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Assessment of aerobic and anaerobic stabilization for biological waste sludges from leather and textile industries

Elif Pehlivanoglu-Mantas*, Duygu C. Ozturk

Environmental Engineering Department, Istanbul Technical University, Istanbul 34469 Turkey
Tel. +90 533 399 9167; Fax. +90 212 285 3781; email: elif.pehlivanoglu@itu.edu.tr, ozturkdu@itu.edu.tr

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ABSTRACT

Sludges from wastewater treatment plants are considered hazardous waste unless they are adequately stabilized to decrease total and dissolved organic carbon (TOC and DOC) concentrations below the standards for disposal of wastes into landfills. There are several methods to define stabilized sludge such as specific volatile suspended solids (VSS) load or leveling off of the VSS concentration. However, evaluation of sludge stabilization may not be as straightforward as these methods suggest. In this study, aerobic and anaerobic stabilization were applied to industrial sludges from two different industries (i.e., leather and textile) to decrease organic content of the sludges below hazardous waste levels. Aerobic sludge treatment provided better organics removals compared to anaerobic sludge treatment for leather industry with a VSS removal of 38% and a TOC removal of 65%. For textile industry, both aerobic and anaerobic treatment resulted in similar decreases in VSS (~ 50%) and TOC (~ 60%) concentrations. Although aerobic sludge stabilization was established after approximately 30 days for both leather and textile industries, as suggested by specific VSS loads, organic content of stabilized sludges did not decrease sufficiently to comply with the TOC/DOC standards for landfill disposal and stabilized sludges are still classified as hazardous waste.

Keywords: Hazardous waste; Industrial wastewater; Sludge stabilization; Specific VSS load

1. Introduction

Although biological processes are important for domestic and industrial wastewater treatment, waste sludge generated during these processes creates an important environmental problem due to its high pollution concentration and high water content. Moreover, waste sludge from wastewater treatment plants (WWTP) requires additional treatment prior to its final disposal and the cost of sludge disposal makes up nearly half of the total operational costs of a WWTP [1]. The amount of municipal sludge generated per capita in Turkey (17–45 g dry weight/ca.day) [2,3] is lower than the amount of sludge generated in Europe (60–90 g dry weight/ca.day) [4] and currently, 5–10% of sludge generated in Turkey is used in agriculture. Sludge incineration is widely used in Europe, however, up to now, cost of incineration and lack of proper/properly operated incinerators have prevented incineration becoming widely used in Turkey. Therefore, despite its deficiencies, most of the non-stabilized excess biological treatment sludge is disposed to a landfill. To prevent leaching of toxic organic pollutants and heavy metals from wastes in landfill areas to surface water and groundwater, hazardous waste which is defined by listing upper limits for several parameters such as arsenic, cadmium, sulfate, fluoride, BTEX and PCBs in the Regulation for Control of Hazardous Waste [5] cannot be disposed of in a landfill. Even if all the other parameters listed in the regulation may indicate a "non-hazardous" waste and hence meet the disposal criteria, most treatment sludges are

*Corresponding author.

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considered hazardous due to their high TOC and/or DOC concentrations (measured in the eluates of sludge cakes). Since only non-hazardous waste can be disposed of in a landfill, the organic carbon content of treatment sludges has currently become a critical parameter in sludge management in Turkey. Nevertheless, concentrations of organics may be decreased to acceptable limits using appropriate sludge stabilization technologies. For example, VSS removal percentages for high-rate completely mixed mesophilic anaerobic digesters at solids retention times of 15 and 30 days are 56% and 65%, respectively [6]. However, the different characteristics of domestic and industrial wastewater sludges may lead to a difference in the decrease of VSS and or TOC/DOC values. It is known that complex organic materials such as peptidoglycan, teichoic acids and complex polysaccharides which are found in bacterial cell walls make the digestion of biological sludge harder due to the rate limiting cell lysis step [7] and similar complex organics which can be found in industrial wastewaters may require higher solids retention times. Moreover, the nature of inorganic components of the sludge may control the rate of mineralization of organic matter in the sludge [8]. Toxicity caused by inorganic components such as heavy metals or interactions between organic matter and mineral surface which may prevent the degradation of organic matter may be given as examples for the effect of inorganic components on the degradation of the organic matter of the sludge [8].

In this study, aerobic and anaerobic stabilization were used for treatment of sludges generated from two different industrial wastewater treatment plants. Experiments were conducted to evaluate sludge stabilization and waste classification of sludges for landfill disposal based on their TOC and DOC values.

2. Materials and methods

Grab sludge samples were taken from wastewater treatment plants (WWTP) of two organized industrial districts: a leather industry and a textile industry (WWTP1 and WWTP2, respectively). The flowrate of WWTP1 is 13,000 m^3/d and the activated sludge system has a sludge retention time (SRT) of approximately 14 days. The flowrate of WWTP2 is 36,000 m^3/d and the SRT of the activated sludge reactor is kept above 15 days.

Both aerobic and anaerobic stabilization of sludges were conducted in laboratory scale systems, using 5 L-cylinder tanks and 1 L-Erlenmeyer flasks, respectively. Both systems were kept at constant temperature (20 ± 0.5°C for aerobic and 35 ± 0.5°C for anaerobic stabilization). Aerobic stabilization tanks were continuously supplied with oxygen in addition to being mixed by magnetic stirrers to keep the dissolved O_2 concentration above 2 mg/L. pH of the aerobic system was kept at 7.0 ± 0.5 using $NaHCO_3$ as well as an appropriate acid or base solution (0.1 N HCl or NaOH), if necessary.

Anaerobic tanks were kept on an orbital shaker at 125 rpm and were buffered with 0.5 g/L $NaHCO_3$. At the beginning of anaerobic stabilization experiments, anaerobically digested sludge from a WWTP which receives domestic and industrial wastewater was used to inoculate the systems (5% v/v) and N_2 gas was used to strip out O_2 gas.

Laboratory analyses were conducted on sludge samples and sludge cakes (both real and lab-prepared) as well as on sludge cake eluates prepared according to Turkish Standards (TS EN 12457-4) [9]. pH, solids content, suspended solids (SS) and volatile suspended solid (VSS) analyses were conducted according to APHA Standard Methods [10], whereas total organic carbon (TOC) and dissolved organic carbon (DOC) were measured using high temperature combustion with a TOC analyzer according to Turkish Standards (TS 8195) [11] with a Shimadzu TOC-5000A analyzer. Sludge cakes were prepared by centrifuging samples taken from the completely mixed reactors for 5 min at 5000 rpm. In addition, oxygen uptake rate (OUR, mg/L/h) measurements were conducted on day 0 and day 20 with an oxygen meter (WTW OXI DIGI Level II) to assess the viability of aerobic sludges. Batch OUR experiments were initiated with sludges spiked with 500 mg COD/L acetate and a nitrification inhibitor (Formula 2533TM-Hach Company, USA) was added to prevent nitrification activity during OUR measurements. Dissolved O_2 concentrations were measured every 30 s and OUR was calculated for dissolved O_2 concentrations between 8 and 3 mg O_2/L.

3. Results and discussion

Characteristics of sludges and sludge cakes taken from WWTPs are provided in Section 3.1, whereas results based on observation of different parameters measured during aerobic and anaerobic stabilization are provided in Sections 3.2 and 3.3, respectively.

3.1. Sludge characterization

VSS/SS ratio in sludges obtained from WWTP1 and WWTP2 (Table 1) are 0.52 and 0.58, respectively. Although the mean ratio of VSS/SS for domestic wastewater sludge is approximately 0.7–0.8 [12], this ratio is usually smaller for municipal WWTPs which receive other sources of wastewater in addition to domestic wastewater [13]. TOC/VSS ratios are 0.59 and 0.5, for WWTP1 and WWTP2, respectively. TKN values are in

Table 1
Characterization sludge and sludge cakes obtained from WWTPs. WWTP1 and WWTP2 represent WWTP of a leather and textile industry, respectively.

	WWTP1 (mean ± std.dev)	WWTP2 (mean ± std.dev)	WWTP1 sludge cake (mean ± std.dev)	WWTP2 sludge cake (mean ± std.dev)
VSS (mg/L)	14,000 ± 212	26,000 ± 275		
VSS/SS	0,52	0,58		
TOC (mg/L[1] or mg/kg[2])	8,215 ± 328[1]	12,880 ± 515[1]	104,700 ± 4000[2]	198,200 ± 7900[2]
DOC (mg/L)	366 ± 13	230 ± 9	80 ± 3	210 ± 9
TKN (mg/L)	1,483 ± 65	1,643 ± 13		
NH_4-N (mg/L)	186 ± 3	126 ± 2		
Solids content (%)			34	14

the order of literature values reported to be approximately 1.5–4% of total dry weight [6].

TOC values of the sludge cakes were similar to values reported in the literature for industrial and municipal sludges (95,400 to 265,200 mg/kg) [14]. Although Oleszczuk et al. reported that the mean TOC value in the municipal sludges was 12% higher than in the municipal-industrial sludges [14], no similar trend was observed when the values for industrial sludges are compared to values obtained from the three main municipal WWTPs in Istanbul, Turkey (78,300, 156,300 and 256,000 mg TOC/kg) [15].

These results suggest that sludge cakes from both WWTPs cannot be accepted into a landfill according to “Hazardous Waste Control Regulation” [5] due to high TOC and DOC contents. Therefore, aerobic and anaerobic stabilization experiments were conducted to check the applicability of these processes for further treatment of WWTP sludges.

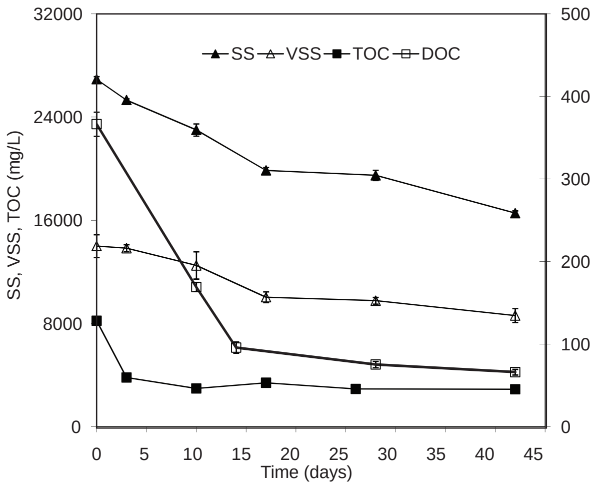

Fig. 1. VSS, SS, TOC and DOC concentrations during aerobic stabilization of WWTP1. The temperature and pH were kept at 20 ± 0.5°C and 7.0 ± 0.5, respectively.

3.2. Aerobic stabilization

3.2.1. Leather industry

VSS, SS, TOC and DOC values were measured during aerobic stabilization of WWTP1 sludge which comprised of a 1:1(v/v) mixture of primary and biological sludges from WWTP1 to represent the real life conditions (Fig. 1). pH did not fluctuate considerably during aerobic stabilization and was approximately 8.3.

Both VSS and SS concentrations decreased approximately 38% during the 42 day-aerobic stabilization. A similar decrease (% 42) was observed in OUR after 20 days. VSS/SS ratio did not change considerably. TOC concentration in the aerobic reactor was 8215 mg/L at day 0 and it decreased to approximately 3000 mg/L at day 3 after which the TOC concentration leveled off. DOC concentration in the aerobic reactor decreased by 80% in 42 days.

TOC and DOC concentrations were also measured in eluates of lab-prepared sludge cakes (Fig. 2) because the standards listed in hazardous waste regulations are based on the measurements of TOC and DOC in the eluates of the sludge cakes [5,9]. TOC concentrations decreased from 104,000 mg/kg to approximately 48,000 mg/kg within the first 5 days; however, a similar decrease in DOC values was not obtained. Although TOC values were approximately 40,000 mg/kg at the end of the 42-day stabilization period, DOC values stayed above the criterion for non-hazardous waste (i.e., 50 mg/L).

3.2.2. Textile industry

Sludge from WWTP2 was diluted 4:5 (v:v) prior to aerobic stabilization due to its high organic content. Changes in VSS, SS, TOC and DOC concentrations corrected for dilution are depicted in Fig. 3. pH fluctuated around a value of 8 with a minimum and maximum value of 7.3 and 8.5, respectively. During the 41 day-aerobic stabilization, removal for SS and VSS were 45%

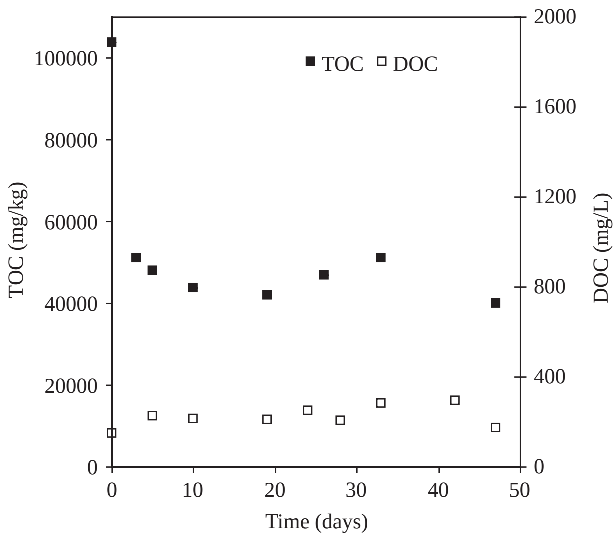

Fig. 2. TOC and DOC concentration in lab-prepared sludge cakes during aerobic stabilization of WWTP1.

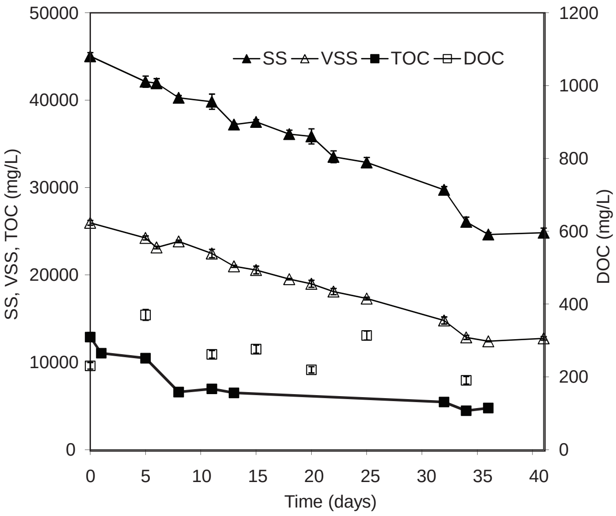

Fig. 3. SS, VSS, TOC and DOC concentrations during aerobic stabilization of WWTP2. The temperature and pH were kept at 20 ± 0.5°C and 7.0 ± 0.5, respectively.

and 51%, respectively, corresponding to a decrease in VSS/SS ratio from 0.58 at day 0 to 0.50 at day 41. The decrease in OUR (52%) between day 0 and day 20 was similar to the decrease in the VSS concentration (data not shown).

TOC concentration decreased from approximately 12,900 mg/L to 4800 mg/L, corresponding to a decrease of 63%. DOC concentration fluctuated throughout the experiment and the decrease in DOC concentration was less than 20%.

TOC concentration in eluate of lab-prepared sludge cake (Fig. 4) was 30,000 mg/kg at day 0 which is the upper TOC limit for non-hazardous waste criteria and TOC concentration decreased nearly 35% during stabilization. However, no decline was observed in DOC concentrations which fluctuated around 200 mg/L.

3.3. Specific VSS load

Specific VSS load of a sludge (gVSS/ca.day) has been used to evaluate stabilization of aerated sludge with values between 16 and 22 gVSS/ca.day indicating stabilized sludge and values above 22 gVSS/ca.day indicating unstabilized sludge [16,17]. Stabilization of aerobic sludges of WWTP1 and WWTP2 occurred after approximately 26 and 32 days, respectively (Fig. 5). However,

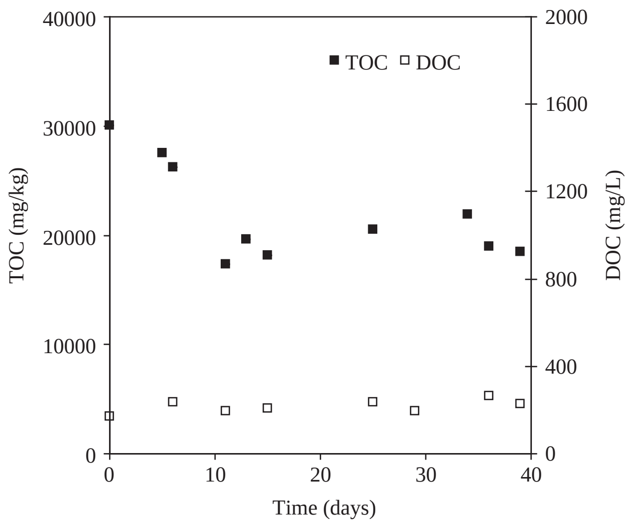

Fig. 4. TOC and DOC concentration in lab-prepared sludge cakes during aerobic stabilization of WWTP2.

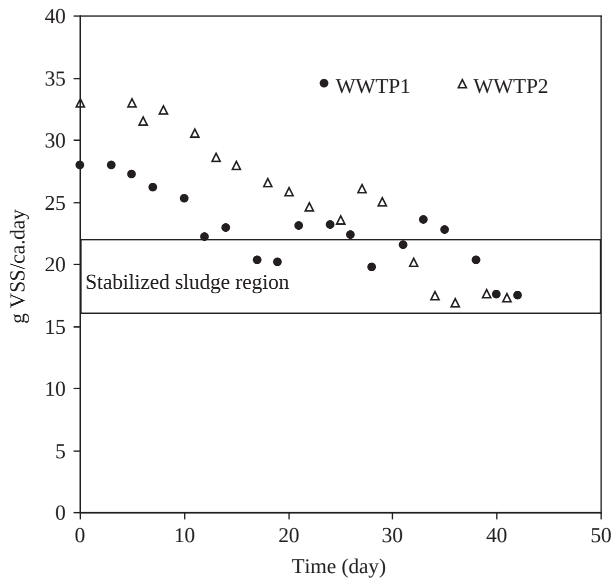

Fig. 5. Specific VSS loads for WWTPs. The stabilized sludge region (between 16 and 22 gVSS/ca.day) indicates stabilized sludge.

it is noteworthy that specific VSS production method is probably more suitable for domestic sludges or municipal sludges with little industrial input. Characteristics of sludge as well as operation conditions of WWTPs may affect the results of this methodology. Therefore, although results may indicate sludge stabilization, sludge may not meet other criteria of stabilized sludge.

3.4. Anaerobic stabilization

3.4.1. Leather industry

Changes in SS, VSS, TOC and DOC concentrations during anaerobic stabilization of sludge from WWTP1 are depicted in Fig. 6. Average pH was 7.7. SS and VSS removal after 49 day-anaerobic stabilization were 19 and 31%, respectively. However, these removal percentages were reached at day 31 and concentrations leveled off afterwards. VSS/SS ratio decreased from 0.52 at day 0 to 0.45 at day 49. TOC concentration decreased by 45% and reached 4500 mg/L at day 49. DOC concentration increased from approximately 370 mg/L to nearly 850 mg/L at the end of anaerobic stabilization which could be explained by the formation of fermentation products such as volatile fatty acids, ethanol and lactate [18,19] which were not measured in this study.

Changes in TOC and DOC concentrations in lab-prepared sludge cakes are provided in Fig. 7. TOC concentration decreased steadily from 103,700 mg/kg to approximately 36,000 mg/kg at day 40 and it did not change considerably for the last 10 days of stabilization. DOC concentration, however, increased from 150 mg/L to 800 after 20 days, but then decreased to 100 mg/L at the end of the stabilization period.

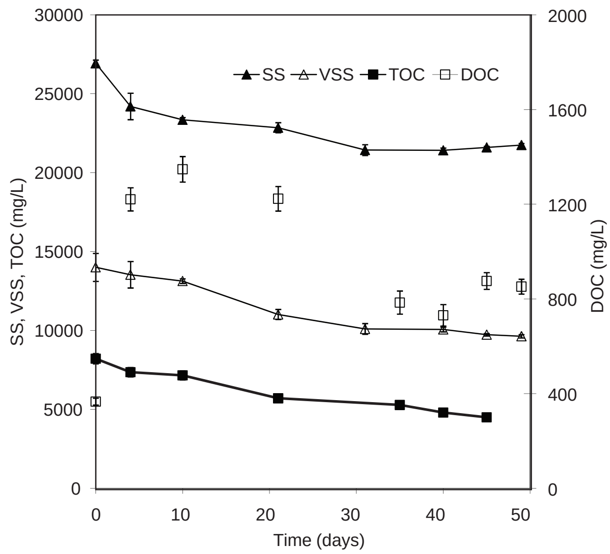

Fig. 6. SS, VSS, TOC and DOC concentrations during anaerobic stabilization of WWTP1. The temperature was kept at 35 ± 0.5°C.

3.4.2. Textile industry

Changes in SS, VSS, TOC and DOC concentrations during anaerobic stabilization of WWTP2 are provided in Fig. 8. pH did not change significantly during stabilization and had an average value of 7.5. Decrease in SS and VSS concentrations after 39 day-stabilization were 37% and 54%, respectively. VSS/SS ratio decreased from 0.58 at day 0 to 0.42 at day 39. TOC concentration decreased to 4570 mg/L, corresponding to a removal of 65%, whereas DOC concentration increased significantly by approximately an order of magnitude, from 230 mg/L to 2280 mg/L.

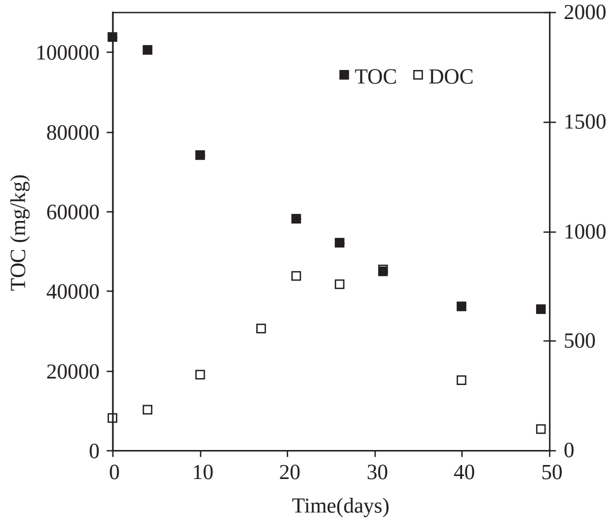

Fig. 7. TOC and DOC concentration in lab-prepared sludge cakes during anaerobic stabilization of WWTP1.

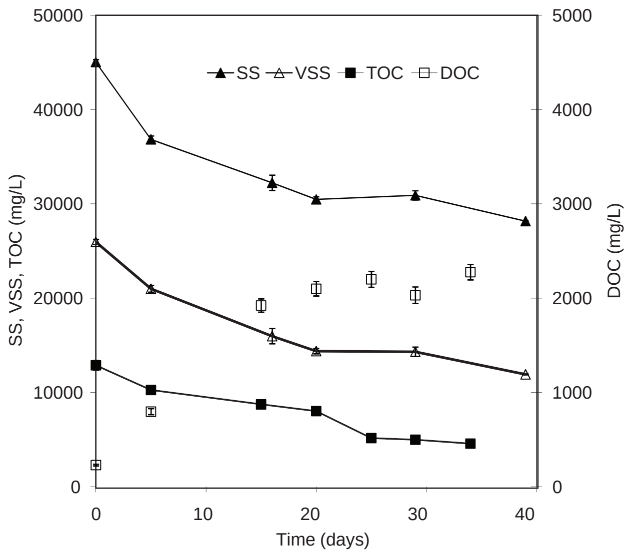

Fig. 8. SS, VSS, TOC and DOC concentrations during anaerobic stabilization of WWTP2. The temperature was kept at 35 ± 0.5°C.

TOC concentration measured on lab-prepared sludge cakes decreased from approximately 30,000 mg/kg to 24,400 mg/kg after 35 days (Fig. 9). Unlike this trend, there was an increase from 170 mg/L to approximately 560 mg/L in DOC concentrations in 5 days. DOC concentrations, then, decreased to 320 mg/L after 39 days. These changes in DOC concentration may be due to the formation and degradation of anaerobic hydrolysis products in the reactor similar to anaerobic stabilization of leather industry sludges.

Removal rates obtained in this study for aerobic and anaerobic stabilization of sludges are similar to results obtained in other laboratory-scale experiments [20]. For sludges of WWTP1, aerobic stabilization had better VSS and TOC removals than anaerobic stabilization. A similar result was obtained by Parravicini et al., which suggested that hydrolysis of residual particulate organic matter in stabilized sludge might occur more efficiently in the presence of oxygen [17]. In this study, however, VSS and TOC removals were similar for aerobic and anaerobic stabilization of sludges of WWTP2. Similarities in VSS removal for aerobic and anaerobic stabilization suggest that the presence or absence of oxygen does not affect the hydrolysis of residual organic matter in textile industry wastewater sludge.

Although aerobic and anaerobic stabilization did not result in compliance with non-hazardous waste standards for TOC and/or DOC concentrations, specific VSS loads were in the range of stabilized sludge after 26 and 32 days for aerobic stabilization of WWTP1 and WWTP2, respectively. A similar result was obtained in a study conducted by Parravicini et al., where the disposal standards for mechanically/biologically treated solid waste were not met after anaerobic or aerobic stabilization, although oxygen utilization rate and specific VSS load indicated sludge stabilization [17]. This inconsistency suggests that parameters used for the evaluation of sludge stabilization such as specific VSS load may work for domestic sludges, but care is needed to evaluate the stabilization of industrial sludges. Therefore, parameters such as phospholipids concentration [21] which can be used for both aerobic and anaerobic systems may be useful for the evaluation of sludge stabilization.

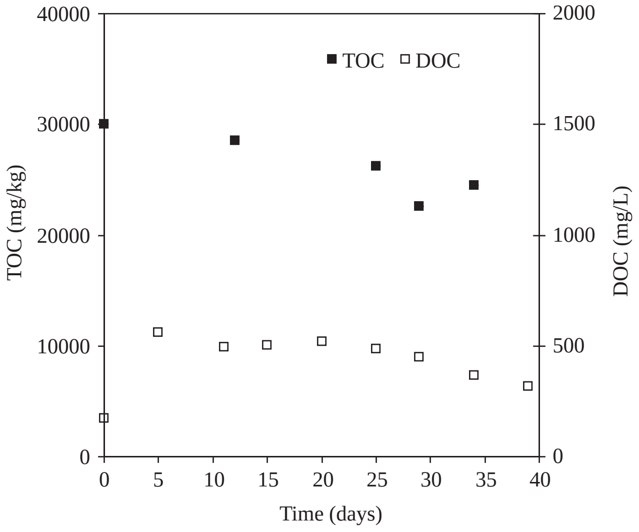

Fig. 9. TOC and DOC concentration in lab-prepared sludge cakes during anaerobic stabilization of WWTP2.

Standards for non-hazardous waste disposal in Turkey are very similar to those in EU, however, strong characteristics of wastewaters generated in Turkey leads to higher TOC and/or DOC concentrations in wastewater sludge. Therefore, when aerobic or anaerobic stabilization alone cannot meet the disposal standards, several pre-treatment steps (e.g., mechanical, chemical or thermal treatment) can be applied as sludge disintegration methods. These methods enhance biodegradation by disrupting cell walls and eliminating the rate limiting-hydrolysis step. Application of ultrasound prior to anaerobic stabilization, for instance, can increase biodegradability by approximately 50% [7]. Also, two biological treatments can be used in sequence to decrease organic matter content of the sludge. For example, using additional anaerobic or aerobic stabilization steps after anaerobic stabilization enhances biodegradability of residual organic matter in digested sludge by 10 and 22%, respectively [17].

4. Conclusion

To prevent or minimize negative impacts of sludges such as uncontrolled microbial activity and odor problems after their final disposal, stabilization of sludges is required. There are several parameters that can be used to evaluate the stabilization level of sludges and among those parameters, the decrease in physico-chemical parameters such as VSS/SS and TOC/DOC as well as specific VSS loads were used in this study. Aerobic and anaerobic stabilization were applied to sludges of which the sludge cakes are considered hazardous and hence unsuitable for disposal in landfills. However, neither aerobic nor anaerobic stabilization of the sludge decreased TOC and/or DOC concentrations measured in the lab-prepared sludge cakes below the standards of non-hazardous waste as specified in "Regulation for Control of Hazardous Waste" Appendix 11A [5]. Therefore, although stabilization of sludges as well as a reduction in sludge volume can be obtained with biological sludge stabilization, physical, chemical and biological sludge disintegration methods or a combination of these methods may be required for appropriate disposal of industrial sludges.

When biological sludge stabilization is conducted alone or with a pretreatment, use of several spectroscopic methods such as FT-IR spectroscopy or solid-state ^{13}C Nuclear magnetic resonance can be valuable with which not only the quantity of organic matter as a collective parameter, but rather the structure of organic matter in sludges can be obtained. These methods can provide insight into the effect of different stabilization techniques on the composition of organic material. For cases where organic content cannot be decreased sufficiently to classify the sludge in question as non-hazardous waste with other stabilization methods, sludge incineration could be used as a terminal remedy.

Acknowledgements

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