Comparative evaluation of biogas recovery during anaerobic treatment of aircraft deicing fluids at increased ratios in domestic wastewater

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Abstract

In this study, anaerobic treatability of domestic wastewater contaminated with two different types of aircraft deicing fluids (ADFs) at different ratios (i.e., Type 1: 0.9%–9.7% and Type 2: 1.8%–12.5%) were comparatively investigated with the control reactors using batch systems operated at mesophilic temperature (35°C). In this respect, the threshold Type 1 and Type 2_ADF ratios indicated inhibition on the microbial cultures were determined according to the biogas yields during the incubation time. The highest biogas yields were calculated as about 0.22 and 0.25 m³/kg tCOD fed in the bioreactors having 0.9% Type 1_ADF and 1.8% Type 2_ADF, respectively. However, when tCOD removals were also taken into account; 3.4% Type 1_ADF and 1.8% Type 2_ADF represented the upper concentration limits excluding the control reactors. Because the reactors with more than 3.5% Type 1_ADF and 2.0% Type 2_ADF indicated significant inhibition on microbial cultures with considerable reductions in biogas yields and organic material removals. Hence, ADF-contaminated wastewaters are of great concern for anaerobic reactors that require careful control at full-scale treatment facilities.

Keywords: Aircraft deicing fluids; Anaerobic reactor; Inhibition; Methane yield; Propylene glycol

1. Introduction

According to the air transportation statistics of Turkey, annual total aircraft traffic (domestic and international) was more than 1.5 × 10⁶ in the past 2 years [1]. Accordingly, the amount of pollutants at airports has increased drastically especially due to the spent aircraft deicing/anti-icing fluids used at high amounts at the airports for flight safety. Because any snow or ice on a critical surface of an aircraft must be removed before departure during flight operations at frosted conditions [2]. De-icing/anti-icing activities take place during the winter months and extend depending on weather conditions. Hence, seasonally generated wastewaters may have great variations in strength from the beginning to the end of the season. Aircraft deicing fluid (ADF) is composed of mainly ethylene glycol (EG) and propylene glycol (PG) with water, wetting agents, and dye. There are four ADF types commonly used with different glycol and additive contents such as corrosion inhibitors [3,4]. For example, Type 1_ADF contains about 90% glycol, 8% water, and <2% additives [5]. Besides, Type 1_ADF has short holdover times with lower viscosity that flows away faster from the aircraft providing relatively short protection against frost, ice, and snow. On the other hand, Type 2_ADF, which is a non-Newtonian (pseudoplastic) fluid, has longer holdover times. Type 2_ADF contains polymeric thickener which prevents quick flowing from the aircraft surface; hence it provides much longer protection [6]. Since these fluids are...
concentrated, they are diluted with hot water (55°C–80°C) before they are instantly sprayed under pressure. Following this application, the spent ADF is discharged through the grids/channels found in the special parking areas at the airports (de-icing pads). These wastewaters contaminated by ADFs are commonly stored in a storage tank which needs to be emptied after a certain time. There are specific regulations and standards regarding the construction, installation, and operation of the storage tank systems for deicing products. The collection system and storage facilities also require periodic cleaning and maintenance [6].

Despite many advantages of air transport (e.g., the safest, quickest, and most convenient means of traveling long distances), airports are large-scale polluters of the environment [7]. The primary environmental concern with deicing/anti-icing operations has been attributed to the glycols and to their high organic strength. It was reported that the COD concentration of the sample taken from a centralized deicing facility was up to $6.0 \times 10^4$ mg/L. Their abundant use and biodegradability lead to oxygen depletion from surface waters receiving uncontrolled runoff [8]. It was reported that the aqueous solubilities of the glycol- and acetate-based ADFs from the surfaces of the airports could result in high organic loadings due to runoff and pose serious toxicity in receiving waters [9]. Sulej et al. [7] also reported that run-off waters generated by airport operations lead to a serious hazard to the environment because they might contaminate the air, water, and soil. Zitomer et al. [10] also emphasized the importance of ADF management at airports since annual ADF usage could be more than 40 million liters at large airports in the United States. It was also reported that this ADF consumption would eventually lead to the production of aircraft deicing runoff with a 5-d biochemical oxygen demand concentration up to $10^4$ mg/L. Besides, attention has shifted to the potentially toxic effects from the aforementioned additives, specifically corrosion inhibitors [11]. Hence, runoff waters from the surrounding of the airports have been attracting greater interest due to potentially negative impacts of ADF-contaminated wastewaters produced at high amounts as a result of a fast increase in airport activity in the last decades.

Sulej et al. [7] reported that the waters due to rainfall and/or snowmelt running off the various surfaces at airports have very complex composition and these fluids might reach the nearest municipal wastewater treatment plant (WWTP) at certain ratios through the sewerage system. Because off-site treatment of airport deicing stormwater is usually done by discharging deicing runoff through the sanitary sewer system to a WWTP for treatment and disposal [10]. According to Switzenbaum et al. [12], central WWTPs are almost always the most economical method of treating deicing chemical runoff, if sufficient biological loading capacity is available. However, anaerobic on-site pretreatment might be feasible when the capacity is limited. On the other hand, direct anaerobic discharge is an off-site treatment alternative by trucking the concentrated deicing runoff to the plants where anaerobic digesters are available. Apparently, anaerobic treatment is one of the most appropriate options for treating the wastewaters contaminated by the ADFs due to the increased production of methane gas [10]. Previous studies also emphasized that domestic wastewater could be successfully treated by up-flow anaerobic sludge bed (UASB) reactor because of its simplicity, low investment and operation costs [13,14]. This technology has been also demonstrated for EG- and PG-based ADFs, so that diluted ADF wastewater up to 20,000 mg/L COD concentration could be successfully treated with 85%–98% removal efficiency at a volumetric organic loading rate (OLR) as high as 10 g COD/L/d [15]. During anaerobic treatment, it is also possible to recover a renewable energy source with a biogas production yield of 0.24 m³/kg COD having 77% methane content [16]. Schoenberg et al. [17] also studied anaerobic treatment of the propylene glycol-based Type 1_ADF and near-complete anaerobic degradability was reported with a first-order degradation rate constant of 3.5 L/d under mesophilic conditions. However, high ADF feed concentrations substantially affected degradability. Besides, Sulej et al. [7] reported that the toxicity of runoff water samples including ADFs might be very high and might reach LC50 (i.e., the lethal concentration 50 presenting the dose causing the death of 50% of individuals in a population after a given time) values of 85%. Therefore, the ratio of ADF in the influent wastewater should be determined before they are treated by anaerobic technologies to foresee to what extent these fluids could be treated without causing any inhibition on the microbial cultures.

Hence, the aim of this study was to investigate anaerobic treatability of domestic wastewater contaminated with two different types of ADFs at different ratios (i.e., Type 1: 0.9%–9.7% and Type 2: 1.8%–12.5%) in order to find out the threshold concentrations at which inhibition occurred. In this scope, the inhibition effect of both ADF types on anaerobic microorganisms was assessed using the biogas yields by monitoring ultimate CH₄ productions in the batch reactors operated at mesophilic temperature (35°C).

2. Materials and methods

2.1. Substrate and inoculum sources

Concentrated Type 1_ and Type 2_ADF samples were provided from one of the airports in Istanbul which were propylene glycol (C₃H₆O₃)-based fluids containing water, corrosion inhibitors, wetting agents, and dye. Total COD (tCOD) concentrations of raw Type 1_ and Type 2_ADF samples were 540,000 and 631,000 mg/L, respectively. Other characteristics of raw Type 2_ADF were also as follows: 88%, propylene glycol; 20 cp, viscosity; and 8.7–9.7, pH. Raw domestic wastewater was obtained fresh from the package wastewater treatment units of an airport which was under construction in Istanbul during the study. The characterization of the raw domestic wastewater was as follows: 7.33 ± 0.19, pH; 359 ± 15 mg CaCO₃/L, alkalinity; 491 ± 129 mg/L, tCOD, 305 ± 38 mg/L, soluble COD (sCOD); and 201 ± 24 mg/L, total suspended solids (TSS). On the other hand, Table 1 presents the characteristics of domestic wastewater contaminated with Type 1_ADF and Type 2_ADF at different increased ratios at the start-up (t = 0 d) of the batch study. The reactors were seeded with the granular sludge taken from the anaerobic reactor of a paper/cardboard industry operated at mesophilic conditions (VS/TS = 50%). The granular sludge was crushed by a kitchen grinder before being added into the batch reactors [18].
2.2. Bioreactors and operating conditions

Anaerobic treatment was conducted in N2-flushed 1-L glass flasks (i.e., the total volume of the reactors), which were closed tightly by special covers. For the first set; reactors were run with the addition of substrate (585 mL) and the seed sludge (120 mL) (v/v = 1/5) including Type 1_ADF with the following ratios; 0% (control_substrate with only domestic wastewater), 0.9%, 2.9%, 3.4%, 5.2%, and 9.7%. For the second set; reactors were run with the addition of substrate (480 mL) and the seed sludge (120 mL) (v/v = 1/4) including Type 2_ADF with the following ratios; 0% (control_substrate with only domestic wastewater), 2.7%, 4.8%, 8.3%, and 12.5%. Hence, the respective active reactor volumes of the sets were 700 and 600 mL. Initial ADF ratios in both sets were determined as about 95,000 mg/L which corresponded to the wastewater contaminated with ca. 10% Type 2_ADF.

In this context, the anaerobic flasks were run as batch reactors at six sets of ADF feeding conditions. Both experimental sets were installed according to be incubated for 5, 12, 26, and >70 d. In this context, a total of 24 (i.e., 6 × 4) reactors for the substrates and 1 single background reactor including only the seed (control_inoculum) were set-up at the first operating day. All reactors were run at identical conditions and they were mixed twice a day manually while incubated at 35°C constant room temperature (i.e., mesophilic) until the changes in cumulative biogas production volumes were negligible and stopped. After the characterization of initial substrates (Table 1) from the complete mixture (t = 0 d); anaerobic treatment performance was monitored for more than 70 d (t = last day).

2.3. Analytical procedure

Total COD (tCOD), soluble COD (sCOD), total and volatile suspended solids (TSS and VSS), and alkalinity parameters were measured according to Standard Methods [19]. For COD experiments; dichromate closed-reflux method was used and concentrations were measured by HACH DR/2010 spectrophotometer (USA). The HI 2211-02 HANNA model pH meter was used for pH analyses (Hanna Instruments Ltd., Bedfordshire). The biogas was daily monitored using a manometer (i.e., Lutron Electronic Enterprise, Taiwan) in the headspaces of the reactors before the produced gas pressures were released by injection needles. Then the biogas volume (mL) in each reactor was calculated under the standard conditions. Gas contents of the reactors were analysed by the advance optima process (ABB model) gas analyser with thermo-magnetic and infrared photometers [20]. Volatile fatty acids (VFAs) were measured by gas chromatography (Agilent Technologies, 6890N, USA) equipped with a flame ionization detector and a capillary column (DB-FFAP 125-3232) after filtering the samples through 0.22 µm filters. Propylene glycol ratios were measured by the Bellingham + Stanley Abbe type refractometer (Model 60/70, Bellingham + Stanley Ltd., UK).

3. Results

Inhibition effects on anaerobic microbial cultures were assessed by monitoring ultimate methane gas production. Liu et al. [21] also reported that the methane yield (m3 CH4/ kg CODremoved) could be a useful parameter to assess the performance of an anaerobic digester. It was reported that in the case of inhibition, methane production decreases due to the fact that methanogenic archaea undergo longer lag time than acidogenic bacteria [22]. Hence, VFAs are accumulated inside the bioreactors, pH values drop, and eventually methanogenesis fails in the anaerobic process [23].

In this respect, the changes in total VFA concentrations were monitored in the batch reactors (Fig. 1). VFA analyses indicated compatible results with the pH values so that VFAs could not be consumed when ADF ratios were more than 3.4% (Fig. 1a) and 1.8% (Fig. 1b) for Type 1 and Type 2 ADFs, respectively. Accordingly, the decrease in pH occurred with the accumulation of VFAs due to high organic loadings in the reactors which also led to an inhibition effect especially on the methanogens. In this scope, alkalinity analyses were also conducted at different operating times. In the batch reactors at the last operating day, alkalinity (i.e., all more than 1,500 mg CaCO3/L) tended to increase gradually compared with initial values. On the other hand, pH values indicated noticeable changes for both ADF types. For Type 1 ADF; pH values of the initial samples at t = 0 d were between 7.33 and 7.57. However in the last operating day (t = 73 d); although pH values of the final samples were between 7.29 and 7.70 for the reactors having 0%–3.4% Type 1 ADF, pH values dropped to 6.44 and 5.96 for the reactors having 5.2% and 9.7% Type 1 ADF, respectively (Fig. 1a). Results of the batch system with Type 2 ADF indicated similar findings so that pH values were between 7.20 and 7.51 in the initial samples. Although respective pH of the final samples for the reactors

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Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Type 1_ADF (%)</th>
<th>Type 2_ADF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.34, 7.38, 7.40, 7.34, 7.33</td>
<td>7.5, 7.51, 7.49, 7.41, 7.29</td>
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<tr>
<td>Alkalinity* (mg/L)</td>
<td>520, 520, 540, 500, 600</td>
<td>800, 840, 760, 700, 800</td>
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<tr>
<td>tCOD (mg/L)</td>
<td>816, 6033, 11535, 16596, 23528</td>
<td>54,825, 828, 4,461, 13,542, 25,146</td>
</tr>
<tr>
<td>sCOD (mg/L)</td>
<td>392, 5,750, 10,617, 15,292, 22,938</td>
<td>359, 4,267, 11,542, 25,146</td>
</tr>
<tr>
<td>sCOD/tCOD, %</td>
<td>48, 95, 92, 92, 97</td>
<td>43, 95, 84, 85</td>
</tr>
</tbody>
</table>

*as CaCO₃
having 0% (control) and 1.8% Type 2_ADF were 7.67 and 7.48; pH values dropped to between 5.24 and 5.88 in the last operating day for the reactors having Type 2_ADF within the range between 2.7% and 12.5% (Fig. 1b). Hence, the pH values with ADF ratios more than 3.4% for Type 1_ADF and more than 1.8% for Type 2_ADF decreased in all bioreactors throughout the incubation period. This finding indicated that appropriate pH range (i.e., 6.7–7.4) could not be achieved for most methanogenic bacteria to function at high organic loadings due to high ADF ratios [24].

Similarly, COD removals were compatible with the pH results so that dramatic reductions were observed from 86% in the reactor with 0.9% to less than 10% in the reactors having 5.2% and 9.7% Type 1_ADF ratios (Fig. 2a). In control reactors, having both ADF types indicated the same tCOD removal of about 69%. On the other hand, during the operation of the reactors with Type 2_ADF at increased ratios; the decrease in organic matter removal was also observed when ADF ratio was higher than 1.8% in the reactors. Total and soluble COD removals decreased down to ca. 11% at 12.5% Type 2_ADF from about 63% at 1.8% Type 2_ADF (Fig. 2b). A dramatic decrease in COD removals was due to VFAs accumulation, because VFAs could be only consumed in the reactor having 0.9%–3.4% for Type 1_ADF in Fig. 1a. On the other hand, almost complete VFAs consumption was observed in the reactor having 1.8% Type 2_ADF (Fig. 1b). Hence, VFAs accumulation was apparent in the reactors when Type 1_ and Type 2_ADF ratios were 5.2% to 9.7% and 2.7% to 12.5%, respectively (Fig. 1b). Gao et al. [25] reported that VFA/alkalinity ratios should be between 0.40 and 0.80 for effective anaerobic degradation. Hence, when alkalinity values were taken into account; performance instability was observed in the reactors due to the fact that VFA/alkalinity ratios increased to more than 2.0. Similar results were also reported by Liu et al. [21] who explained significant decrease in the methane content of the produced biogas from 55% to 20% at increasing OLR from ca. 2.0 to 6.0 g COD/L/d by the impact of VFA/alkalinity ratio on both acidogenesis and methanogenesis. Elreedy et al. [26] also reported the prevalence of acidogenesis and acetogenesis over methanogenesis due to a gradual increase in VFAs production through the
compartments of an anaerobic packed bed baffled reactor operated at an OLR of 4.0 g COD/L/d.

Biogas yields were also calculated at increased ADF ratios based on the influent tCOD concentrations using the cumulative biogas productions obtained till the last operating day. According to the results, high biogas productions with respective methane contents of ca. 63% and 59% could be acquired during anaerobic batch treatment of domestic wastewater contaminated with Type 1_ and Type 2_ADF until certain ratios (Figs. 3a and b). Results in terms of biogas yields and tCOD removals, 3.4% Type 1_ADF and 1.8% Type 2_ADF represented the upper concentration limits of the experimental design. Accordingly, biogas yields were between 0.11 and 0.22 m³/kg tCOD_infl for 0.9%–3.4% Type 1_ADF whereas the biogas yield was 0.25 m³/kg tCOD_infl for 1.8% Type 2_ADF. Biogas yield decreased down to 0.07 m³/kg tCOD_infl when Type 2_ADF ratio increased to 2.7% in the reactor (Fig. 4). On the other hand, such dramatic biogas decrease was observed when Type 1_ADF was 5.2% in the reactor. Hence, Type 2_ADF was more toxic to anaero-

bobic microbial cultures and showed inhibition effect at lower ratios compared with Type 1_ADF ratio in the wastewater. This might be due to the fact that Type 2_ADF had higher amounts of additives and polymeric thickener in order to provide longer holdover times. These results were comparable with those reported in recent studies. For example, decrease in the biogas yield was also observed by Tham and Kennedy [27] who reported that biogas production stopped and anaerobic toxicity assays indicated significant microbial inhibition at concentrations ≥2% ADF owing to high VFA concentrations (i.e., more than 2,000 mg/L) as well as high OLRs. In our study, we found similar findings indicated inhibition in the reactors having more than 2.5% ADF ratios. Because, as already explained, high ADF ratios caused accumulation in VFAs leading to low pH values not in the optimum range for the methanogens. Moreover, Marin et al. [3] reported that COD removal efficiency reduced from 92% to 77% when OLR was increased from 0.75 to 3.0 g COD/L/d in an anaerobic reactor treating ADF at mesophilic temperature. Besides, Liu et al. [21] also reported that as the average OLR increased to about 6 kg COD/m³/d; sharp reductions in pH, COD removal, gas production, and methane percentage of the biogas were observed together with rapid VFAs accumulation in the effluent. Hence although the UASB reactor was a promising technology and efficient for the treatment of wastewaters contaminated with ADF (i.e., including propylene glycol) at a certain content, the pathway and efficiency of anaerobic degradation was strongly influenced by OLR.

4. Conclusions

In the present study, the effect of two different types of ADFs on anaerobic performance in batch reactors treating domestic wastewater contaminated with Type 1_ and Type 2_ADF was investigated. In this respect, optimum ADF ratios in domestic wastewater were determined in order to foresee their inhibition effect on anaerobic microorganisms. The findings of the study indicated satisfying biogas yields and high COD removals at certain ADF ratios and hence, anaerobic treatment of ADF-contaminated domestic wastewater could be applicable at controlled feeding and operating conditions with high energy productions. However, ADF ratios ≥ 2.5% led to significant reductions both in COD removal and in biogas yield (i.e., from 0.22 to 0.11 and from 0.25 to 0.07 m³/kg tCOD_infl at 3.4% and 2.7% Type 1_ and Type 2_ADF ratios, respectively) indicating inhibition due to VFAs accumulation at high organic loadings.
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References