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Co-digestion of mixed industrial sludge with municipal solid wastes in anaerobic simulated landfilling bioreactors

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Abstract

In this study, the feasibility of the anaerobic co-digestion of a mixed industrial sludge with municipal solid wastes (MSW) was investigated in three simulated anaerobic landfilling bioreactors during a 150-day period. All of the reactors were operated with leachate recirculation. One of them was loaded only with MSW (control reactor); the second reactor was loaded with mixed industrial sludge and MSW, the weight ratio of the MSW to mixed industrial sludge was 1:1 (based on dry solid) (Run 1); the third reactor was loaded with mixed industrial sludge and MSW, the weight ratio of the MSW to mixed industrial sludge was 1:2 (based on dry solid) (Run 2). The VFA concentrations decreased significantly in Run 1 and Run 2 reactors at the end of 150 days. The pH values were higher in Run 1 and Run 2 reactors compared to control reactor. The differences between leachate characteristics, the biodegradation and the bioefficiency of the reactors were compared. The NH_4–N concentrations released to leachate from mixed sludge in Run 1 and Run 2 reactors were lower than that of control reactor. The BOD_5/COD ratios in Run 1 and Run 2 reactors were lower than that of control reactor at the end of 150 days. Cumulative methane gas productions and methane percentages were higher in Run 1 and Run 2 reactors. Reductions in waste quantity, carbon percentage and settlement of the waste were better in Run 1 and Run 2 reactors compared to control reactor at the end of 150 days. Furthermore, TN and TP removals in waste were higher in reactors containing industrial sludge compared to control. The toxicity test results showed that toxicity was observed in reactors containing industrial mixed sludge.

Keywords: Municipal solid waste; Bioreactor; Mixed industrial sludge; Co-digestion; Simulated anaerobic landfilling bioreactor

1. Introduction

An interesting option for improving yields of anaerobic digestion of solid wastes is co-digestion. The benefits of co-digestion include: dilution of potential toxic compounds, improved balance of nutrients, synergistic effect of microorganisms, increased load of biodegradable organic matter and better biogas yield. Additional advantages include hygienic stabilization and increased digestion rate [1]. In anaerobic digestion, co-digestion is the term used to describe the combined treatment of several wastes with complementary characteristics, being one of the main advantages of anaerobic technology.

Landfills are employed for solid and hazardous waste disposal. Unfortunately, many of these sites have not been properly operated and the leachate contains high concentrations of COD, ammonia, VFA and heavy metals. Anaerobic simulated landfilling bioreactors work as anaerobic sludge digesters for more economic sludge digestion and acceleration of waste stabilization to enhance the methane gas recovery [2]. Compared with conventional sanitary landfills, simulated anaerobic landfilling bioreactors provide the potential for more rapid, complete and predictable attenuation of solid waste constituents and reduce the environmental pollution. The co-digestion of solid wastes with industrial sludge in simulated anaerobic landfilling reactors increase the mixed solid waste bioefficiency and improve the leachate characteristics.

Co-digestion of municipal solid waste (MSW) with sludge from yeast wastewater treatment plants has a significant effect on the quality of leachate [3]. Anaerobic co-digestion of the organic food fraction of the municipal solid wastes, with pri-

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mary sewage sludge, produces high quality biogas, resulting in a suitable renewable energy source [4]. Sosnowski et al. [1] showed that the anaerobic co-digestion of sewage sludge and MSW seems to be an attractive method for environmental protection and energy savings.

As aforementioned, although many studies [5–8] are related to co-digestion of MSW with sewage sludge, agricultural wastes, animal wastes, olive oil, pig slurry, swine manure, and cattle manure [9,10] there are limited studies on the co-digestion of MSW with toxic industrial sludge in simulated anaerobic landfilling bioreactors. For instance, Pohland and Gould [11] studied the effects of co-digestion of municipal refuse and industrial waste sludge in landfilling reactors. The reactors containing lowest metal plating sludge did not inhibit the conversion of readily degradable organic compounds. Therefore, the purpose of this research is to evaluate the effects of co-digestion of mixed industrial sludge with municipal solid waste in simulated anaerobic landfilling bioreactors in order to compare the leachate quality and the reactor bioefficiencies. Therefore, the COD removals, the VFA, the ammonia levels, pH variation in leachate samples and the methane gas productions in laboratory scale simulated anaerobic landfilling reactors were monitored. Furthermore, toxicity test results were compared in leachate samples.

2. Methodology

2.1. Lab-scale anaerobic simulated landfill bioreactor

Stainless-steel cylindrical bioreactors 10 cm in diameter and 30 cm in height were constructed to treat the mixed industrial sludge by mixing it with municipal solid wastes and to collect the biogas. The schematic configuration of these reactors is shown in Fig. 1. These bioreactors were operated in batch mode at a temperature of 35–40 °C under anaerobic conditions. The leachate was collected at the bottom section of the solid waste reactor and the effluent was recycled to the top of the reactor with a peristaltic pump. There were two separate ports on the top of the reactor for the addition of simulated rainwater, measurement of the methane, total gas productions and for recirculation of the leachate.

2.2. Operating protocol for simulated landfill reactors

All the anaerobic simulated landfill reactors were loaded with solid waste and mixed industrial sludge at different ratios. The first (control reactor, no industrial sludge added), the second (Run 1) and the third reactors (Run 2) were operated with 300 ml of leachate recirculation since it was effective in enhancing the degradation rate of the waste, and the gas production in anaerobic simulated landfilling bioreactors. Furthermore, the recirculation of leachate in anaerobic landfilling reactors accelerates the organic matter hydrolysis, converting it into organic acids and methane [2]. Table 1 shows the operating conditions for all reactors through 150 days. The weight ratio of the MSW to mixed industrial sludge was 1:1 (dry solid basis). The weight ratio of the MSW to mixed industrial sludge was 1:2 (dry solid basis). Fifty millilitres of anaerobic sludge was added to all the reactors in order to provide methanogenic conditions. Fifty millilitres of tap water was added to all the reactors in order to simulate the rainwater. The characterization of the industrial sludge and MSW is shown in Tables 2a and 2b. No heavy metal was determined in the MSW. The municipal solid wastes were collected from the kitchen of the Engineering Faculty in Dokuz Eylul University Campus. The mixed industrial sludge was taken from the belt filtering system of the mixed sludge originating from the textile, metal plating, electronic, chemical and plastic industries at the Manisa Organized Industrial District. The TS and VS concentrations were 3200, 3800, 4500 mg/l; and 4500, 6500, 8200 mg/l in control, Run 1 and Run 2 reactors, respectively.

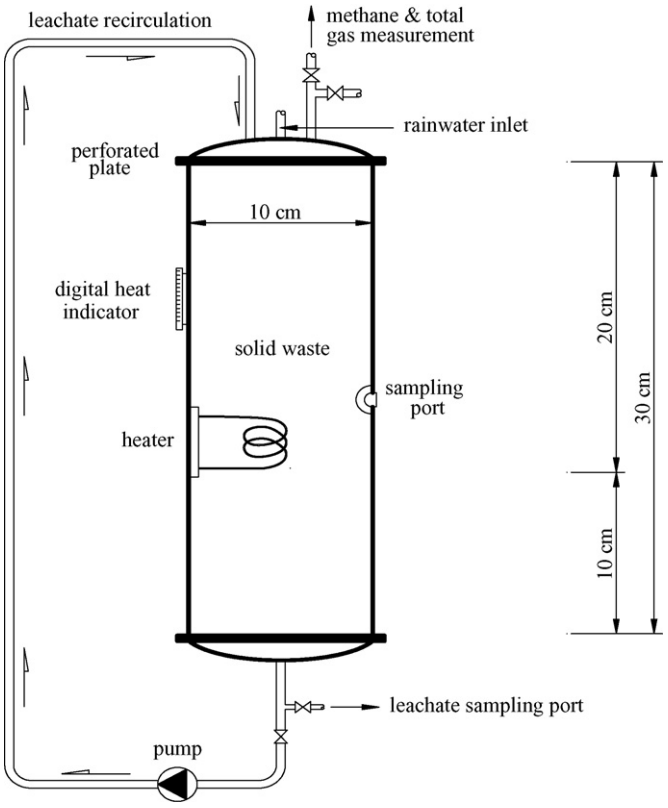

Fig. 1. Schematic configuration of simulated anaerobic landfilling bioreactor.

Table 1
Operation conditions

	Control reactor	Run 1	Run 2
Loading date (kg COD/kg VS day)	1.93	1.19	0.96
Quantity of waste (g)	1200	1200	1200
Weight ratio (MSW to industrial sludge)	Mixed industrial sludge was not added	1:1	1:2
Recirculation	With	With	With
Recirculation volume (ml/day)	300	300	300
Water content (%)	90	82	68
Organic matter	95	87	79
C (%)	52.8	48.3	43.9
Operation time (day)	150	150	150

Table 2a
Characterization of mixed industrial sludge

Characteristics	Measured value	Characteristics (mg/l)	Measured value
Water content (%)	67	Cr	0.05
Organic matter (%)	70	Zn	0.44
C (%)	38.8	Cu	0.14
Total nitrogen (mg/l)	1300	Pb	0.062
Total phosphorus (mg/l)	790	Fe	10.36
Ammonium nitrogen (mg/l)	86	Mn	0.3
AOX (μg/l)[a]	800	Ni	0.03
Sulfate (mg/kg wet waste)	680	Cd	0.02

[a] AOX: adsorbable organic halogens.

2.3. Analytical procedure

The analytical analysis in this study was performed following the procedures given by Ağdağ and Sponza [12]. Organic matter, water content, volatile solid (VS), carbon (C), in municipal waste samples and COD concentrations in leachate samples were detected following the Standard Methods [13]. BOD_5 was measured using the WTW Oxi Top IS 12 system. Total nitrogen (TN), total phosphorus (TP) and ammonia-nitrogen were measured using spectroquant kits numbered 14,537, 14,543 and 14,752 in a photometer Merck SQ 300. The heavy metal and sulfate analyses (Pb, Zn, Cd, etc.) were performed following the Standard Methods [13] using an atomic adsorption spectrometer UNICAM 929. The pH was determined immediately after sampling to avoid any change due to CO_2 stripping, using a pH meter, type NEL pH 890. Total volatile fatty acid (TVFA) concentrations in the leachate samples were measured using Anderson and Yang [14] method. Gas productions were measured by liquid displacement method. Total gas was measured by passing it through a liquid containing 2% (v/v) H_2SO_4 and 10% (w/v) NaCl [15]. Methane gas was detected using a liquid solution containing 3% NaOH (w/v) [16]. Methane percentage was monitored with a digital methane meter (Drager Pac Ex).

Inert COD content of leachate was determined with glucose comparison method developed by Germirli et al. [17] in soluble COD. AOX was measured using Heraous AOX-MT200 analyzer.

Anaerobic toxicity assay (ATA) test was performed at 37 °C using serum bottles with a capacity of 115 ml as described by Owen et al. [18] and Donlon et al. [19]. Serum bottles were filled with the leachate samples at dilution rates of 0, 25, 50, 75 and 100%. Vanderbilt mineral medium was added to give a constant glucose-COD concentration of 3000 mg/l indicating the presence of non-limiting substrate conditions in the serum bottles. Six hundred and sixty-seven milligrams per litre of sodium thioglycollate was added to the serum bottles to provide the reducing conditions. Twenty-five millilitres of anaerobic sludge with a volatile solid concentration of 4000 mg/l was added to the assay bottles taking from the anaerobic treatment plant of a yeast industry in İzmir (Pakmaya, Yeast Industry). Furthermore, 5000 mg/l of $NaHCO_3$ was added for maintaining the neutral pH and providing suitable methanogenic activity, respectively. The glucose-COD in the serum bottles was stochiometrically replenished to 3000 mg/l with stock Vanderbilt solution after 3 days of exposure to leachate wastewater. Duplicate controls were performed through the assay, containing no-leachate. All the results are the mean values of duplicate sampling. Methane productions were monitored through 3 days of incubation periods in every serum bottle.

Table 2b
Characterization of MSW

Characteristics	Measured value	Characteristics	Measured value
Water content (%)	98	Cr	0
Organic matter (%)	95	Zn	0
C (%)	49	Cu	0
Total nitrogen (mg/kg)	1300	Pb	0
Total phosphorus (mg/kg)	500	Fe	0
Ammonium nitrogen (mg/kg)	75	Mn	0
AOX (μg/kg)	0	Ni	0
Sulfate (mg/kg wet waste)	0	Cd	0

Toxicity to the bioluminescent organism *Vibrio fisheri* was assayed using n the LUMIStox measuring system following DIN 38412 L34 and L341 [20]. LUMISmini type photometer (Dr. Lange Company) was used for the toxicity teast. All samples were serially diluted with 2% NaCl (w/v) solution. Each assay was performed at pH 7.0 and a temperature of 15 °C. Sodium chloride (2%) was used as the control. Inhibition percentage (H%) values refer to the decreasing activity in samples causing inhibitory effect of test substances (leachate samples) during the light emission. The inhibition was evaluated as follows [21]:

Percent inhibition (H)	Result
$0 < H < 5$	Non-toxic
$5 < H < 20$	Possibly toxic
$20 < H < 90$	Toxic

All the data given in the figures and in the tables are the mean of duplicate samplings.

3. Results and discussions

3.1. Removal efficiencies in leachate samples

3.1.1. COD variations

COD was monitored as an indicator parameter of the organic strength of the leachate. Fig. 2 shows the daily variation of COD concentrations in leachate for the control (no sludge addition), Run 1 (waste to sludge ratio 1:1) and Run 2 (waste to sludge ratio 1:2) reactors through 150 days of operation period. The initial COD concentration in leachate samples collected from the control, Run 1 and Run 2 reactors were 27,415, 19,004 and 17,109 mg/l, respectively. The initial COD value of the control reactor was higher than the others since it contained a high proportion of readily degradable organic substances. The maximum COD values in the leachate samples taken from the reactors containing mixed industrial sludge (Run 1 and Run 2) were 31,104 and 28,105 mg/l, respectively, on day 15. The maximum COD value was 43,719 mg/l on day 25 in control reactor. In the fol-

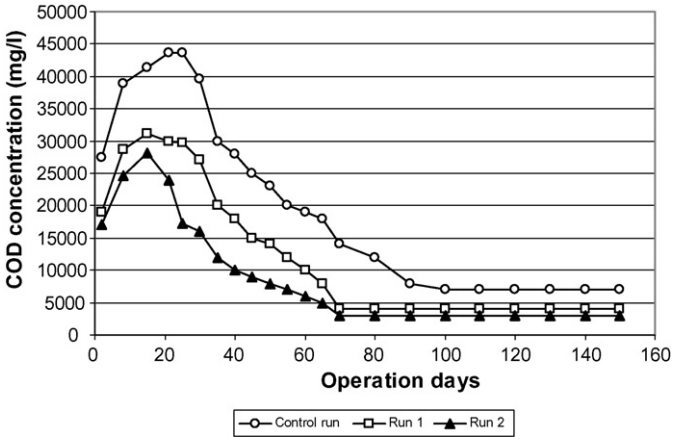

Fig. 2. Variation of COD concentrations in leachate samples.

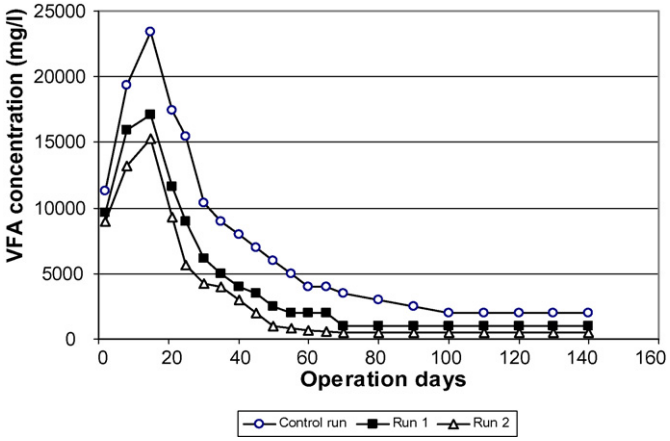

Fig. 3. Variation of VFA concentrations in leachate samples.

lowing days the COD concentrations decreased to a stable level on days 100 and 70 in control and Run 1, Run 2 reactors, respectively. The COD concentrations were 8000, 4000 and 3000 mg/l, in control, Run 1 and Run 2 reactors, respectively, in the aforementioned days and remained constant until day 150 (see Fig. 1). The final COD concentrations in Run 1 and Run 2 reactors were lower than the control. This could be attributed to nutrients and to trace heavy metal concentrations present in mixed industrial sludge which activated the methanogenic archaea. The COD removal efficiencies measured between maximum COD and final COD concentrations were 83, 87 and 89% in control, Run 1 and Run 2, reactors. The COD concentrations remained stable for the last 50 days of operationing, indicating the stabilization of organic substances in all reactors On the other hand, the COD concentrations in Run 1 and Run 2 reactors reached a stable level in a relatively short time compared to control. In contrast to our results, the study performed by Pohland and Gould [2,11], showed that the COD values were higher than the control reactor in reactors containing metal plating. They found that the decrease in COD was slower in reactors containing heavy metal than the control reactor. In our study, the heavy metal concentrations were lower in reactors containing mixed sludge (see Table 2a) No heavy metal was observed in MSW (see Table 2b). Therefore, the heavy metals supported the growth of anaerobic bacteria in Run 1 and Run 2 reactors, as reported by Speece [22].

The result of this study showed that co-digestion of mixed industrial sludge with MSW in simulated anaerobic landfill reactors has a positive effect in the decrease of COD concentrations in leachate since the heavy metals were utilized by the anaerobic methanogenic microorganisms as reported by Stroot et al. [23].

3.1.2. VFA variations

The concentration of VFA is an important parameter because it indicates the degree of stability of the anaerobic process. As shown in Fig. 3 the initial VFA concentrations in leachate samples were 27,415, 9650 and 8669 mg/l in control, Run 1 and Run 2 reactors, respectively. The maximum VFA concentrations in control, Run 1 and Run 2 were 23,413, 17,105 and 15,303 mg/l and then they started to decrease. The VFA concentrations in leachate samples reached a stable level by days 100 and 70 in control, Run 1 and Run 2 reactors, respectively. The VFA removal efficiencies measured between maximum level of VFA and final concentrations were 91, 94, and 96% in control, Run 1 and Run 2, respectively. This shows that at high COD concentrations a high VFA was obtained. The degradation of organic substances at high concentrations in initial phase of the fermentation increased the VFA levels. The VFA must have been converted to methane via methanogenic bacteria. The lower VFA concentration in reactors containing mixed industrial sludge could be attributed to the low COD concentrations through hydrolysis of organic compounds.

In the leachate samples taken from the reactors containing industrial sludge the growth of acidifying bacteria, which are able to hydrolyze the insoluble substrates, resulted in high VFA concentration [24]. However, in this study the leachate samples in Run 1 and Run 2 reactors exhibited low VFA concentrations compared to control reactor. Different suggestions were reported about the effects of sewage and industrial sludge on the VFA concentrations in leachate samples. Schmidell et al. [26] reported that a high quantity of the sewage sludge within the solid waste reactor has a low VFA concentration. On the other hand, in the study carried out by Pohland and Gould [11], the VFA concentration of the reactor receiving industrial sludge was higher than that of the control reactor.

TVFA/bicarbonate alkalinity (TVFA/BA) ratio provides information which can be used to determine the stability of the anaerobic reactor. If the acid concentrations (H_2CO_3 and TVFA) exceed the available alkalinity, the reactor will sour, severely inhibiting microbial activity, especially the methanogens [22]. If the TVFA/BA ratio is lower than 0.4, the reactor is stable. When the TVFA/BA ratio is lower than 0.8, the reactor system is moderately stable or unstable as reported by Behling et al. [25]. The VFA/BA ratios were 0.40, 0.35 and 0.20 in control and Run 1 and Run 2 reactors, respectively, on day 70. This shows that Run 1 and Run 2 reactors were stable.

3.1.3. NH_4–N variations

The results of the NH_4–N concentrations measured in leachate samples over periods of time from the control, Run 1 and Run 2 reactors are shown in Fig. 4. The highest NH_4–N con-

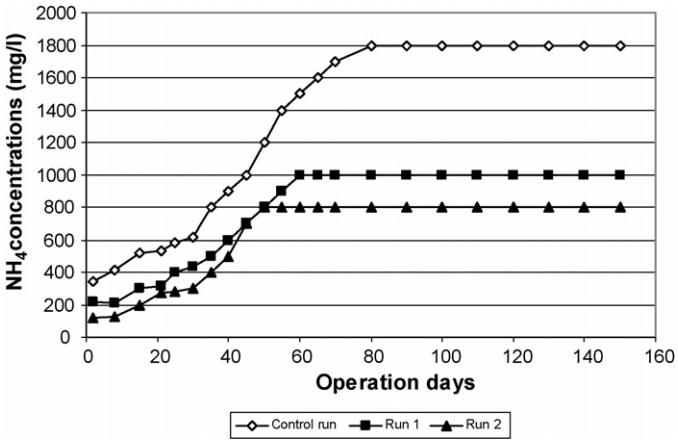

Fig. 4. Variation of NH_4–N concentrations in leachate samples.

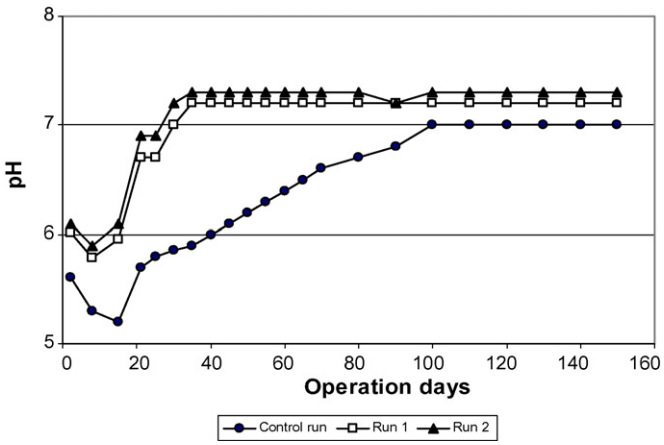

Fig. 5. Variation of pH levels in leachate samples.

centrations were 1800, 1000 and 800 mg/l in control, Run 1 and Run 2 reactors through the mineralization of organic nitrogenous compounds and remained stable for the last 50 days of operation through 150 days of total operation. These results showed that the mineralization of organic nitrogenous compounds was terminated. It was observed that the NH_4–N concentrations in control reactor was higher than that of Run 1 and Run 2 reactors since the control reactor contained more nitrogenous organic compounds such as proteins and amino acids. The TN concentrations in waste were higher in control reactor as compared to Run 1 and Run 2 (TN = 10,395, 6000 and 4195 mg/kg in waste of control, Run 1 and Run 2 reactors, respectively, in first day of operation). The lower NH_4–N concentrations in the leachate samples of the Run 1 and Run 2 reactors could be explained by the inhibition of proteolysis by the heavy metals in mixed industrial sludge, resulting in insufficient degradation of nitrogenous organics. In other words, protein degrading microorganisms are very sensitive to heavy metals, sulfate and other toxic substances. Marttinen et al. [27], reported that a landfill leachate treatment is normally focused on the removal of organic nitrogenous, carbonaceous matters and ammonia nitrogen levels since all three parameters are quite important for possible inhibition of methane production under anaerobic conditions. It is important to note that the major part of the nitrogen in the solid waste bioreactors is in the organic form as reported by Marttinen et al. [27].

3.1.4. pH variations

The variation of pH profiles over time is illustrated in Fig. 5. As can be seen in this figure, the initial pH of the leachates from the control, Run 1 and Run 2 reactors were 5.61, 6.02 and 6.1, respectively. The low Ph is due to the high concentrations of VFA which are produced by acetogenic bacteria and inhibit the methanisation process. The pH value in control reactor remained stable by day 100 (pH 7). The pH values in Run 1 and Run 2 reactors were measured as 7.2 by day 35. After this day the pH in both reactors remained constant until day 150. This study showed that the pH values in reactors containing mixed industrial sludge were higher than that of control reactor.

Warith [5] found that the highest pH value was in the reactor containing sewage sludge among the control and nutrient added reactors. Similarly, in our study, the pH values of the industrial sludge added reactors was found to be approximately 7.0–7.3 during the last 50 days of the anaerobic incubation confirming the results obtained by Warith [5]. Similarly, in a study carried out by Pohland and Gould [11], it was shown that the pH value of the reactor containing metal plating industrial sludge was higher than the pH value of the control reactor.

3.1.5. BOD_5, inert COD concentrations, BOD_5/COD ratios and TOC test results

In order to study the proportion of biodegradable organic carbon in the leachate it was decided to determine the BOD_5/COD ratios. Table 3 shows the BOD_5, COD concentrations, BOD_5/COD ratios and TOC values in the leachate samples of all the reactors measured for days 21, 40 and 150. The BOD_5 values were 40,500, 25,000, 21,242 and 18,000 mg/l on day 21 in control, Run 1 and Run 2 reactors, respectively. The BOD_5 values decreased to 700, 600 and 200 mg/l on day 150. Ninety-seven, 97 and 98% BOD_5 removal efficiencies were observed in the aforementioned reactors, on day 150. The highest BOD_5 decreases occurred in Run 2 reactor. The experimental results indicate that, the addition of mixed industrial sludge did not retard the decreasing in BOD_5 removals. In contrast to the results obtained in this study the research carried out by Warith [5] showed that the highest BOD_5 value occurred in the reactor containing industrial sludge. The BOD_5/COD ratio indicates the changes in the amount of biodegradable compounds in the leachate. Initially, all the reactors have high BOD_5/COD ratios (approximately 0.92, 0.83 and 0.75%) indicating the low degradability of leachate as reported by Quasim and Chiang [3]. On day 150, the BOD_5/COD ratios decreased to approximately 0.18, 0.15, and 0.06 in control Run 1 and Run 2 reactors, respectively. These ratios indicate the presence of a highly biodegradable leachate. In other words, these BOD_5/COD ratios show the increasing biodegradability of organics due to solubilization of organic substances through methanogenesis. As the organic content biodegradation of MSW occurred, the BOD_5/COD ratio decreased. This decrease indicated that the organic wastes were degraded through fermentation phase which demonstrated a decreasing biodegradability due to methane formation. The

Table 3
Variation of BOD_5 and TOC concentrations and BOD_5/COD ratios in leachate samples

	Control reactor			Run 1			Run 2		
	Day 21	Day 40	Day 150	Day 21	Day 40	Day 150	Day 21	Day 40	Day 150
COD (mg/l)	43618	28000	7000	30005	18000	4000	23995	10000	3000
BOD_5 (mg/l)	40500	12000	700	25000	10000	600	18000	5000	200
BOD_5/COD ratio	0.92	0.42	0.1	0.83	0.55	0.15	0.75	0.5	0.06
TOC (mg/l)	20400	7000	500	14000	5200	400	10500	3200	170

BOD_5/COD ratio of the control reactor was the lowest. This result indicated that the organic waste in the control reactor was not converted efficiently to methane via methanogenesis.

The results of inert COD assays in leachate samples showed that inert COD level was found to be approximately 8, 13 and 15% in control, Run 1 and Run 2 reactors, respectively, on day 70 (data not shown). The high inert COD levels in reactors containing mixed industrial sludge could be attributed to AOX and heavy metals. This indicates that the COD of leachate samples could be treated approximately up to 85–90%. This is the maximum soluble COD removal efficiency reached in the simulated landfill reactors under favorable anaerobic conditions [28].

TOC give an indication of the amount of organic substrate in the leachate. TOC value of the Run 2 reactor was the lowest on day 150. TOC values in control and Run 1 reactor decreased to 500 and 400 mg/l from initial values of 20,400 and 14,000 mg/l, respectively. The accumulation of carbon dioxide in the reactors caused increases in TOC concentrations through anaerobic degradation [29]. TOC values measured in all anaerobic reactors exhibited similar trend to the results obtained by Quasim and Chiang [3].

3.1.6. Determination of leachate toxicity using anaerobic toxicity assay (ATA) and lumistox tests

Table 4 illustrates the results of the ATA tests, indicating the quantities of methane produced from the serum bottles containing glucose (control) and leachate samples through six hours and three days of anaerobic incubation. At the end of the ATA test, it was found that there was a significant toxicity in reactors containing mixed industrial sludge (especially in Run 2) under anaerobic conditions since decreases in methane gas productions were observed. This can be explained by the AOX and heavy metal content of reactors containing mixed industrial sludge. No toxicity was observed in control reactor since no toxic or inhibitory organic/inorganic chemicals were contained in this reactor. When the leachate percentage was increased in the serum bottles for control reactors, the quantity of methane produced increased, indicating the utilization of leachate as a suitable carbon source by the methanogenic microorganisms through anaerobic degradation. On the other hand, the methane gas productions decreased in serum bottles containing mixed industrial sludge, indicating the toxicity of the mixed sludge taken from the textile, metal plating, electronic, chemistry and plastic industries in Manisa Organized Industrial District.

Tables 5a–5c show the percent inhibitory (H%) effects of leachate taken from the control, Run 1 and Run 2 reactors, respectively. Leachate samples taken from the Run 1 and Run

Table 4
ATA test results in leachate samples of all reactors

	Quantity of methane (ml/day) ($n = 3$ mean value)	
	After 6 h	After 3 days
Glucose 0% leachate (control)	32	35
Glucose 0% leachate (control)	31	35
25% leachate (control reactor)	35	36
50% leachate (control reactor)	39	40
75% leachate (control reactor)	44	48
100% leachate (control reactor)	50	53
25% leachate (Run 1)	26	27
50% leachate (Run 1)	24	26
75% leachate (Run 1)	20	20
100% leachate (Run 1)	12	14
25% leachate (Run 2)	15	18
50% leachate (Run 2)	10	12
75% leachate (Run 2)	8	8
100% leachate (Run 2)	3	2

Table 5a
The percent inhibitory effects of leachate samples from the control reactor

Inhibition H (%)	Time (min)	Dilution factor (G_L)			
		1	5	10	20
H_5	5	90	71	60	41
H_{15}	15	93	74	65	45
H_{30}	30	95	75	69	49

Table 5b
The percent inhibitory effects of leachate samples from the Run 1 reactor

Inhibition H (%)	Time (min)	Dilution factor (G_L)			
		1	5	10	20
H_5	5	91	72	61	44
H_{15}	15	93	75	66	46
H_{30}	30	96	78	73	56

Table 5c
The percent inhibitory effects of leachate samples from the Run 2 reactor

Inhibition H (%)	Time (min)	Dilution factor (G_L)			
		1	5	10	20
H_5	5	92	77	66	47
H_{15}	15	96	78	68	53
H_{30}	30	99	82	76	62

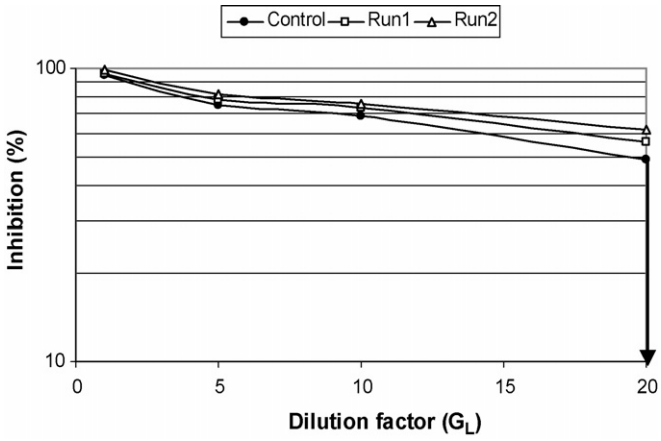

Fig. 6. Dilution factor (GL).

2 reactors were found to be toxic according to Environmental Protection Service (EPS) for the toxicity test using luminescent bacteria ($20 < H < 90$) [16]. If the percent inhibitory value ($H\%$) varied between 20 and 90%, the effect was toxic [17]. 1/1, 1/5, 1/10 and 1/20 dilution rates were applied on leachate samples to determine the dilution factor (G_L) indicating the IC_{50} values (dilutions inhibited 50% light intensity of *Vibrio fisheri* of leachate samples). Fig. 6 shows the G_L values indicating the IC_{50} values of leachate samples. As can be seen in this figure, the IC_{50} value of the control reactor was 20 while the IC_{50} value of the Run 1 and Run 2 reactors were approximately 35 and 45. It can be concluded that the leachate samples inhibited 50% of the light intensity of the luminescence bacteria *Vibrio fisheri* even when diluted 35 and 45 times in Run 1 and Run 2 reactors, respectively. Tables 5a–5c showed that the addition of mixed industrial sludge generated toxicity on methanogenic bacteria present in the simulated anaerobic landfill bioreactors.

3.2. Methane gas productions and methane percentages in simulated anaerobic landfilling bioreactors

The quantity of methane in control, Run 1 and Run 2 reactors are shown in Fig. 7. As can be seen in this figure, the maximum cumulative methane gas production was recorded as 3000, 4000 and 5000 l in control, Run 1 and Run 2 reactors, respectively, at the end of 100 and 70 days, respectively. After these days no methane production was determined, indicating the stabilization of organic substances. Therefore, the cumulative methane gas productions remained constant for the last 50 days of operation. The reason for the high cumulative methane gas productions in Run 1 and Run 2 reactors is the rapid degradation of organic wastes in these reactors. The nutrients and heavy metals in the mixed industrial sludge increased the activity of methanogens since the growth of methane bacteria was stimulated by heavy metals at trace concentrations [22]. Similarly, Sosnowski et al. [1] found that high cumulative methane gas productions were observed in reactors containing industrial sludge, compared to reactors containing sewage sludge. However, Cecchi et al. [29] reported that cumulative biogas production of mixtures increased with increasing proportions of MSW.

Methane percentages in control, Run 1 and Run 2 reactors are shown in Fig. 8. Methane percentage in control, Run 1 and Run 2 reactors still increased through 100 and 70 days of operation period. The maximum methane percentages were 59, 70 and 72%, respectively, in control, Run 1 and Run 2 reactors. The methane percentages were measured as 0 on days 100 and 70 for control, Run 1 and Run 2 reactors, respectively. These results showed that degradation of organic substances based on COD and VFA stopped in all the reactors during the last 50 days of operation periods. Methanogenesis process and methane gas percentages were faster in reactors added mixed sludge than that of the control reactor. Methane yields were 5, 6.89 and 8.5 g CH_4-$COD_{removed}$/kg VS_{added} in control, Run 1 and Run 2 reactors, respectively. This indicates that industrial sludge addition provided a balanced environment for growth of methanogens resulting in high methane gas production and high COD removals in Run 1 and Run 2 reactors.

3.3. Bioefficiency of anaerobic process

It was found that the maximum mass of removed COD was equal to 6.8, 8.34 and 15.3 g in control, Run 1 and Run 2 reac-

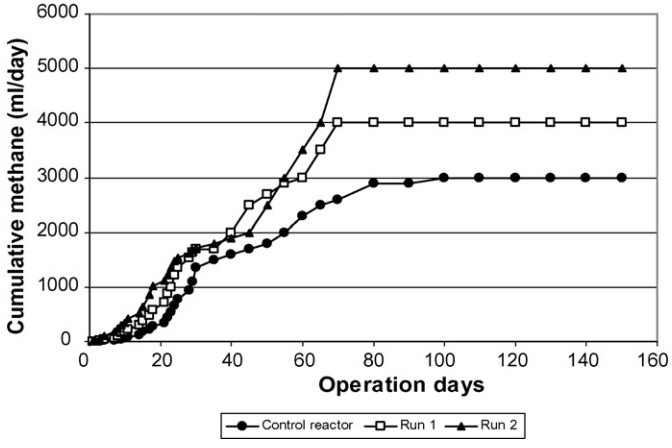

Fig. 7. Variation of cumulative methane gas production in simulated anaerobic landfilling bioreactor.

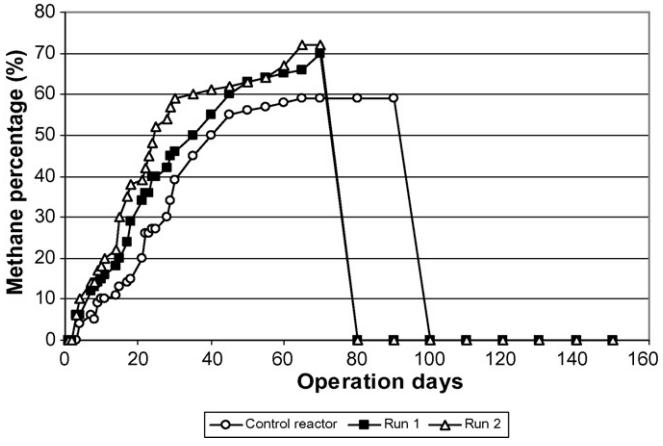

Fig. 8. Variation of methane percentage in simulated anaerobic landfilling bioreactor.

tors on day 70. Using these values, and taking into consideration the methane gas produced, it can be concluded that 80% of COD was removed in the control reactor and was converted to methane. Eighty-seven and 89% of $COD_{removed}$ were converted to methane in Run 1 and Run 2 reactors, respectively, on day 100.

As shown, the calculated methane yield was higher in Run 2 since the presence of heavy metals and AOX stimulated the growth of methanogenic bacteria and the methanogenesis. Furthermore, the nutrients in industrial sludge increased the rate of methane production and methane percentages. The control reactor exhibited lower anaerobic efficiency since it did not contain the heavy metals necessary for the growth of methanogens.

3.4. Comparison of the characteristics of the mixture of MSW and mixed industrial sludge in simulated anaerobic landfilling reactors

As can be seen in Table 6 the organic matter in control reactor decreased from 95 to 15%. The percentage of organic matter reductions in control, Run 1 and Run 2 reactors were 84, 88, and 91%, respectively, through 150 days of incubation period. It was observed that the reactors containing mixed industrial sludge exhibited better organic matter reductions. Similarly, in the study realized by Schmidell et al. [26]; the organic matter reduction decreased when the industrial sludge quantity was increased. The settlements efficiencies were 73, 83 and 90% in control Run 1 and Run 2 reactors, respectively. It can be concluded that the organic wastes settled better in reactors industrial sludge compared to control reactor Similarly, the study performed by Warith [5] showed that the lowest settlement was achieved in industrial sludge added reactors. The reductions in waste quantity were 87, 93 and 95% in control, Run 1 and Run 2 reactors, respectively, on day 150. It is important to note that, settlement is a very important parameter affecting the landfilling economy. The other parameters measured in waste samples in three anaerobic landfilling reactors are shown in Table 6.

In order to compare the efficiencies of wastes and leachate samples a mass balance was performed in all simulated anaerobic reactors. Since the leachate was recycled in simulated landfilling reactor the mass of investigated parameters was added to the data obtained in dry wastes. All the parameters in biosolid reactors were calculated per gram in dry wastes by taking into consideration the water content of the waste quantity. For calculation of the leachate characteristics the leachate volume was taken as 0.350 l and all the data was given as mg with the exception of C (see Table 7) The total TN masses were 2472, 2085 and 1483 mg in control Run 1 and Run 2 reactors, respectively, at the beginning of the anaerobic incubation. The total TN masses decreased significantly to 735, 406 and 294 mg in control, Run 1 and Run 2 reactors, respectively, on day 150. The NH_4–N ratios in total TN were 7, 5.75 and 4.51%, respectively, in control, Run 1 and Run 2 reactors, respectively, at the beginning of the study. This shows that the remaining nitrogen constituent were the organic nitrogenous compounds. It was shown that the total NH_4–N levels increased from 174, 120 and 67 mg to 637, 352, and 282 mg in control, Run 1 and Run 2 reactors, respectively, on day 150. The main reason for increases of the total NH_4–N originated from the leachate since the ammonia produced from the degradation of nitrogenous organic substances in wastes pass to the leachate. C mass decreased from 81, 69 and 45 g to 8.2, 4.1 and 2.8 g in control, Run 1 and Run 2 reactors. 89, 94 and 94% C removals were obtained in the aforementioned reactors. High C removals in reactors containing industrial sludge could be attributed to the high methane production through high methanogenic activity in Run 1 and Run 2 reactors (see Fig. 7). The phosphorous in reactors originated from the MSW and industrial sludge. A significant amount of TP originated from the leachate. TP levels decreased from 679, 434 and 305 mg to 158, 76 and 38 mg in control, Run 1 and Run 2 reactors. No heavy metals were detected in control reactors. The heavy metals

Table 6
Characteristics of the mixture of MSW and mixed industrial sludge in simulated anaerobic landfilling reactors

	$t = 0$ day			$t = 150$ days		
	Control	Run 1	Run 2	Control	Run 1	Run 2
Water content (%)	90	82	68	30	20	10
Organic matter (%) (in DS)	95	87	79	15	10	7
% C (in DS)	52.8	48.3	43.9	8	5	4
TN (mg/kg) (in waste)	10395	6000	4195	1000	800	350
TP (mg/kg) (in waste)	2165	695	435	500	110	65
NH_4–N (mg/kg) (in waste)	450	400	205	70	40	20
Waste height (cm)	30	30	30	8	5	3
Waste quantity (g)	1200	1200	1200	150	80	50
Cr (mg/kg)	0	0.02	0.04	0	0.01	0.02
Zn (mg/kg)	0	0.24	0.36	0	0.18	0.26
Cu (mg/kg)	0	0.09	0.10	0	0	0.02
Pb (mg/kg)	0	0.01	0.039	0	0	0.01
Fe (mg/kg)	0	7.41	9.13	0	4.95	7.18
Mn (mg/kg)	0	0.1	0.2	0	0	0.01
Ni (mg/kg)	0	0	0.01	0	0	0
Cd (mg/kg)	0	−0	0.01	0	0	0

Table 7
Characterisation of analyzed parameters in waste and leachate samples

Operation days	Parameters	TN (mg)	TP (mg)	NH_4–N (mg)	C (g)	Cr (mg)	Zn (mg)	Cu (mg)	Pb (mg)	Fe (mg)	Mn (mg)	Ni (mg)	Cd (mg)
$t = 0$ day	Control reactor (in waste)	1247	259	54	65	0	0	0	0	0	0	0	0
	Leachate	1225	420	120	16	0	0	0	0	0	0	0	0
	Total	2472	679	174	81	0	0	0	0	0	0	0	0
	Run 1 reactor (in waste)	720	84	48	58	4.3×10^{-3}	5.1×10^{-2}	1.9×10^{-2}	3.4×10^{-2}	1.6	2.1×10^{-2}	0	0
	Leachate	1365	350	72	11	7×10^{-3}	0.1	4.2×10^{-2}	1.4×10^{-2}	3.3	0.1	0	0
	Total	2085	434	120	69	11×10^{-3}	0.15	6.1×10^{-2}	4.8	4.9	3.32		
	Run 2 reactor (in waste)	503	43	24.6	38	1.5×10^{-2}	0.4	1.34×10^{-2}	4.5×10^{-2}	3.5	7.6 × 10-2	3.8 × 10-3	3.8 × 10-3
	Leachate	980	262	42.35	7	1.7×10^{-2}		4.9×10^{-2}	1.75×10^{-2}	3.7	0.14	0.07	1.4×10^{-2}
	Total	1483	305	67	45	3.2	0.41	6.4×10^{-2}	6.25×10^{-2}	7.2	0.21	0.07	0.01
$t = 150$ days	Control reactor	105	53	7.35	8	0	0	0	0	0	0	0	0
	Leachate	630	105	630	0.2	0	0	0	0	0	0	0	0
	Total	735	158	637	8.2	0	0	0	0	0	0	0	0
	Run 1 reactor (in waste)	56	6	2.24	3	1×10^{-3}	1.1×10^{-2}	2.5×10^{-3}	0	0.3	0	0	0
	Leachate	350	70	350	1.1	3.5×10^{-3}	9.8×10^{-2}	2.8×10^{-2}	0	1.9	0	0	0
	Total	406	76	352	4.1	4.5 × 10-3	10.9×10^{-2}	0.03	0	2.2	0	0	0
	Run 2 reactor (in waste)	14	3	1.9	1.9	9×10^{-4}	0.01	9×10^{-4}	4.5×10^{-4}	0.3	4.4×10^{-4}	0	0
	Leachate	280	35	280	0.9	1×10^{-2}	9.8×10^{-2}	1.75×10^{-4}	1.4×10^{-3}	2.8	0	0	0
	Total	294	38	282	2.8	0.01	0.10	10.7×10^{-4}	1.85×10^{-3}	3.1	4.4×10^{-4}	0	0

The parameters were calculated from the concentrations given in Table 6 by taking into consideration the quantities in dry waste for control, Run 1 and Run 2 reactors. The parameters in leachate samples were calculated by taking into considerations the leachate and the rainwater volumes.

Table 8
Characterization of heavy metals in leachate samples for all reactors

	$t = 0$ day			$t = 150$ days		
	Control	Run 1	Run 2	Control	Run 1	Run 2
Cr (mg/l)	0	0.02	0.04	0	0.01	0.02
Zn (mg/l)	0	0.30	0.40	0	0.28	0.28
Cu (mg/l)	0	0.12	0.14	0	0.08	0.05
Pb (mg/l)	0	0.04	0.05	0	0	0.03
Fe (mg/kg)	0	9.61	10.61	0	5.60	8.2
Mn (mg/l)	0	0.3	0.4	0	0	0
Ni (mg/l)	0	0	0.07	0	0	0
Cd (mg/l)	0	0	0.04	0	0	0

	Control run			Run 1			Run 2		
	Day 21	Day 40	Day 150	Day 21	Day 40	Day 150	Day 21	Day 40	Day 150
COD (mg/l)	43618	28000	7000	30005	18000	4000	23995	10000	3000
BOD_5 (mg/l)	40500	12000	700	25000	10000	600	18000	5000	200
BOD_5/COD ratio	0.92	0.42	0.1	0.83	0.55	0.15	0.75	0.5	0.06
TOC (mg/l)	20400	7000	500	14000	5200	400	10500	3200	170

in reactors originated from the industrial sludge. Some leachate samples contains significant amounts of heavy metals originating from the leaching of heavy metals to leachate from wastes. The heavy metal concentrations measured in leachate samples are shown in Table 8. On the other hand, the methanogenic microorganisms use heavy metals for growth. Therefore, the heavy metal removals were high in leachate and waste samples (see Table 8). The total Cr removal efficiencies were 59 and 99% in Run 1 and Run 2 reactors, respectively, on day 150. The total Fe amounts decreased from 4.9 and 7.2 mg to 2.2 and 3.1 mg in Run 1 and Run 2 reactors, resulting in 55 and 57% removal efficiencies, respectively. Ni and Cd were completely removed in Run 1 and Run 2 reactors, respectively, on day 150. The Pb levels decreased from 4.8×10^{-2} and 6.25×10^{-2} mg to 0 and 1.85×10^{-3} mg in Run 1 and Run 2 reactors resulting in removal efficiencies of 100 and 97%, respectively.

4. Conclusion

In this study, co-digestion of a mixed industrial sludge with MSW was investigated in three simulated anaerobic landfilling reactors. The leachate, MSW and the landfilling reactor characteristics were monitored through 150 days. Reductions in waste quantity, carbon percentage and settlement of the waste were better in control reactor compared to Run 1 and Run 2 reactors. However TN, TP and NH_4–N removals in waste were higher in industrial sludge added reactors compared to control while significant toxicity was observed in industrial mixed sludge added reactors.

Co-digestion of industrial sludge with MSW has a stimulatory effect on methane gas productions and methane percentages in simulated landfilling reactor. The co-digestion of MSW with an industrial sludge ratio of 1:2 gave the highest methane yield of 8.5 g CH_4-$COD_{removed}$/kg VS_{added}. This indicated that co-digestion processed at a higher efficiency than that of MSW alone. Low heavy metal concentrations do not inhibit the conversion of readily biodegradable organic compounds in simulated anaerobic simulated bioreactors.

The TN, TP removals in reactors containing industrial mixed sludge were comparably higher than those obtained in reactors containing only MSW. BOD_5/COD ratios decreased significantly in leachate samples for Run 1 and Run 2 reactors at the end of operation periods. High heavy metals removal efficiencies were obtained in reactors containing industrial sludge. Significant toxicity was observed in reactor containing a MSW to industrial sludge ratio of 1:2.

Co-digestion is a waste treatment method in which different wastes or wastewaters are mixed and treated together. The term "co-fermentation" is synonymously used for "co-digestion". When various wastes are mixed and co-digested, both synergistic and antagonistic outcomes are possible. For example, wastes having heavy metals can be mixed with wastes containing high concentration of organic matter constituents to increase the overall biogas production, reactor efficiency and leachate quality.

This study showed that anaerobic co-digestion of industrial sludge with MSW is a feasible process in the stabilization of the waste and in the treatment of leachate releases from the simulated anaerobic reactors. The supplementation of industrial sludge to MSW in simulated anaerobic bioreactors is a viable alternative for recovering high energy in the form of biogas with 72% methane content while at the same time improving the leachate quality.

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