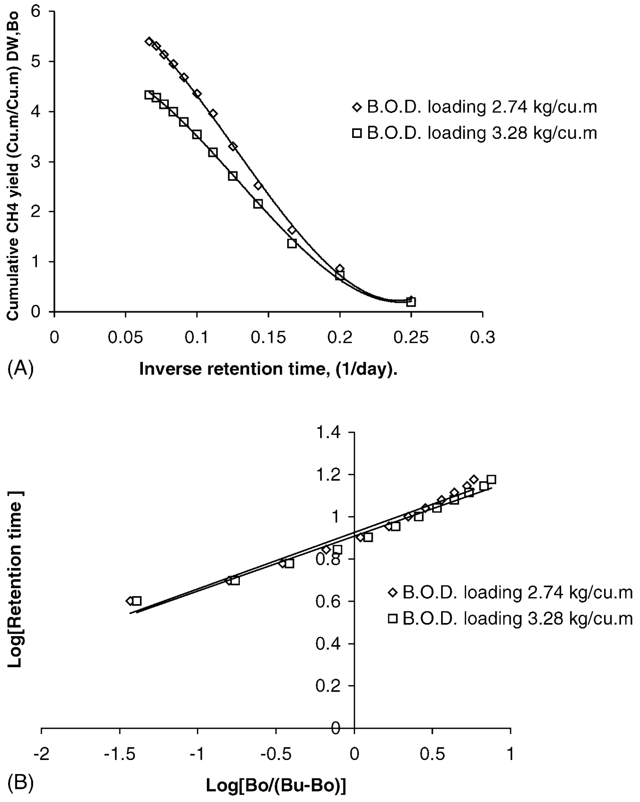

Fig. 6. (A) Plot of cumulative methane yield against inverse retention time at digestion temperature 55 °C for different BOD loading. (B) Plot of log $(B_0/(B_u - B_0))$ against log (retention time) at digestion temperature 55 °C for different BOD loading.

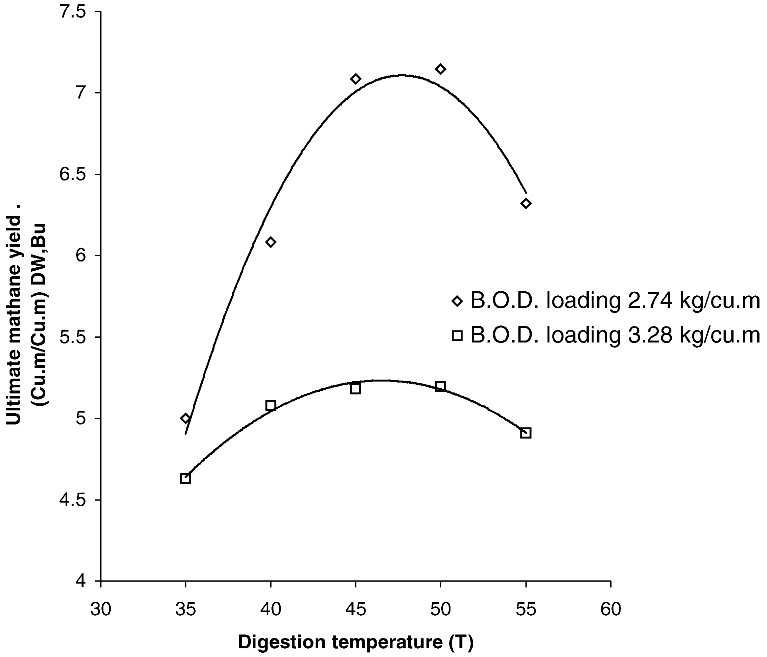

Fig. 7. Variation of ultimate methane yield with digestion temperature at different BOD loading.

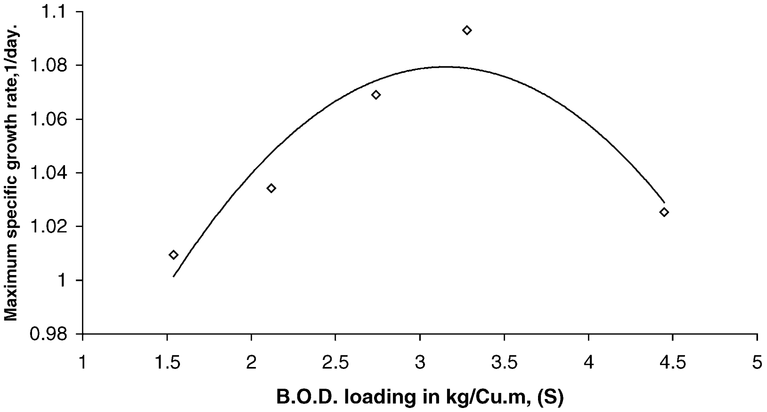

Fig. 8. Variation of maximum specific growth rate with BOD loading at 35 °C digestion temperature.

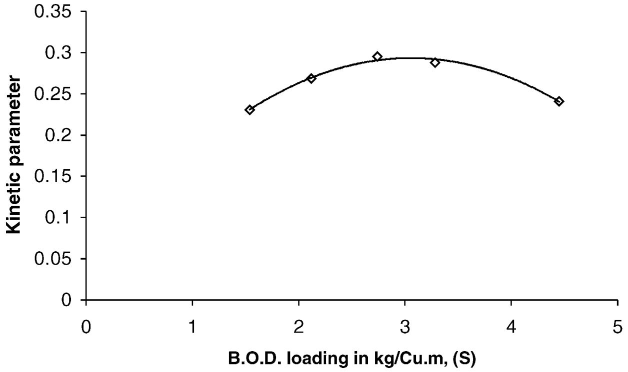

Fig. 9. Variation of kinetic parameter with BOD loading at 35 °C digestion temperature.

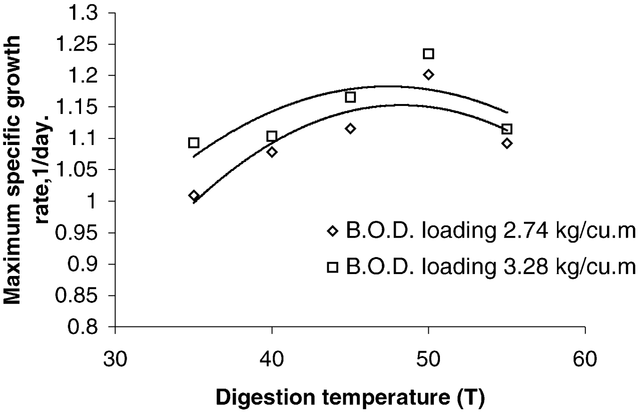

Fig. 10. Variation of maximum specific growth rate with digestion temperature at different BOD loading.

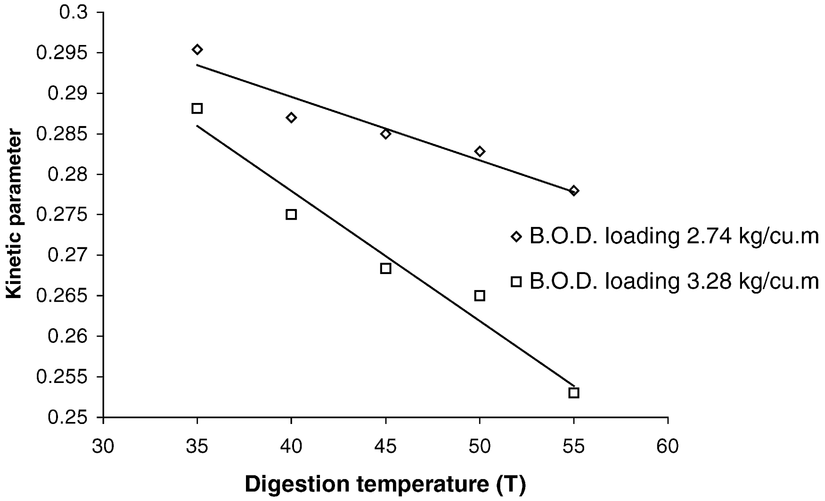

Fig. 11. Variation of kinetic parameter with digestion temperature at different BOD loading.

Table 5
Results of experimental parameters for different digestion temperatures at BOD loading of 3.28 kg/Cu m and for retention time of 14 days

Digestion temperature (°C)	Total volume of biogas produced (m^3/m^3 at STP)	Total volume of CH_4 produced (m^3/m^3 at STP)	Total volume of CO_2 produced (m^3/m^3 at STP)	% CH_4 (average)	% CO_2 (average)	Residual BOD (kg/Cu m)	Percent reduction of BOD	Ultimate methane yield (Cu m/ Cu m DW) [Bu]	μ_m	k
35	5.473	3.955	1.5176	72.28	27.72	0.55	83.23	4.6296	1.093	0.2881
40	5.896	4.3138	1.5822	73.17	26.83	0.52	84.14	5.081	1.103	0.275
45	6.03	4.39	1.631	72.95	27.05	0.5	84.37	5.1814	1.1658	0.2684
50	6.257	4.58	1.675	73.23	26.77	0.459	86.01	5.1957	1.2345	0.265
55	5.96	4.335	1.625	72.74	27.26	0.45	85.28	4.9107	1.115	0.253

The kinetic parameter (k) which is a measurement of the overall performance of the digester depends on BOD loading, and the BOD loading for which k is maximum is 3.0514 kg/Cu m as found out from Fig. 9. The equation which fits the curve is,

$$k = -0.0272S^2 + 0.166S + 0.0397 \tag{10}$$

It has been further observed from Fig. 10 and Tables 4 and 5 that μ_m shows non-linear relationship with digestion temperature for a given BOD loading. Eqs. (11) and (12) fit the curves well of Fig. 10 for BOD loading of 2.74 and 3.28 kg/Cu m respectively.

$$\mu_m = -0.0011T^2 + 0.1102T - 1.5023 \tag{11}$$

$$\mu_m = -0.0013T^2 + 0.1289T - 1.8894 \tag{12}$$

Fig. 11 shows that kinetic parameter (k) varies linearly with digestion temperature for both BOD loading of 2.74 and 3.28 kg/Cu m, and kinetic parameter decreases with increase in digestion temperature. By graphical analysis the relationship between kinetic parameter and digestion temperature can be represented by Eqs. (13) and (14) for BOD loading of 2.74 and 3.28 kg/Cu m respectively.

$$k = -0.0008T + 0.3207 \tag{13}$$

$$k = -0.0016T + 0.3421 \tag{14}$$

4. Conclusion

The present investigation is a systematic study of biomethanation of distillery wastes in mesophilic and thermophillic range of temperatures, which reveals that there is enormous effect of digestion temperature and substrate concentration in terms of BOD and COD loadings on the yield of biogas and also on the methane content in the biogas. It has further revealed that bacterial growth continued significantly up to 7 days of retention time after which decaying of the bacteria has occurred and bacterial action has been very insignificant after 14 days of retention time. Maximum total biogas yield as well as methane yield have been obtained for BOD loading of 2.74 kg/Cu m at 50 °C digestion temperature within the range of digestion temperature experimented with. It has been found that variation of kinetic parameter with temperatures follow a linear relationship whereas variation of maximum specific growth rate (μ_m) with temperature and both μ_m and k with BOD loadings exhibit non-linear behaviour. It is also found from mathematical analysis that μ_m is maximum at 50.09 °C digestion temperature for BOD loading of 2.74 kg/Cu m, and the BOD loading for which μ_m and k are maximum are 3.15 and 3.0514 kg/Cu m respectively at 35 °C. It also reveals that maximum percentage reduction of BOD has occurred at digestion temperature of 55 °C for BOD loading of 2.74 kg/Cu m within the range of parameters experimented with.

Acknowledgements

Fellowship support to Mr. Saikat Banerjee from Council of Scientific and Industrial Research, India, is gratefully acknowledged.

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