Desalination 251 (2010) 58–63

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Improving anaerobic biodegradability of biological sludges by Fenton pre-treatment: Effects on single stage and two-stage anaerobic digestion

Gulbin Erden *, A. Filibeli

Dokuz Eylül University, Department of Environmental Engineering, Tinaztepe Campus, 35160, Buca-Izmir, Turkey

ARTICLE INFO

Article history:
Received 7 August 2009
Received in revised form 28 September 2009
Accepted 28 September 2009
Available online 21 October 2009

Keywords:
Anaerobic digestion
Biological sludge
Fenton process
Sludge minimization

ABSTRACT

In the present study, the effects of Fenton process on anaerobic sludge bioprocessing were investigated. A ratio of 0.067 g Fe(II) per gram H_2O_2, and 60 g H_2O_2/kg dried solids (DS) was applied to biological sludge samples preceding anaerobic sludge digestion. Single stage anaerobic digestion under thermophilic conditions is compared with two-stage anaerobic digestion (mesophilic digestion prior to thermophilic digestion). The comparison is in terms of solid reductions and specific methane productions. Fenton processed sludge gives higher solid reduction and higher methane production for each experiment. The highest reduction in sludge's solids was observed in a reactor operated under thermophilic conditions. The second stage digestion under mesophilic conditions did not induce extra solid reduction. However, it facilitated higher methane. Another observation is that, Fenton process led to decrease the biosolids' resistance to dewatering in terms of capillary suction time (CST), but had no effect on sludge dewatering on belt-press application.

1. Introduction

Anaerobic digestion of waste activated sludge (WAS) is often slow due to the rate limiting cell lysis step [17]. In order to improve hydrolysis and anaerobic digestion performance, floc disintegration was developed as the pre-treatment process of sludge to accelerate the anaerobic digestion and to increase the degree of stabilization [4,32]. Sewage sludge disintegration can be defined as the destruction of sludge by external forces. The forces can be of physical, chemical or biological nature. A result of the disintegration process is numerous changes of sludge properties [21]. The changes may be summarized as disruption of microbial cells in the sludge, thereby destroying the cell walls and releasing the cell content; breaking up or disrupting the cell walls, so that substances protected by the former are released and dissolved; and opening up the cell walls of organisms, so that the substances contained in the cell are solubilized [30]. Increased stabilization degree of sludge with disintegration process provides less sludge production, more stable sludge and more biogas production comparing the classical anaerobic digestion [31]. Ultrasonic treatment [3,14,25,26,29,34,35], ozone oxidation [5,20,33], mechanical disintegration [16,23], alkaline treatment [6,18], thermal treatment [2] and biological hydrolysis with enzymes [1,15] were investigated for sludge disintegration purpose by several researchers in half-scale and lab-scale plants. Fenton process is one of the commonly used advanced oxidation techniques. Fenton's reagent is a mixture of H_2O_2 and ferrous iron. The ferrous iron initiates and catalyses the decomposition of H_2O_2, resulting in the generation of highly reactive hydroxyl (OH) radicals [12]. The OH radical is the main reactant in the process capable of decomposing a number of organic substances via oxidation. The rate and extent of the Fenton reactions are dependent on system parameters including, iron and hydrogen peroxide concentration, and solution pH. The application of the Fenton process for disintegration of WAS may cause two phenomena: solubilization and mineralization of sludge solids. Part of activated sludge is mineralized to carbon dioxide and water while part of sludge is solubilized to biodegradable organics, which are easily accessible and can be digested much faster in later biological process than sludge in a particular phase. Takumura et al. [28] applied the similar advanced oxidation method of photo-Fenton reaction to WAS in a batch photo reactor for disintegration purpose; soluble chemical oxygen demand (SCOD) was achieved at highest level in the presence of 4 g H_2O_2/L, 40 mg Fe(II)/L, and 3000 mg MLSS/L, $pH = 3$ for 6 h reaction time and effective disintegration was obtained. At longer than 6 h retention time, COD was decreased and mineralization occurred. Nickel and Neis [24] applied Fenton process to thickened sludge and they noted optimum activity in the presence of 25 g H_2O_2/kg DS, and 1.67 g Fe(II)/kg DS, $pH = 3$ and at ambient temperature and pressure. In these conditions Fenton process resulted in a considerable reduction of dried solid (DS) and volatile solid (VS) contents in the filter cake of approximately 20%, an improved dewaterability with a 30% reduction of the sludge volume, and a 30% increase of the cake DS-content when compared with the untreated sludge sample. In another study, biological sludge is processed with 0.07 g Fe(II) per gram of H_2O_2 and 50 g H_2O_2/kg DS at $pH = 3$ and Fenton

---

* Corresponding author.
E-mail address: gulbin.erden@deu.edu.tr (G. Erden).

0011-9164/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2009.09.144

processed sludge were digested in laboratory scale digester consisting 1 L batch reactor at mesophilic and a 26.6% reduction in VS was recorded [7]. In our previous study, 0.067 g Fe(II) per gram of H_2O_2 and 60 g H_2O_2/kg DS was found as optimum dose using Box–Wilson Experimental Design Method. Biological sludge was processed with 0.067 g Fe(II) per gram of H_2O_2 and 60 g H_2O_2/kg DS at pH = 3, and 25.4% reduction in VS was obtained in 8.5 L lab-scale digester operated with a 5 day sludge retention time at mesophilic conditions. VS reduction in the reactor fed with Fenton processed sludge was 1.53 times greater than in the control reactor at the end of the 20th operation day [11]. In this study, the same ratio of 0.067 g Fe(II) per gram H_2O_2, and 60 g H_2O_2/kg DS was applied to biological sludge samples preceding anaerobic sludge digestion. Single stage anaerobic digestion under thermophilic conditions was compared with two-stage anaerobic digestion (mesophilic digestion prior to thermophilic digestion). The comparison was in terms of solid reductions and specific methane productions.

2. Materials and methods

2.1. Sludge characterization

Waste activated sludge (WAS) was sampled from the municipal wastewater treatment plant in Izmir, which has extended aeration activated sludge plant with nutrient removal facilities. At the start-up of the reactors, inoculum sludge was taken from a full-scale upflow anaerobic sludge blanket (UASB) reactor treating beer industry wastewater. Dried solids (DS), volatile solids (VS), pH, electrical conductivity (EC), and CST are analyzed to determine the characteristics of sludge. Results are shown in Table 1. All analyses are according to the procedures given in the Standard Methods [27]. pH and electrical conductivity measurements were carried out with a 890 MD pH meter and a YSI Model 33 conductivity-meter, respectively.

2.2. Experimental procedure

2.2.1. Fenton process

In Fenton experiments, a ratio of 0.067 g Fe(II) per gram H_2O_2, and 60 g H_2O_2/kg dried solids (DS) was applied to a 1.5 L sludge sample. This dose combination is from an optimization study which is using Box–Wilson Statistical Design Method. Disintegration degree (DD) [22] was used as a system response for evaluation of floc disintegration. The results were given in our previous study [11]. The Fe(II)/H_2O_2 ratio used in this study is in agreement with [24]. Fenton process is carried out by adjusting the pH to 3 with H_2SO_4. The second step is the addition of Fe(II) at certain concentrations. After this, H_2O_2 is added to the sample. The mixed sample is stirred at 100 rpm for 60 min. After reaction, the sample is neutralized with $Ca(OH)_2$. In Fenton experiments, ferrous ($FeSO_4 \cdot 7H_2O$) is used as the source of Fe(II), ferrous ($FeSO_4 \cdot 7H_2O$) is of analytical grade from Merck. Hydrogen peroxide solution (37% (w/w)) in stable form, H_2SO_4 (98–99%) and NaOH are all of analytical grade from Merck.

Table 1
Properties of waste activated sludge and anaerobic inoculum sludge.

Parameters	Activated sludge	Anaerobic inoculum sludge
pH	7 ± 0.2	8.22 ± 0.1
Electrical conductivity (EC, μS/cm)	7.21 ± 1.42	3.12 ± 0.3
Redox potential (ORP, mV)	35 ± 2	− 185 ± 3
Dried solids (DS, %)	1.81 ± 0.36	7.5 ± 0.3
Volatile solids (VS, %)	54.44 ± 1.92	82.5 ± 1.9
Suspended solids (SS, mg/L^{-1})	13500 ± 650	72800 ± 3986
Volatile suspended solids (VSS, mg/L^{-1})	9500 ± 348	65250 ± 4265
Capillary suction time (CST, s)	142.5 ± 16.48	400 ± 15.9
Crown press application		
Final cake solids (%)	10.31	–
Particle size (μm)		
Surface weighted mean D [3,2]	18.444	221.876
Volume weighted mean D [4,3]	77.212	1094.572
d (0.1)	9.970	121.798
d (0.5)	46.496	1204.415
d (0.9)	160.299	1583.540

2.2.2. Anaerobic digestion studies

Four lab-scale anaerobic reactors are used in sludge digestion. Two of them are operated as control reactors without Fenton's application, where the others are fed with Fenton processed sludge. In the first stage of anaerobic digestion studies, two lab-scale anaerobic reactors with the volume of 13.5 L were operated at 55 ± 2 °C in thermophilic conditions. Control reactor is marked as TC, and the reactor fed with Fenton processed sludge is marked as TF. In the second stage of anaerobic digestion, 8.5 L lab-scale anaerobic reactors operated at 37 ± 2 °C in mesophilic conditions were used. The control reactor was coded as TMC and the reactor fed with Fenton processed sludge was coded as TMF. In the second stage, sludge taken to the TC was fed to the reactor coded as TMC and sludge taken to the TF was fed to the reactor coded as TMF. The reactors were heated and the temperature was kept constantly by heat transfer oil jacket which is constructed from a stainless-steel. This reactor is operated with PLC for both stages. Mechanical mixers were used in the reactors. In the start-up phase, inoculum sludge was fed to reactors. After that, 1/2 volume of the reactor content was withdrawn and the same volume of activated sludge was fed to the reactors. In our previous study [11], different sludge retention times were carried out for the same sludge samples in mesophilic conditions. 5 day sludge retention times gave the best results in terms of stabilization degree. Hence, all reactors were operated as semi batch system with a 5 day sludge retention time in digestion studies. To see the temperature effect on anaerobic biodegradability of sludge, sludge retention time in reactors operated in thermophilic conditions was chosen as the same in reactors operated in mesophilic conditions. In semi batch systems with 5 days of sludge retention time, 1/5 of the total volume of sludge in reactors was withdrawn to the reactors and the same volume of sludge content was fed everyday during the operation period. During the 30 day operation period, 2.7 L of sludge was withdrawn and the same volume of sludge content was fed to the TC and TM reactors, then 1.7 volume of sludge from the TC and TM were withdrawn to the TMC and TMF respectively, and every day the same volume of sludge was fed to the TMC and TMF.

2.3. Analytical methods

For system evaluations, pH and temperature were monitored daily while alkalinity, volatile fatty acid (VFA), and electrical conductivity values were measured three times in a week. For performance evaluations, total dried solids (DS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), protein contents, particle size distribution, daily total gas and methane productions, and CST were measured during the operation period. DS, VS, SS and VSS analyses were regularly done according to the Standard Methods [27]. CST values were analyzed with a Triton A-304 M CST-meter. Particle size distributions were monitored by using a Malvern Mastersizer 2000QM analyzer. The belt-press simulator of crown press supplied from Phipps and Bird, Richmond, VA was used for evaluation of dewatering properties of sludge. Sludge slurry (200 mL) was drained through a screen and the volume collected after 2 min was measured. The solids remaining on the screen were then pressed and the final cake solids determined. Methane productions were determined by liquid displacement method. In this method gas passes through the distilled water including 3% (w/v) NaOH [13]. Due to the lack of digital device to measure the amount of gas produced, gas valves of the reactors were first closed for about 1 h and then opened. The liquid displacements were converted to the daily productions. Specific methane productions (SMP) were determined as $mLCH_4/gVS$ based on volatile solids and daily methane productions. Gas components (CO, CO_2, and H_2S) were analyzed by a Dräger model X-am 7000 multi gas analyzer. Volatile fatty acid (VFA) measurements were