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Research Article

Co-digestion potential of different industrial sludge sources and impact on energy recovery

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ABSTRACT

Co-digestion potential of the wastewater treatment sludges produced at two industries with different characteristics was investigated in anaerobic batch reactors operated at mesophilic (35±2 °C) condition. The sludge sources selected were from a food industry producing edible oil and from a textile industry producing woven fabric. Reactor performance was evaluated by the conventional parameters as well as by monitoring the biogas production during co-digestion of both industrial sludges at equal mixing proportions. Results indicated that both of these sludge sources had substantial biogas production potential with a cumulative biogas yield more than 425 mL/g-VSS_{fed} whereas it was about 5-fold lower only for the food sludge. On the other hand, chemical oxygen demand (COD) removal reached to about 90% during co-digestion with a well recovery of pH value and alkalinity concentration for sufficient buffering at the end of incubation. Therefore, by the combination of different industrial sludges through co-digestion; higher digestion performance and improved methane yield could be achieved due to better balanced substrate and nutrients. Regarding the initial heavy metals in the supernatant phase of the mixed sludge; iron (Fe), zinc (Zn), nickel (Ni), aluminum (Al), and manganese (Mn) could be removed from 56% to 80% while no apparent removals were observed in cadmium (Cd) and lead (Pb) at the end of operation. Hence, these potential toxic pollutants in the digestate should be taken into consideration while deciding the most appropriate resource recovery and ultimate disposal methods.

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INTRODUCTION

It has been still a major challenge to treat the wastewaters produced at several industries owing to their different characteristics that depend on the raw materials used during the production stage. Hence, most industries are required to construct their own treatment plants due to the complexity of these wastewaters which can be problematic to be treated in municipal wastewater treatment plants (WWTPs). Wastewaters from food industries producing edible oil are generally rich in chemical oxygen demand (COD), total dissolved and suspended solids, oil and grease, fats, and phosphate that cause high organic and inorganic loading rates in bioreactors. Besides, if discharged to receiving water bodies without subjected to any treatment, wastewater from edible oil production would lead to rapid de-oxygenation and irreversible damage to aquatic life [1, 2]. On the other hand, wastewaters of textile industries mostly contain various parameters characterized by high strength pollutants such as COD, suspended solids, color, toxicity, and

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turbidity due to the usage of a wide range of chemicals and dyes during textile processing which severely threaten the soil and receiving waters [3, 4]. Therefore, the reduction at the source and application of the most efficient methods of treatment should be the major focus of industrial sectors. Additionally, sludge produced in the industrial WWTPs remains a challenge for many industries due to inefficient and limited waste management strategies especially in developing countries Additionally, sludge produced in the industrial WWTPs remains a challenge for many industries due to inefficient and limited waste management strategies especially in developing countries. For example, huge amounts of wastewater, organic solid waste and inorganic residues are generated in the processing and refining oilseed for the production of edible oil. Instead of producing economically valuable products or generating energy from these wastes, residues, and by-products; most edible oil industries prefer landfilling for the ultimate disposal of the produced sludge. However, conversion of waste to energy as a form of resource recovery should be the preferable route for managing the organic wastes from all industrial facilities [5, 6].

In this context, since industrial waste sludges are generally well-known with their high COD and total solids (TS) contents, they become very suitable for anaerobic digestion (AD) processes that have been widely applied for volume reduction and biogas generation with low operating cost [7]. However, fluctuations in organic loading rate (OLR), heterogeneity of wastes, or the presence of the inhibitors can result in unstable processes. Besides, initial substrate characteristics such as C/N ratio, pH value, etc. could make some feedstocks not suitable for AD technology which has been used extensively for converting organic compounds to biomethane -especially co-digestion of appropriate biological industrial sludges with other waste sources- for achieving a sustainable industrial sludge management [8]. Hence, the combination of different wastes through co-digestion has been recommended in recent years. Compared to mono-digestion (i.e., with only one substrate), co-digestion provides the simultaneous digestion of two or more feedstocks and it has been indicated to be beneficial for its economic viability, improved biogas yields, and its ability to prevent some of the operating problems due to imbalanced nutrients, existence of heavy metals, toxic materials, or recalcitrant compounds [9]. According to Alrawashdeh [10], co-digestion of the olive mill wastes with sewage sludge was recommended to improve biogas generation due to a better nutrient balance. On the other hand, heavy metals can be found in olive mill waste in high concentrations and it was reported that substrate biodegradability was enhanced by co-digestion [11]. Kumar et al. [12] also recommended co-digestion of textile sludge (aerobic waste sludge) with manure at equal ratios with a biogas production of ca. 525 mL/g-TS_{added} while no obvious biogas production occurred when only textile sludge was digested.

Stabilized sludge by anaerobic digestion contains organic matter and other substances needed by plants for growth, e.g., nitrogen, phosphorus, potassium, calcium and magnesium, and thus it can be used in agriculture as fertilizer or soil conditioner. However, the content of heavy metals detectable in soils may cause toxicity which makes them as the most important limitation in the use of sludge for agricultural purpose. Because, the application of stabilized sludge onto soils could affect the potential availability of heavy metals which are found in several forms in the soil such as solid phases, free ions in soil solution, soluble organic-mineral complexes, or adsorbed on colloidal particles. Hence, soils can store and accumulate heavy metals to some extent owing to their adsorption capacity. The most unwanted heavy metals in stabilized sludge that are highly toxic for the living organisms are cadmium, chromium, nickel, lead, and mercury [13–17]. Since acidification of soils leads to an increase in solubility and absorption rate of heavy metals; pH plays the main role for the fate of the metal compounds in the environment. According to the study by Babel and del Mundo Dacera [13]; the heavy metals could be dissolved and could exist in solution when acid was added to the sludge through the process of exchanging the protons (from the acid) by solubilization of heavy metals in sludge. On the other hand, it was also reported that solids content also had an impact on the solubilization rate of the heavy metals. The metal removal efficiency during bacterial leaching of heavy metals from anaerobically digested sludge decreased with an increase in solids concentration of sludge. Hence generally, lower pH and lower solid content favored metal solubilization for anaerobically digested sludge [13, 14]. Accordingly, if the soil has strong acidification potential; the release of heavy metals bonded with oxides of manganese, aluminum and iron as well as other minerals increases. Among the metals, cadmium had the highest mobility (i.e., at a pH value of 6.5) with chromium and phosphorus whereas zinc was up to 60% bonded by the oxides of manganese and iron [14]. The inhibiting level and toxic effect of Fe, Ni, Pb, Zn, Cu, and Cr on the digestion process were investigated in previous studies and it was reported that adding some of the heavy metals not only decreased the efficiency of biogas production but also affected the COD and solid reduction [11, 18]. Moreover, heavy metals toxicity was observed in the following order: Cu > Ni > Pb > Cr > Zn > Fe in a previous study by Alrawashdeh et al. [11]. Regarding the ultimate disposal of the industrial stabilized sludge as the by-product of the sludge digestion process, heavy metal content can make composting, land application, sanitary landfilling, and incineration options not suitable [19]. In case of land application as the ultimate disposal method, the major inorganic constituents in sludge (Fe, Al, Ca, or P), as well as the characteristics of the soil (i.e., the sludge is laid on) have strong impact on the mobility of heavy metals as organic matter decays. Besides, each heavy metal has different characteristics (with exchangeable, adsorbed and organically-bound fractions) independent of sludge type and they are likely to be mobile to some degree once applied onto land and mobilization of metals may result from dissolution of the carbonate fractions of Cd, Pb, and Ni or oxidation of the sulfide fraction of Cu [13].

Hence, the aims of this study were to investigate mesophilic anaerobic co-digestion potential of two sludge sources from food and textile industries while presenting the impact on reactor performance and biogas recovery as well as to assess the change in the concentrations of heavy metals during the digestion period.

MATERIALS AND METHODS

Sludge Samples and Inoculum Used

The food and textile sludge samples with respective TS contents of 8.5% (volatile content of ~89%) and 0.5% (volatile content of ~45%) were supplied by a food industry producing edible oil and by a textile industry producing woven fabric, finishing cotton and mixed fiber woven cloth both located in Lüleburgaz/Kırklareli/Türkiye. The food sludge (FdS) was provided from the decanter unit –where the mixed biological and chemical sludges are thickened- of the existing WWTP of the investigated industry. The textile sludge (TxtS) used as the substrate was the biological sludge from the extended air activated sludge system provided before the thickener unit of the existing WWTP treating the wastewater produced from several units (e.g., desizing, bleaching, mercerization, drying, dyeing, washing, etc.) of the investigated industry. Raw sludge samples from the food and textile industry indicated the following characteristics, respectively: pH 4.20 and 7.11, alkalinity 2725 and 1075 mg $CaCO_3$/L, 85565 and 2730 mg tCOD/L, 84078 and 4415 mg TS/L, 786 and 11 mg TP/L, 0.054 and 3.31 mg NH_4^+-N/L. Heavy metals in raw sludge samples from the food and textile industry indicated the following concentrations, respectively: 1370 and 21 mg Al/L; 1.66 and 6.1 mg Cu/L; <0.001 and <0.001 mg Cd/L; 0.12 and 0.1 mg Cr/L; 91.5 and 14.6 mg Fe/L; 1.3 and 0.3 mg Mn/L; 0.164 and 0.121 mg Ni/L; <0.010 and 0.095 mg Pb/L; 11 and 0.59 mg Zn/L. Moreover, the FdS was rich in oil and grease with about 13900 mg/L. The inoculum was obtained from a mesophilic anaerobic digester treating the sewage sludge produced at a municipal WWTP (İstanbul, Türkiye) with TS content of about 6.6%.

Batch Reactors and Operating Conditions

The assays were carried out in two sets (i.e., Set I and Set II) at mesophilic condition (35±2 °C) in 1 L glass bottles which were used as reactors with a working volume of 700 mL. Each flask was run with the same inoculum in a 1:6 ratio ($v_{inoculum}/v_{substrate}$). Moreover, co-digestion of food and textile sludges was applied at equal mixing proportions of 1:1 (v/v). During set-up of the batch study, the reactors were configured only for co-digestion at Set I as FdS+TxtS (1:1) (300 + 300 = 600 mL) + inoculum (100 mL) whereas for mono- and co-digestion at Set II as follows: (i) FdS (600 mL) + inoculum (100 mL); (ii) TxtS (600 mL) + inoculum (100 mL); (iii) FdS+TxtS (1:1) (300 + 300 = 600 mL) + inoculum (100 mL). The flasks were also designed to be opened at different operating periods (i.e., for Set I at the 5th, 26th, 41st, and last day whereas for Set II at the 7th, 16th, 30th, 47th, and last day) to conduct experimental analyses during hydrolysis, acidogenesis and methanogenesis phases. Initial samples were immediately taken for t=0 d analyses. Since the FdS used in this study was acidic with a pH of 4.2, the pH of the flasks including FdS was adjusted to 7.0 with 1.0 N NaOH during set-up. In order to measure the methane production of only the inoculum, the inoculum was also incubated without the addition of substrates. After the addition of the sludge samples; each bottle was closed tightly and sealed with a cap and a rubber septum. Then, the headspace of each reactor was flushed with the gas mixture of 80% N_2 and 20% CO_2 for 2 minutes to establish anaerobic conditions inside the reactors. The reactors were then kept in an incubator at 35±2 °C and operated as batch systems while they were shaken manually once a day during the incubation period. The experimental set-up was done minimum in triplicates and average biogas values were calculated.

Analytical Procedure

The solids, COD, and alkalinity were determined according to Standard Methods [20]. Total COD (tCOD) and soluble COD (sCOD) experiments were conducted according to dichromate open-reflux method. For sCOD experiments, the samples were filtered through 0.45 µm syringe PVDF filters. After addition of dichromate and acid solutions; samples were kept at 150 °C for 2 hours and COD concentrations were measured by behr TRS 300 control device. The pH measurement was done using a pH meter (Hach Lange HQ/40 D model) and alkalinity measurement was done by titrating with 0.02 N H_2SO_4 acid solution till the pH dropped down to 4.5. Total phosphorus (TP) concentration of the samples was measured by the Thermo ICP-OES Spectrophotometer (iCAP 6300 Duo) according to the same procedure as explained below for the determination of heavy metals.

For the measurement of heavy metals (iron, Fe; zinc, Zn; nickel, Ni; aluminum, Al; manganese, Mn; cadmium, Cd; lead, Pb; copper, Cu; and chromium, Cr), the samples were prepared according to the EPA 200.7 method in the liquid (i.e., supernatant of the digestate) and in the solid (i.e., digested sludge) phases which were taken from the batch sets during the study [21]. For heavy metal analysis in the digested sludge, samples were oven-dried at 50 °C and then crushed into pieces. A homogeneous sample with an amount of 0.4 g (±0.1) was put into a microwave vessel for acid extraction (i.e., respectively with 9 and 3 mL of nitric and hydrochloric acid). Then, the samples were burned at 160 °C, allowed to cool down to room temperature, quantitatively transferred to a volumetric flask, diluted to 50 mL with distilled water, and mixed thoroughly. The concentrations of all investigated heavy metals were measured by the Thermo ICP-OES Spectrophotometer.

The biogas generation was measured using a manometer (Lutron PM 9107 model) before being released from each flask by an injection needle. The measured biogas values were then converted from pressure unit (mbar) to volume unit (mL) under the standard conditions (0 °C and 1 atm). During the study, biogas production at the headspace of

Table 1. Initial substrate characteristics in the batch sets

Parameter	Unit	Set I	Set II		
		Co-digestion	Mono-digestion		Co-digestion
		[FdS+TxtS (1:1)]	[FdS]	[TxtS]	[FdS+TxtS (1:1)]
tCOD	mg/L	12,331±5[a]	16,300±77	261±33	8682±77
sCOD	mg/L	2417±10	10,035±42	110±2	4805±69
pH[b]	–	7.0	7.0	7.65	7.0
Alkalinity	mg/L	1705	2725	1075	1625
TSS	mg/L	21,742±330	56,398±429	5779±159	26,818±152
VSS	mg/L	16,924±384	47,425±250	3322±14	22,099±142

a: Average±Standard deviation; b: Initial pH was adjusted to 7.0 with 1.0 N NaOH in the reactors with FdS.

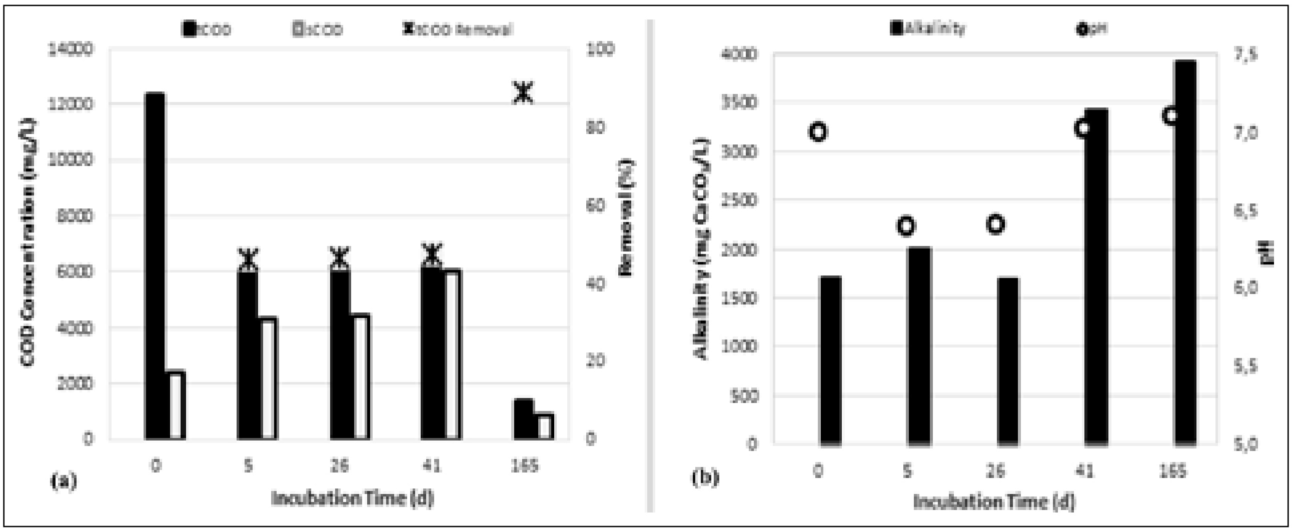

Figure 1. Profile of **(a)** COD; **(b)** pH and alkalinity during anaerobic co-digestion during Set I [FdS+TxtS (1:1)].

each flask was monitored daily till the last incubation day (i.e., until daily biogas productions ceased in the bioreactors and cumulative biogas volume reached to a constant value).

RESULTS AND DISCUSSION

In this study, the potential of using anaerobic co-digestion of two different sludge sources (i.e., from textile and food industries) was tested at equal mixing proportions compared to mono-digestion of single industrial sludge and the initial substrate characteristics are presented in Table 1.

Results of Set I revealed that tCOD removal reached about 90% during co-digestion with a pH value higher than 7.0 at the end of the digestion period. The tCOD profile is shown in Figure 1a whereas pH and alkalinity profile is shown in Figure 1b during anaerobic co-digestion of the investigated industrial sludge sources at equal ratios in Set I. Although the pH value at 41-d reactor indicated about 7.0 in Set I, the pH value was still lower than 7.0 at 47-d reactor in Set II co-digesting both sludge samples. On the other hand, the pH values were 6.57 and 7.24 in the reactors digesting only FdS and TxtS, respectively. This showed the significance of co-digestion, especially of the FdS. However, although digestion performance could not be monitored between the 47th and last days of operation; respective pH values were of 7.28, 7.95, and 7.66 in the reactors with FdS, TxtS, and (FdS + TxtS) at the end of incubation. Also, TP concentration was substantially removed in the liquid part with more than 50% (i.e., from 366 mg/L to 180 mg/L) after digestion. On the other hand, regarding the initial heavy metals concentrations in the liquid phase (i.e., supernatant of the digestate) of the mixed sludge; iron (Fe), zinc (Zn), nickel (Ni), aluminum (Al), and manganese (Mn) could be removed from 56% to 80% while no apparent removals were observed in cadmium (Cd) and lead (Pb) at the end of operation for both sets. Although heavy metals except copper (Cu) and chromium (Cr) indicated compatible profile in both sets; no apparent reduction in Cu and Cr concentrations was observed in the Set I (Table 2) whereas final concentrations of these heavy metals were determined lower compared to the initial values in the Set II [22].

Accordingly, Fe, Zn, Ni, Al, and Mn were reduced from 32% to 77% and from 55% to 99% in the FdS and TxtS digestates with 53% and 28% TP removals, respectively. The biogenic sulfides produced result in insoluble complexes with heavy metals and then precipitated. Since the main removal mechanisms of heavy metals from digestate/liquid phase are precipitation and adsorption onto sludge; bicarbonate and phosphate in bioreactor, and biogenic sulfides that might be produced under sulfate reducing conditions might favor their removal [23]. On the other hand, the heavy metals present in the sludge can be dissolved and then exist in solution in the case of acid addition with the exchange of the protons (from the acid) by solubilization of heavy metals in sludge. Hence, one of the most important factors affecting the solubilization of metals in sludge is pH and metals solubilization increases with lower pH values. In a study by Aktaş [24], the metal removal mechanisms are listed as follows: (i) a metabolism-independent process (passive uptake) through ion-exchange phenomena, (ii) complexation with negatively charged groups, and (iii) adsorption and precipitation by extracellular polymeric substances (EPS).

In this study, respective heavy metal concentrations in raw food sludge and textile sludge were measured as 1370 and 21 mg Al/L; 1.66 and 6.1 mg Cu/L; <0.001 and <0.001 mg Cd/L; 0.12 and 0.1 mg Cr/L; 91.5 and 14.6 mg Fe/L; 1.3 and 0.3 mg Mn/L; 0.164 and 0.121 mg Ni/L; <0.010 and 0.095 mg Pb/L; 11 and 0.59 mg Zn/L. Xiao et al. [25] also reported that Cu, Ni, Zn and Cr were the detected heavy metals in the effluents of food industry. Textile industries, on the other hand, are known as the facilities discharging a large amount of heavy metal due to the fact that these metals might be naturally present in textiles. Moreover, heavy metals might penetrate into textile fibers as a result of production and dyeing processes; protective agents used during storage; the wide usage of chemicals, colorants, and other additives (e.g., caustic soda, sodium carbonate, etc.) during the manufacturing processes. For example, Cr, Ni, Zn, Pb, Cu, and Cd are used for the production of colour pigments in textile dyes. Besides, different heavy metals such as Co, Cu, and Cr are found within the dye chromophores used in textile industry [26]. According to Kaur et al. [27], the heavy metal contents of a textile industry effluent were measured in the order of Co > Cd > Pb > Zn > Cr > Cu with respective concentrations 1.69, 1.33, 0.14, 0.13, 0.06, and 0.03 mg/L. Hence, the content of heavy metals in sludge might be different according to the source of wastewater, the sludge treatment process, the geography, industrial characteristics, and the economic welfare of the city as described in Xiao et al. [25] who also reported higher levels of heavy metals in municipal sludge which were collected from regions with higher industrial facilities.

Although heavy metals can be stimulatory, they might be inhibitory, or even toxic for biochemical reactions. Accordingly, the industrial sludge that contains considerable amount of heavy metals should be avoided for any biogas production through AD. Especially, heavy metals have the potential to affect anaerobic microorganisms including methanogens depending on their concentrations which might cause reduction in the performance of biological metal removal and in biogas generation as well [23, 24, 28]. Regarding the inhibitory effect of the four heavy metals investigated by Altaş [24], the IC50 values (i.e., the concentrations that cause a 50% reduction in the cumulative methane production over a fixed period of exposure time), were found to be as Zn=7.5 mg/L, Cr=27 mg/L, Ni=35 mg/L, and Cd=36 mg/L when glucose was used as the carbon source. For the 50% inhibiting concentration of Cu^{2+} to acetoclastic and hydrogenotrophic methanogens was reported by Karri et al. [23] as about 21 and 9.0 mg/L, respectively whereas the activity of an acetate-degrading methanogenic enrichment culture was inhibited by 50% at about 67 mg Pb/L. According to Table 2 in this particular study; Zn, Cr, Ni, and Cd in the initial combined sludge sample were measured far below aforementioned IC50 values indicating the inhibitory effect on methane-producing anaerobic sludge. The effects of some metals on methane production from food waste were also investigated by Zhang et al. [29] who reported that biogas generation was substantially dependent on the supplementation of Fe, Co, Mo, Ni elements; however, excessive Fe and Ni addition (i.e., 1000 and 50 mg/L, respectively) indicated toxicity to methanogens. They also reported the optimal dosages for Fe as 100 mg/L and for Ni as 5 mg/L which indicated the highest methane yield (504 mL/g VS_{added}) with an increment of about 36% compared to the control reactor in the absence of these metals. Hence, according to Table 2; Fe was measured as about 70 mg/L in the initial combined sludge sample which was again below that toxic concentration reported by Zhang et al. [29]. Abdel-Shafy and Mansour [28] also reported that the presence of heavy metals during AD decreased the efficiency of the biological process, gas production and volatile organic matter removal and even methanogenic bacteria inhibition was observed. It was reported that this inhibition was due to accumulation of organic acid intermediates which was dependent on heavy metals. The toxicity of the investigated metals was obtained in the following order: Hg < Cd < Cr (III); hence, the presence of these toxic heavy metals in organic waste should be avoided or controlled during AD. Abdel-Shafy and Mansour [28] defined inhibitory level of a heavy metal as that caused a radical decrease in the gas production. On the other hand, they defined toxic limits as the concentration at which total gas production was reduced by 60% from control reactor. Results indicated inhibiting concentrations as 125, 170, and 775 mg/L whereas toxic

Table 2. Change in heavy metals concentrations in the liquid phase during anaerobic co-digestion in Set I [FdS+TxtS (1:1)]

Heavy metal	Initial (mg/L)	Final (mg/L)	Reduction (%)
Iron (Fe)	69.64	14.03	80
Nickel (Ni)	1.410	0.320	77
Manganese (Mn)	2.140	0.737	65
Zinc (Zn)	13.62	5.182	62
Aluminum (Al)	663.2	289.2	56
Copper (Cu)	2.124	2.018	5
Chromium (Cr)	0.748	0.747	–
Cadmium (Cd)	0.002	<0.002	–
Lead (Pb)	0.095	0.167	–

limit values as >250, >340, and >1550 mg/L for Hg, Cd, and Cr (III), respectively. In Kadam et al. [30], IC50 values for some heavy metals during methanogenesis were presented. Accordingly, they reported that for Cr, Zn, Ni, Cd, Cu, Pb, and Co; IC50 values were about 15, 16, 400, 8, 13, 67, and 0.8 mg/L, respectively. They also reported optimum values of Zn, Cd, Fe, Ni, and Cu for an effective AD as 5.0, 0.1, 0–1000, 0.8–4.0, and 5.0–30 mg/L, respectively.

In this context, many studies reported large differences in the inhibitory concentrations of metals which might be due to some factors such as the change in; the biofilm structure, the precipitation and adsorption of soluble metals, EPS concentration of sludge, and the dense distribution at the outer layer of the inoculum sludge especially in granular form. Even the variations in the sludge characteristics might have significant effect on the inhibitory concentrations of heavy metals on anaerobic microorganisms [24].

Since, heavy metals are commonly found in stabilized sludge, there has been an increased concern about its direct re-use in agriculture as fertilizer due to the limitation of the heavy metal concentration according to regulations in recent years. Hence, source control of industrial discharges is required by; (i) controlling the processes and materials used during the production stage at the facilities, (ii) removal and controlled disposal of hazardous constituents before reaching to the waste stream, (iii) separation of highly contaminated industrial effluents from the domestic wastewater, and (iv) pretreatment before municipal collection system [13]. It was reported that the share of industrial effluents has been still increasing in the overall mass of sewage sludge which also leads to high heavy metal content with the most toxic ones as cadmium, lead, arsenic and mercury. Heavy metals occur in different forms and can be absorbed by clay minerals, hydrated iron oxides and organic matter. Heavy metals also appear in the form of inorganic compounds (e.g., oxides, phosphates, carbonates, sulphates, sulphides). When the metals occur in a soluble and exchangeable form, they are released to the environment most easily (nickel, cadmium). However, when the metals are found in bonded form (i.e., with carbonates, phosphates, sulphides and oxides of manganese, iron, chromium and zinc) they are less easily released to the environment. On the other hand, heavy metals can prevent iron metabolism, whereas iron can prevent from absorption and transportation of other components, e.g. phosphorus [14]. According to chemical speciation of heavy metals in anaerobically digested sludges; Cd, Cr, Cu, Pb, Mn, Ni, and Zn seem to predominate in the following forms: Cd in carbonate and residual forms; Cr in organic and residual forms; Cu in residual and organic forms; Pb in carbonate and organic forms; Mn mostly in organically bound form; Ni in carbonate and residual forms; and Zn mostly in organically bound form. Among the heavy metals, Cu changed most easily into its chemical (i.e., sulfide precipitated) form which increased as AD continued further. Besides, when compared to the chemical forms of Zn and Ni before and after the AD process; the degree of Cu stabilization was higher [13].

Babel and del Mundo Dacera [13] already emphasized the importance of the removal of some heavy metals from especially agro-industrial sludge to levels below the regulatory standards of that country to make the sludge suitable for land application and to be used in agriculture. They reported that removals attained for the metals were 30% for Cu, 59% for Mn and 39% for Ni, for anaerobically digested sludge. In this particular study, compared to initial raw sludge samples; all the investigated heavy metals concentrations except cadmium indicated a positive change (i.e. the increases were between 11% in nickel and 52% in lead) in the final digested sludge samples taken from the co-digester (with food and textile sludge sources). For example in Set I, the results of the heavy metals in the solid phase of the combined sludge sample were as follows (rounded values in mg/kg): 17000 for Al; 85 for Cu; <1.25 for Cd; 37 for Cr; 3000 for Fe; 54 for Mn; 30 for Ni; 5.1 for Pb; and 290 for Zn. On the other hand in Set II; the results of Al and Fe in the solid phase of the FdS and TxtS samples were respectively as follows (rounded values in mg/kg): 23000 and 4160; and 3600 and 4530 whereas the results of other investigated heavy metals in the solid phase of the FdS, TxtS, and the combined sludge samples were respectively as follows (rounded values in mg/kg): 74, 280, 158 for Cu; <1.25, <1.25, <1.25 for Cd; 32, 113, 59 for Cr; 56, 127, 96 for Mn; 28, 135, 60 for Ni; 4.6, 13.5, 12.7 for Pb; and 305, 698, 502 for Zn [21]. Nevertheless, the measured heavy metals in the solid phase of the digested sludge did not exceed the permissible level specified in the related regulation of Türkiye [31]. Because, according to Annex I-B Limit Values (mg/kg DS); heavy metals concentrations must not exceed the following values (mg/kg): 1000, Cu; 10, Cd; 1000, Cr; 300, Ni; 750, Pb; and 2500, Zn [31]. However, the mercury and pathogen contents should be also below the limit values in order to assure their usage by laying on soil for agricultural purposes.

Kadam et al. [30] also studied permissible values of some heavy metals to be used as fertilizer in Eropean Union (EU). Accordingly, the permissible values for Zn, Cd, Ni, and Cu metals were reported as 200, 1.0, 50, and 100 mg/kg, respectively. Kaur et al. [27] also investigated the contents of some heavy metals in the soil of the agricultural field collected from the neighborhood of textile industries. They reported that Cd, Cr, Co, Cu, Pb, and Zn were detected as 1.33, 16.43, 214.60, 13.63, 57.33, and 92.52 mg/kg, respectively.

In another study by Xiao et al. [25], distribution characteristics of typical heavy metals in sludge from WWTPs in China was investigated. Moreover, the variation in sludge composition containing wastewaters from different facilities from metallurgical, chemical, food and metal industry was evaluated. Accordingly, heavy metal levels were in the order of Zn > Cu > Cr > Ni > Pb > As > Hg > Cd, ranging from 154 to 2970 mg/kg, 28 to 1150 mg/kg, 10 to 136 mg/kg, 9 to 262 mg/kg, 0 to 79 mg/kg, 12.1 to 41.6 mg/kg, 0.67 to 19.50 mg/kg and 0.21 to 2.77 mg/kg, respectively. Besides, according to the typical heavy metal distribution in sludge; Hg, Zn and Cu were apparently affected by the degree of industrial intensity, while the distribution in Ni, Cd, Pb, As and Cr were more even. Regarding the sludge with wastewater from the food industry; Cu, Ni, Zn and Cr content in sludge increased significantly whereas Ni and Zn content in sludge with wastewater from the printing and dyeing industry increased at a great extent. Hence, it was concluded that the heavy metal content in sludge may vary and can be affected by several factors mainly the source of wastewater [25].

In this study, biogas productions were also monitored during the incubation period of both sets except the lockdown periods due to pandemic situation. Daily and cumulative biogas production during co-digestion of FdS and TxtS in Set I, during mono-digestion of FdS in Set II, and during co-digestion of FdS and TxtS in Set II are illustrated in Figure 2a–c, respectively. According to the biogas results, both sludge sources used in this study had substantial biogas production potential when anaerobically digested together (i.e., at least 325 and 425 mL/g-VSS$_{fed}$ in Set I and Set II, respectively); however, each industrial sludge alone had much lower biogas production (i.e., at least 80 mL/g-VSS$_{fed}$ for FdS in Set II). In the reactor digesting only TxtS indicated about 50 mL cumulative biogas result in Set II. Hence, the results from this study showed that co-digestion not only reduced the environmental pollution and health risks from the selected industries but also recovered useful energy [22].

In conclusion, co-digestion proposed a sustainable management method for the sludge produced at the WWTPs of appropriate industries. Moreover, since majority of industrial sludges are generated in much smaller quantities; it is considered that co-digestion would also provide potential of using the available anaerobic digesters of the industries producing higher amounts of sludge in adjacent areas [8].

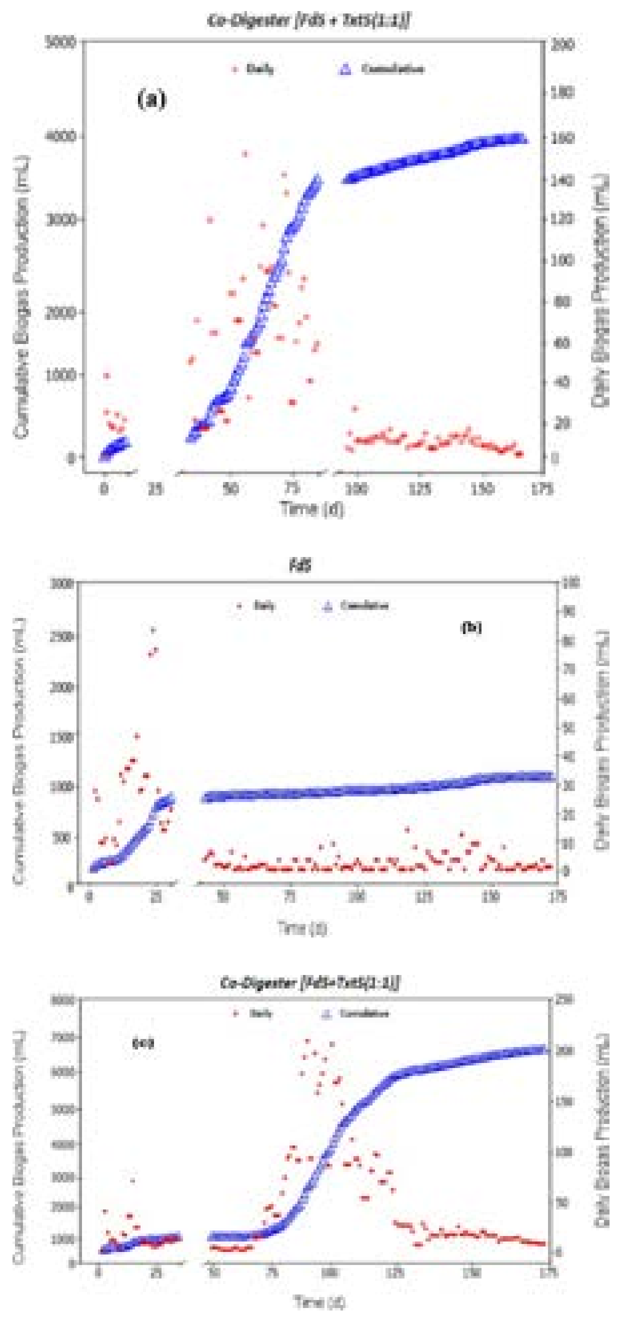

Figure 2. Daily and cumulative biogas production during anaerobic; **(a)** co-digestion in Set I [FdS+TxtS (1:1)], **(b)** mono-digestion in Set II [FdS], and **(c)** co-digestion in Set II [FdS+TxtS (1:1)].

CONCLUSIONS

Results revealed that both of the sludge sources from food and textile industries had substantial biogas production potential during anaerobic co-digestion at mesophilic condition. Accordingly, the cumulative biogas yield was observed more than 425 mL/g-VSS$_{fed}$ for the FdS and TxtS at equal mixing proportions whereas it was about 5-fold lower only for the FdS. Hence, co-digestion yielded a higher amount of biogas compared to mono-digestion where single industrial sludge was digested. Next to the improved biogas yields; results showed better process performance in terms of total COD removal which was about 50% and 90% at the 41st and last days of operation respectively with a well recovery of pH and sufficient buffering capacity in the batch assays. On the other hand, respective total COD removals were 84% and 36% when FdS and TxtS were digested alone. Besides, heavy metals (aluminum, iron, manganese, nickel, and zinc) was substantially reduced from 56% to 80% with more than 50% TP removal in the liquid supernatant of the digestate after co-digestion. These heavy metals were reduced from 32% to 77% and from 55% to 99% in the liquid phases of the FdS and TxtS digestates with 53% and 28% TP removals, respectively. On the other hand, the content of the investigated heavy metals in the solid phase of the digested sludge samples did not exceed the permissible level specified in the related regulations of Türkiye for their usage by laying on soil for agricultural purposes. However, this conclusion should be confirmed by the fact that the mercury and pathogen contents were also below the limit values. Therefore, the use of digested sludge for non-agricultural purposes and land reclamation would essentially be a better alternative.

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DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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