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SONO-OXIDATIVE PRE-TREATMENT OF WASTE ACTIVATED SLUDGE BEFORE ANAEROBIC BIODEGRADATION

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Abstract - The effects of sonication, potassium ferrate (K_2FeO_4) oxidation and their simultaneous combination (called "sono-oxidative pre-treatment") on chemical properties and anaerobic digestion of waste activated sludge (WAS) were investigated and compared comprehensively. Based on chemical parameters, the optimum operating conditions were found to be 0.3 g K_2FeO_4/g total solids (TS) dosage for 2-h individual K_2FeO_4 oxidation, 0.50 W/mL ultrasonic power density for 10-min individual sonication and, lastly, the combination of 2.5-min sonication at 0.75 W/mL ultrasonic power density with 2-h chemical oxidation at 0.3 g K_2FeO_4/g TS dosage for sono-oxidative pre-treatment. The disintegration efficiencies of these methods under the optimized conditions were in the following descending order: 37.8% for sono-oxidative pre-treatment > 26.3% for sonication > 13.1% for K_2FeO_4 oxidation. The influences of these methods on anaerobic biodegradability were tested with the biochemical methane potential assay. It was seen that the cumulative methane production increased by 9.2% in the K_2FeO_4 oxidation reactor, 15.8% in the sonicated reactor and 18.6% in the reactor with sono-oxidative pre-treatment, compared to the control (untreated) reactor.
Keywords: Sludge digestion; Potassium ferrate; Pre-treatment; Sonication; Waste Activated Sludge (WAS).

INTRODUCTION

The activated sludge process is one of the most commonly used biological processes for treatment of both domestic and municipal wastewaters. Inevitably, the formation of large amounts of excess biomass (called "waste activated sludge, WAS") is the most important disadvantage of the activated sludge process. Prior to final disposal of the WAS, it must be treated, because its improper disposal brings about a significant threat for ecological systems due to its highly putrescible nature and its pathogen content (Şahinkaya and Sevimli, 2013a). However, the treatment and disposal of the waste sludge are among the most difficult and expensive problems in the treatment plants. The cost of its treatment and final disposal may also be up to 60% of the total operating cost of the wastewater treatment plants (Wei *et al*., 2003). In order to stabilize the WAS, a high rate anaerobic digester is a widely utilized process with the benefits of mass reduction, methane production, and improved dewatering properties of the digested sludge. However, anaerobic digestion of the waste sludge requires long retention times of up to 20 or more days, since extremely slow hydrolysis of the microorganism cells in the sludge is the rate-limiting step of the digestion process (Nickel and Neis, 2007). For this reason, physical, chemical, biological and combined sludge pre-treatment methods may be used prior to the sludge digestion so as to solubilize the sludge, shorten the retention time in the digester and improve its biodegradation efficiency.

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Ultrasonic pre-treatment (called briefly 'sonication') is one of the most effective and eco-friendly sludge disintegration methods (Pilli *et al*. 2011). Sonication is based on acoustic cavitation, which is the rapid and repeated formation and collapse of microbubbles in a liquid medium, resulting of the propagation of ultrasonic waves. When ultrasonic pressure waves pass through a sludge sample, micron-sized dissolved gas bubbles are generated and collapse in less than a few microseconds during sonication. Their collapse causes extreme increments in temperature and pressure. Temperature and pressure can reach values in the ranges of 500–15000 °K and 100–5000 atm in the collapsing bubbles, respectively (Gogate and Kabadi, 2009). Under these extreme circumstances, both highly reactive radicals (such as $OH^{\bullet}$) and shockwaves, which are able to enhance mass transfer and shear induced processes, are generated in the liquid medium (Gogate and Pandit, 2008). These severe physical forces, named "hydro-mechanical shear forces", are the most powerful at low ultrasonic frequencies around 20 kHz, and are the predominant mechanism of the ultrasonic sludge disintegration, as a natural consequence of acoustic cavitation (Pilli *et al*., 2011). These extremely powerful mechanic forces disrupt the sludge flocs, break up the cell walls and membranes, and release the cellular organic substances into the supernatant of the sludge (Pilli *et al*., 2011). An increase in the ultrasonic power, applied to the sludge, increases the intensity of acoustic cavitation and so enhances the disintegration of sludge, which can be proved by an increase in soluble organic matter fractions and a reduction in particle size (Pham *et al*., 2010). Thus, sonication plays the same role as the biochemical hydrolysis in the digestion process and shortens the hydrolysis of sludge and enhances the anaerobic biodegradation and the production of methane gas (Sahinkaya and Sevimli, 2013b). However, its most important disadvantage is its consumption of high amounts of electrical energy. In order to reduce its capital and operating costs, sonication can be combined with acidification (Şahinkaya, 2015), alkalization (Şahinkaya and Sevimli, 2013b), the Fenton process (Şahinkaya *et al*., 2015) and thermal pre-treatment (Şahinkaya and Sevimli, 2013a). The present work presents a new approach combining sonication with an advanced oxidation method using potassium ferrate (K_2FeO_4).

K_2FeO_4 is a powerful oxidizing agent in the whole pH range (Wang *et al*., 2015) and has a strong potential for disintegration of the waste sludge (Wu *et al*., 2015). In addition, oxidation and reduction products of K_2FeO_4 are not harmful for humans and the environment, as they are essentially iron oxy/hydroxides (Anquandah *et al*., 2013). With these features, K_2FeO_4 is a good alternative oxidizing reagent for sludge pre-treatment. Its oxidative sludge disintegration mechanism is based on the disruption of sludge flocs and destruction of cell walls and membranes by ferrate anion (FeO_4^{2-}) (Wu *et al*., 2015), which is one of the strongest water-stable oxidising species known, so that extracellular and intracellular organic substances are transfered from the solid phase into the aqueous phase of the WAS. Thus, both the rate and efficiency of the sludge digestion are enhanced as a result of the increase in the solubilization of sludge. In a similar study by Ye *et al*. (2012), the effects of K_2FeO_4 oxidation on sludge disintegration were investigated and it was found that the waste biological sludge was effectively disintegrated with increasing doses of K_2FeO_4 up to 0.81 g/g total solids (TS), after a 2-h oxidation period. In another study, Wu *et al*. (2015) examined the influences of K_2FeO_4 oxidation on the disintegration and anaerobic biodegradability of sludge from a municipal wastewater treatment plant. Their results showed that, while maximum sludge disintegration was achieved at a dosage of 500 mg/L (equal to 0.1 g/g TS) K_2FeO_4, cumulative biogas production was augmented by about 44%. Therefore, K_2FeO_4 oxidation was reported as an alternative method for the disintegration of excess biological sludge before anaerobic digestion.

Although there are many research studies on sludge disintegration by individual sonication and oxidation methods, there is not any research on the synergistic effects of the simultaneous combination of sonication and K_2FeO_4 oxidation methods on the disintegration and anaerobic biodegradation of sludge in the literature. Therefore, the main aim of this study is to provide some insight for the improvement of an environment-friendly combined sludge disintegration method. For this aim, the individual and simultaneous influences of sonication and K_2FeO_4 oxidation methods were investigated to enhance both the disintegration and anaerobic biodegradability of the WAS. In order to show the synergistic effects of these methods, sludge disintegration was represented by the disintegration degree (DD_{COD}, as a function of soluble and total chemical oxygen demand concentrations) and extracellular polymeric substances (EPS, which are primarily composed of carbohydrate and protein) in the supernatant. In order to determine the synergistic effects of sono-oxidative pre-treatment on anaerobic biodegradability of the WAS, biochemical methane production (BMP) assays were performed in batch mesophilic reactors.

MATERIALS AND METHODS

Waste Activated Sludge

Sludge samples were obtained from the outlet of a final clarifier of a full-scale municipal wastewater treatment plant. The WAS had a pH of 7.2, total chemical oxygen demand (*tCOD*) of 9100 mg/L, soluble chemical oxygen demand (*sCOD*) of 70 mg/L, total solids (TS) of 9770 mg/L, suspended solid (SS) of 8010 mg/L, volatile suspended solid (VSS) of 5980 mg/L, soluble protein of 35 mg/L and soluble carbohydrate of 25 mg/L. Before the experiments, the sludge concentration was adjusted to 1% TS content through removing or adding supernatant obtained by sludge settlement.

The mesophilic anaerobic seed sludge samples (used in the BMP assay) were collected from an anaerobic sludge digester of an industrial wastewater treatment plant using an activated sludge process. The anaerobic inoculum had a pH of 7.6, *tCOD* of 10145 mg/L, TS of 21800 mg/L, SS of 20610 mg/L, volatile solids (VS) of 3560 mg/L and VSS of 3205 mg/L.

The anaerobic seed sludge and waste activated sludge samples were stored in the dark at +4 °C up to 7 days, before the experiments. All chemicals were of analytical grade. Ultra-pure water was used for all analyses.

Sludge Disintegration Experiments

In order to observe the individual effects of K_2FeO_4 oxidation on the sludge disintegration, the experiments were carried out under different K_2FeO_4 dosages at the original pH of the WAS. The oxidative pre-treatment experiments were performed in a jar tester (Mtops, South Korea) using a 250 mL volume of the WAS. After the addition of K_2FeO_4 to the sludge samples, it was assumed that the oxidation reaction was started and then the reaction mixture was stirred at 60 rpm mixing speed for a 2-h reaction period at room temperature.

Sonication was performed via an ultrasonic homogenizer (Bandelin, Germany) equipped with a TT 13 probe (Bandelin, Germany). Its maximum power output was 200 W at a fixed frequency of 20 kHz, which is the most effective frequency for the sludge disintegration. The ultrasonic power density applied to the sludge was adjusted by the input power setting of the equipment. During the sonication experiments, the sludge samples were not mixed, but were homogenized by the turbulence effect of acoustic cavitation. In the each experimental run, 100 mL of the sludge was placed in a pyrex-glass beaker. The ultrasonic probe was immersed 2 cm into the WAS. Then, the sludge samples were sonicated at low ultrasonic densities (0.50, 0.75 and 1.00 W/mL) for varying sonication times from 1 min to 30 min.

Sono-oxidative pre-treatment is the simultaneous combination of sonication with 2 h - K_2FeO_4 oxidation. In the sono-oxidative pre-treatment experiments, the ultrasonic power density and sonication period were optimized at a fixed potassium ferrate dosage (0.3 g/g TS), since the optimal dosage of K_2FeO_4 was determined as 0.3 g/g TS in the oxidative pre-treatment experiments. After the desired amount of K_2FeO_4 was added to the sludge, the reaction mixture was sonicated and the sono-oxidative pre-treatment was initiated. After sonication, the reaction mixture was kept at room temperature until the end of the 2 h pre-treatment period. The individual sonication and sono-oxidative pre-treatment experiments were carried out at 0.50, 0.75 and 1.00 W/mL at varying sonication periods from 1 min to 30 min. In this way, the contribution of K_2FeO_4 oxidation to the energy efficient sono-oxidative pre-treatment method was determined.

Biochemical Methane Production (BMP) Assay

The anaerobic biodegradability experiments of untreated, chemical oxidized, sonicated and sono-oxidized sludge samples were carried out by BMP tests in the batch mesophilic reactors, according to the study of Eskicioglu *et al*. (2007). In the BMP assays, the anaerobic inoculums (20 mL) were first placed into 125 mL bottles and then the pre-treated or untreated sludge samples (80 mL) were added. After a mixture containing equal parts of $NaHCO_3$ and $KHCO_3$ to achieve an alkalinity of 4000 mg/L (as $CaCO_3$) was added to the bottles, the bottles (120 mL) were sealed. Nitrogen flushing was applied to the batch reactors in order to remove the oxygen. The batch reactors were kept in a darkened temperature-controlled incubator at 36±2 °C, until they stopped producing biogas in the BMP assays. The reactors were shaken manually once a day for proper contact of seed and substrate. Biogas and methane gas were measured daily by the liquid displacement method.

Analytical Procedures

After the pre-treatment experiments, the samples were cooled to room temperature, and all analyses were carried out for samples at room temperature. The samples were used directly for the measurements of TS, SS, VS, VSS and *tCOD* according to the procedures of Standard Methods (APHA/AWWA/WEF, 2005). Before the measurements of soluble carbohydrate, protein and *COD*, the samples were centrifuged at 2500 rpm for 15 min, and the supernatant was filtered through a 0.45 µm membrane filter (Sartorius). Soluble COD was measured in the filtrate according to the Standard Methods (APHA/AWWA/WEF, 2005). The soluble carbohydrate and protein analyses were carried out colorimetrically by the modified Lowry method (Pierce, USA) and phenol–sulphuric acid method (Dubois *et al*., 1956), respectively. Sludge pH and temperature were analyzed using a multi-parameter measuring instrument (Hach Lange, Germany). All measurements were performed in triplicate.

The disintegration degree (DD_{COD}) is the main parameter to evaluate the performance of the pre-treatment methods for sludge disintegration, and was defined as the ratio of *sCOD* increase upon pre-treatment to the maximum possible sCOD increase (Eqn. (1)) (Zhang *et al*., 2007),

$$DD_{COD}\,(\%) = \frac{(sCOD_d - sCOD_0)}{(tCOD - sCOD_0)} \cdot 100 \qquad (1)$$

where $sCOD_d$ is sCOD of the pre-treated sludge (mg/L), $sCOD_0$ is *sCOD* of the raw sludge (mg/L) and *tCOD* is tCOD of the raw sludge (mg/L).

The total volume of biogas was first measured by passing it through a liquid containing 2% (v/v) H_2SO_4 and 10% (w/v) NaCl (Beydilli *et al*., 1998). Then, the volume of methane gas was determined by using a liquid containing 3% NaOH to scrub out the carbon dioxide (CO_2) from the biogas (Razo-Flores *et al*., 1997). The volumes of biogas and methane gas were measured daily or every other day by the liquid displacement method.

RESULTS AND DISCUSSION

Effect of K_2FeO_4 Oxidation on Sludge Disintegration

K_2FeO_4 oxidation experiments were performed with a 2-h oxidation period at room temperature. The results of individual K_2FeO_4 oxidation experiments are presented in Figure 1. As seen from these graphs, the sludge disintegration was improved steadily with increasing K_2FeO_4 dosage up to 0.3 g K_2FeO_4/g TS. The concentrations of sCOD, carbohydrate and protein in the supernatant were increased significantly from 70, 15 and 35 mg/L to 1260, 70 and 240 mg/L at 0.3 g/g TS dosage, respectively. At this dosage, the DD_{COD} value was calculated as 13.1%. This increment was due to the disruption of bacterial flocs as a result of oxidation of the extracellular organic matter, the destruction of cell walls and membranes by ferrate (FeO_4^{2-}), and thereafter the release of organic fractions into the aqueous phase. When the K_2FeO_4 dosage was augmented to 0.4 g/g TS, soluble COD, carbohydrate and protein concentrations were increased negligibly to 1675, 105 and 299 mg/L, respectively. However, a further increase in K_2FeO_4 dosage to 0.5 g/g TS led to a decrease in the concentrations of soluble COD, carbohydrate and protein to 1370, 95 and 275 mg/L, respectively. This decrease might result from the oxidation of organic material in the supernatant by excess K_2FeO_4, since FeO_4^{2-} (ferrate) is a non-selective and powerful oxidizing agent. Therefore, the optimal K_2FeO_4 dosage was determined to be 0.3 g/g TS for the oxidative sludge pre-treatment method in this study. Contrary to this finding, Wu *et al*. (2015) reported that the maximum sludge disintegration was achieved at a dosage of 500 mg/L K_2FeO_4 (equal to 0.1 g/g TS), and that higher dosages reduced the disintegration efficiency by oxidizing the solubilized organic materials. In another study, Ye *et al*. (2012) found that the waste sludge was effectively disintegrated with increasing dosages of K_2FeO_4 up to 0.81 g/g TS, after a 2-h oxidation period. These differences in the results of sludge disintegration experiments are caused mainly by different chemical and biological characteristics of the WAS (such as pH, buffering capacity, bacterial cell content, inorganic ions and organic materials, which can be reacted with non-selective oxidizing ferrate ions) and grade of the K_2FeO_4 reagent utilized in these studies.

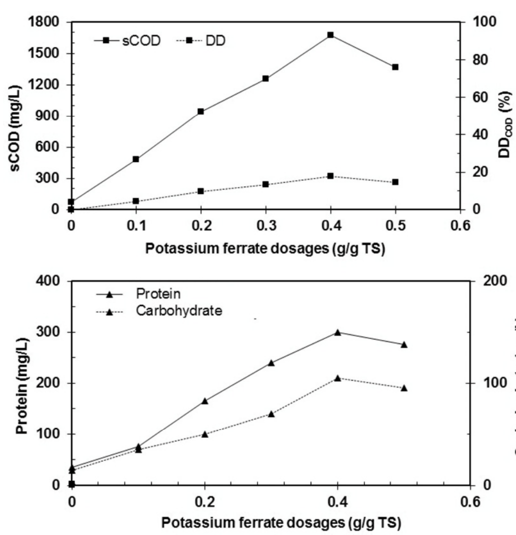

Figure 1: Effect of K_2FeO_4 oxidation on sludge disintegration.

Effect of Sonication on Sludge Disintegration

In order to investigate the influences of sonication period and ultrasonic density at a fixed frequency of 20 kHz, individual sonication experiments were carried out by varying ultrasonic densities from 0.50 to 1.00 W/mL in the time range of 1–30 min. As illustrated in Figure 2, the sludge disintegration was promoted steadily with an increase in ultrasonic density and extending the sonication period. Individual sonication at the densities of 0.50, 0.75 and 1.00 W/mL resulted in a significant increment in the sCOD concentration from 70 to 2450, 2750, 3180 mg/L in the first 10 min, and 3510, 4100, 4395 mg/L in the total sonication period of 30 min, respectively. Based on these sCOD results, the DD_{COD} values were calculated as 26.3, 29.7 and 34.4% for 10 min sonication, and 38.1, 44.6 and 47.9% for 30 min sonication at 0.50, 0.75 and 1.00 W/mL densities, respectively. Soluble carbohydrate and protein concentrations were increased from 15 to 125, 185, 310 mg/L and from 35 mg/L to 595, 845, 1485 mg/L in the first 10 min; soluble carbohydrate and protein concentrations were 240, 275, 410 mg/L and 930, 1255, 1970 mg/L at the end of a 30 min sonication period at 0.50, 0.75 and 1.00 W/mL densities, respectively. The ratios of sCOD concentrations in the first 10 min compared to those at 30 min at the densities of 0.50, 0.75 and 1.00 W/mL were 69, 68 and 72%. Therefore, it was observed that the sludge was disintegrated in two stages: an initial rapid disintegration stage in the first 10 min and a slow stage in the remaining part of the sonication period, as shown in Figure 2. The sludge flocs were rapidly disrupted and the exposed cells were disintegrated in the rapid sludge disintegration stage, while additional cells were exposed and damaged by sonication in the following slow disintegration stage (Huan *et al*., 2009). Similarly, Huan *et al*. (2009), Şahinkaya and Sevimli (2013a), Yan *et al*. (2010) and Zhang *et al*. (2007) also reported that the ultrasonic sludge disintegration occurred in two stages. The reason for this rapid disintegration obtained in the first 10 min was the rapid cavitational effect arising from the collapse of powerful transient bubbles created in fractions of microseconds close to microbial cells (Show *et al*., 2007). As a result, the optimum sonication conditions were found to be 10 min sonication at 0.50 w/mL density by taking the concentrations of soluble carbohydrate and protein into consideration in addition to sCOD and DD_{COD}.

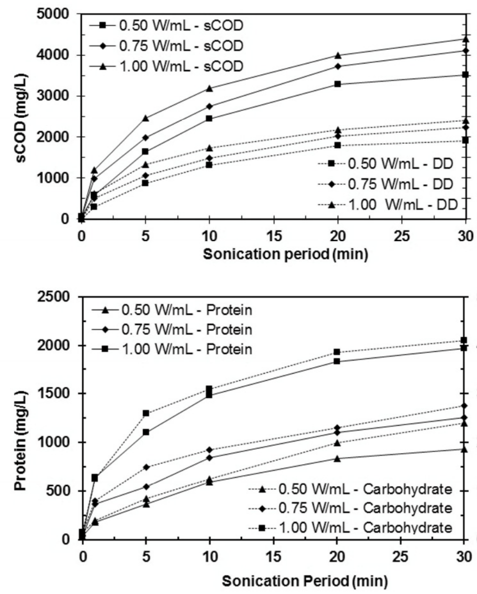

Figure 2: Effect of sonication on sludge disintegration.

Effect of Sono-Oxidative Pre-Treatment on Sludge Disintegration

The influences of ultrasonic density and sonication period in the combined sono- oxidative pre-treatment method were examined to develop a new process consuming less energy than sonication. For this reason, the sono-oxidative pre-treatment experiments was conducted at the constant 0.3 g/g TS K_2FeO_4 dosage (determined as the optimal dosage before).

As illustrated in Figure 3, the degrees of sludge disintegration (DD_{COD}) were apparently higher in the combined method, compared to the individual sonication and K_2FeO_4 oxidation methods. Similar to sonication, the sludge disintegration by sono-oxidative pre-treatment occurred in two stages: a rapid oxidation stage in the first 1 min of the disintegration period and a subsequent slow stage for the remaining part of the disintegration period. However, the rapid sludge disintegration stage was faster, compared to sonication alone. While the sCOD concentration increased considerably from 70 mg/L to 1850, 3150 and 3445 mg/L by sono-oxidative pre-treatment with 1 min-sonication; it was increased to 4890, 5405 and 5675 mg/L with 30-min sonication, respectively. Similar to the increasing trend of the sCOD concentration, the disintegration degree of sludge (DD_{COD}) increased upon prolonging sonication period and increasing ultrasonic density. The

DD_{COD} values were 19.7, 34.1 and 37.4% with sonication of 1 min and 53.4, 59.1 and 62.1% with sonication of 30 min at 0.50, 0.75 and 1.00 W/mL densities, respectively. The soluble carbohydrate and protein concentrations were measured to be 80, 125, 190 mg/L and 445, 600, 905 mg/L by the combined pre-treatment with 1 min-sonication, while they were 300, 320, 400 mg/L and 1120, 1310, 1950 mg/L by the combined pre-treatment with 30 min-sonication at 0.50, 0.75 and 1.00 W/mL, respectively. Therefore, this combined pre-treatment method more efficiently disintegrated the WAS, even at lower ultrasonic densities and shorter sonication periods, compared to individual sonication. In addition, the efficiency of the sono-oxidative method was higher than the total of these two different methods, as summarized in Table 1. As understood from this table, the sludge disintegration was enhanced by synergistic effects as a result of the increasing ultrasonic power applied to the WAS. The proposed mechanism for the synergistic effects is that the sludge flocs were first disintegrated by hydro-mechanical shear forces so that microbial cells released from the disrupted sludge flocs were more effectively exposed to oxidizing FeO_4^{2-}. Thus, more extracellular and intracellular organic substances are released from the solid phase to the aqueous phase of the WAS. On the other hand, as seen from Table 2, prolonging of the sonication period in the combined method caused a decrease in the disintegration efficiency. This decrease in the concentrations of organic materials in the soluble phase might result from the oxidative destruction of cellular organic substances via highly reactive hydroxyl radicals ($OH^{\bullet}$) created by acoustic cavitation and FeO_4^{2-}. Consequently, based on the chemical parameters, the optimal conditions were determined to be 1 min sonication at 0.75 W/mL ultrasonic density at a 0.3 g/g TS K_2FeO_4 dosage for the 2-h sono-oxidative pre-treatment method.

It was noted that, while the energy consumption per unit volume of the WAS was 5 W·min for sonication alone under the determined optimum conditions, it was 0.75 W·min for the combined method in this study (as a function of the multiplication of time with power). In this way, it was proven that the simultaneous combination of sonication with K_2FeO_4 oxidation not only enhances the disintegration efficiency, but also reduces significantly the ultrasonic energy consumption.

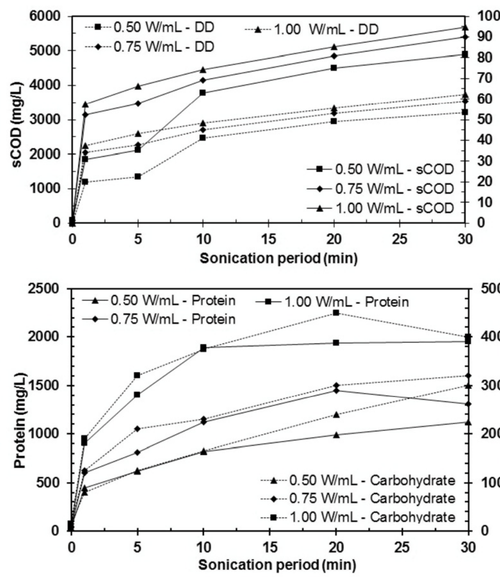

Figure 3: Effect of sono-oxidative pre-treatment on sludge disintegration.

Table 1: Synergistic effects of sono-chemical pre-treatment with 1 min sonication.

Pre-treatment Conditions		DD_{COD} by individual pre-treatment (%)			Actual DD_{COD} by the combined pre-treatment (%)	Syneristic D_{COD} increase (%) (with 1 min - sonication)
K_2FeO_4 dosage (g/g TS)	Ultrasonic Density (W/mL)	K_2FeO_4 Oxidation	Sonication (for 1 min)	Total of DD_{COD} values		
0.3	0.50	13.1	5.7	18.8	19.7	1.1
	0.75		10.1	23.2	34.1	10.9
	1.00		12.4	25.5	37.4	11.9

Table 2: Synergistic effects of sono-chemical pre-treatment with 10 min sonication.

Pre-treatment Conditions		DD_{COD} by individual pre-treatment (%)			Actual DD_{COD} by the combined pre-treatment (%)	Syneristic D_{COD} increase (%) (with 1 min - sonication)
K_2FeO_4 dosage (g/g TS)	Ultrasonic Density (W/mL)	K_2FeO_4 Oxidation	Sonication (for 10 min)	Total of DD_{COD} values		
0.3	0.50	13.1	26.3	39.4	41.1	1.7
	0.75		29.7	42.8	45.1	2.3
	1.00		34.4	47.5	48.5	1.0

Effect of Pre-Treatment Methods on Anaerobic Sludge Digestion

The BMP assays were performed in the batch mesophilic (36±2 °C) anaerobic reactors in order to examine the influences of these three disintegration methods under their own optimum conditions on the anaerobic biodegradability of WAS. The experimental results can be seen in Figure 4. As shown from this graph, sono-oxidative pre-treatment obviously shortens the rate-limiting hydrolysis phase, and promoted the anaerobic biodegradability of the WAS. While maximum substrate usage in the pre-treated reactors happened in the first week of the incubation period; it was seen in the reactor with raw sludge in the third week. This result was expected due to the considerable increment in the solubilization of WAS via the pre-treatment application, prior to the anaerobic digestion (Pilli *et al*., 2011; Şahinkaya and Sevimli, 2013b; Wu *et al*., 2015). In addition, it was observed that there was no toxic effect on the anaerobic digestion of sludge. While biogas and methane productions were increased relatively by 9% and 9.2% in the reactors with K_2FeO_4 oxidation pre-treatment, 10.8% and 15.8% in the reactors with sonication, the utmost biogas (18.3%) and methane (18.6%) productions were achieved in the sono-oxidative pre-treated reactors at the end of a 60-day digestion period of the BMP assay. Furthermore, the sludge stabilization was also enhanced in the batch reactors. Compared to the untreated reactor, the tCOD reductions in the K_2FeO_4 oxidized, sonicated and sono-oxidative pre-treated reactors were improved by 27.3, 30.1 and 44.8%, respectively. Therefore, the sono-oxidative pre-treatment both increased the methane production and improved the stabilization degree of WAS in the anaerobic digester.

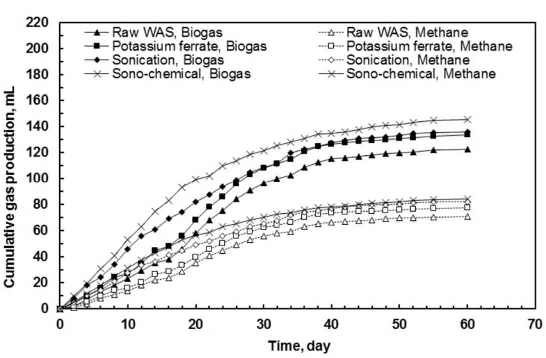

Figure 4: Effects of sludge pre-treatment methods on anaerobic biodegradability.

CONCLUSIONS

The effects of K_2FeO_4 oxidation, sonication, and sono-oxidative pre-treatment methods on both the disintegration and anaerobic biodegradability of sludge were investigated. Based on the experimental data, the following results can be summarized as:

- While the optimum conditions for individual K_2FeO_4 oxidation and sonication methods were 0.3 g/g TS K_2FeO_4 dosage and 0.50 W/mL ultrasonic density for 10-min, the optimized conditions for sono-oxidative pre-treatment was found to be the combination of 1-min sonication at 0.75 W/mL density with 2-h chemical oxidation at 0.3 g/g TS K_2FeO_4 dosage. The disintegration efficiencies of these methods under the optimized conditions were in the following descending order: 37.8% for sono-oxidative pre-treatment>26.3% for sonication > 13.1% for K_2FeO_4 oxidation.
- The mechanism of sono-oxidative pre-treatment may be that the sludge flocs were first disrupted and disintegrated by vigorous hydro-mechanical shear forces (created by sonication) so that microbial cells released from the disrupted sludge flocs were more effectively exposed to oxidative FeO_4^{2-}. Therefore, more organic substances were released into the soluble phase of the WAS, compared to the individual pre-treatment methods.
- The sludge disintegration by sonication and sono-oxidative methods happened in two stages: a rapid and a subsequent slow disintegration stage.
- The anaerobic digestion was enhanced due to the solubilization of particulate organic matter by the sludge pre-treatment. While relative increases in the methane productions were 15.8% in the sonicated reactor and 9.2% in the K_2FeO_4 oxidized reactor, this increment was 18.6% in the sono-oxidative pre-treated reactor, compared to the unpretreated reactor. Moreover, the anaerobic stabilization of the sludge was also clearly augmented by the sono-oxidative pre-treatment.
- As a result, it was proven that the combination of sonication, even at lower ultrasonic densities and shorter sonication periods, with K_2FeO_4 oxidation promoted both the disintegration and the anaerobic biodegradability of WAS. Hence, this new combined method has been found to be a more energy efficient sludge pre-treatment method in this study.

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