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ANAEROBIC BIODEGRADABILITY ENHANCEMENT OF MEAT PROCESSING WASTEWATER SLUDGE BY FENTON PROCESS

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Abstract: In this study, an advanced oxidation process of Fenton Process was applied to meat processing wastewater sludge for the purpose of sludge disintegration before anaerobic digestion. Fenton Process was applied to the meat processing wastewater sludge samples were taken from a treatment plant located in Denizli, Turkey. In the first stage of the study, experiments were carried out to optimize the process conditions in terms of disintegration using Box-Wilson Statistical Design. Ferrous iron and hydrogen peroxide concentrations were chosen as process variable and disintegration degree parameter based on soluble chemical oxygen demand calculations used as process response. 13% of disintegration degree was obtained at 90 gH_2O_2/ kg Dried Solids and 3 g Fe(III)/kg Dried Solids. After optimization studies for disintegration, sludge digestion studies were carried out using Biochemical Methane Potential (BMP) Test. BMP test results showed that Fenton Process can be used as a sludge disintegration purpose and application of Fenton Process before anaerobic digestion causes 33% higher methane gas production comparing the non-pretreated sludge.

Keywords: Anaerobic digestion, disintegration, Fenton process, filterability, meat processing wastewater sludge

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INTRODUCTION

Meat processing industries generate large amounts of wastes and by-products, e.g. carcasses, feet; offal, hides, bones and blood, corresponding to 40–50% of the total animal weight slaughtered (Cuadros et al., 2011). Meat processing industry wastes have a very complex composition and many of these wastes are either not biodegradable or very slow to degrade in biological processes (Rico et al., 2007). Produced sludge in the treatment units is also a problem due to its non-biodegradable fractions and lipid-rich materials content. However, meat processing wastewater sludge represents a good substrate for biogas production in anaerobic digestion; the hydrolysis of complex particulate in the sludge's content is limited digestion process (Masse et al., 2003). Pretreating organic materials prior to anaerobic digestion aims to enhance hydrolysis and thus effects more complete degradation, as bacterial cells are only able to take up small molecules (Luste et al., 2009). Disintegration was developed as pretreatment of organic materials prior to anaerobic digestion of sludge to enhance hydrolysis and to complete degradation. Pre-treatment of sludge with advanced oxidation processes have attracted growing interest for disintegration of treatment plant's sludge. Advanced oxidation processes such as ozone oxidation (Fall et al., 2018; Zhang et al., 2016), ultrasonic treatment (Zielewicz et al., 2016; Erden and Filibeli, 2010), Fenton process (Pilli et al., 2016; Erden and Filibeli 2010a), and its combinations (Neumann et al., 2017; Tian et al., 2015) were investigated by several researchers as biological sludge's disintegration methods. Mechanism of the mentioned methods is based on formation of hydroxyl radical of a powerful oxidizing agent. These methods were applied to biological sludge samples and there is no study about disintegration of industrial oily sludge with Fenton process.

RESULTS AND DISCUSSION

Sludge

Meat processing wastewater sludge was sampled from a local meat processing wastewater treatment plant in Denizli, Turkey. The properties of meat processing sludge are given in **Table 1**. All analyses were done according to procedures given in Standard Methods (Standard Methods, 2005) and were repeated three times. The values represent the mean of the measurements.

Table 1. Sludge characterization

Parameter	Value
pH	7.06
EC, electrical conductivity (μS)	1845
Alkalinty (mg/L)	2370
SS , suspended solids (mg/L)	6100
TS, total solids (%)	2.9
OM , organic matter (%)	85.6
SRF, specific resistance to filtration (m/kg)	$1.99*10^{12}$
CST, capillary suction time (s)	189.7
COD_s, soluble chemical oxygen demand (mg/L)	240

Fenton Process

Fenton pre-treatment was applied to 1.5 L sludge sample. This method was carried out by firstly adjusting the pH of the sludge to 3 using H_2SO_4. Second step was the addition of Fe(II) at certain concentrations. After this period, different H_2O_2 concentrations were added to the sample. The mixed sample was stirred at 100 rpm for 60 min. After reaction, the sample was neutralized with $Ca(OH)_2$. In Fenton experiments, ferrous ($FeSO_4.7H_2O$) used as source of Fe(II), was analytical grade and purchased from Merck. Hydrogen peroxide solution (37% w/w) in stable form, H_2SO_4 (98–99%) and $Ca(OH)_2$ were all provided from Merck. An amount of 1000 mg/L Fe(II) stock solution was prepared for further dilution to obtain a solution of desired concentrations. Fe(II) stock solution was stored at dark place to prevent oxidation of Fe(II).

Box-Wilson Experimental Design

Box–Wilson experimental design is a response surface methodology, which is an empirical modeling technique, devoted to the evaluation of the relationship of a set of controlled experimental factors and observed results (Mantha et al., 1998). For Fenton process, the significant variables like H_2O_2 and Fe(II) concentration were chosen as the independent variables. H_2O_2 concentration varied between 10 and 100 g/kg while Fe(II) concentration was ranged from 1 to 5 g/kg. The experimental conditions determined by the Box–Wilson experimental design method are presented in **Table 2**. The experiments consist of four axial (A), four factorial (F), and central points (C). The central point was repeated three times resulting in 11 experiments in total. The Statistica 5.0 Computer Program was used for the determination of model. Disintegration degree (DD, %), was chosen as the response for evaluation of disintegration performance of Fenton processed sludge. The response function is given below;

$$E = b_0 + b_1X_1 + b_2X_2 + b_{12}X_1X_2 + b_{11}X_{12} + b_{22}X_{22} \qquad (1)$$

where E is the predicted response function, b_1 and b_2 are the linear coefficients, b_{12} is the cross product

Table 2. The experimental conditions determined by the Box–Wilson experimental design method

Run	X_1 (g H_2O_2/ kg KM)	X_2 (g Fe(II)/ kg KM)
A_1	100	3
A_2	10	3
A_3	55	5
A_4	55	1
F_1	86.8	1.6
F_2	23.2	1.6
F_3	86.8	4.4
F_4	23.2	4.4
C	55	3

coefficient and b_{11} and b_{22} are the model coefficients. The combined effects of variables were evaluated by an analysis of variance (ANOVA). The quality of the fit model as dominated by the coefficient of determination of R^2 and its statistical significance was controlled by the *F*-test in the same program.

Biochemical Methane Potential (BMP) Test

The BMP test was applied to both raw and disintegrated samples (S) for comparison purpose. Anaerobic stock culture was used as inoculum (I). The culture was obtained from the anaerobic digestion unit of Pakmaya Industry in Izmir, Turkey. The stock basal medium (BM) was prepared in distilled water (Speece, 1996). BMP tests were carried out in a 150mL serum bottle with 60mL reaction. The ratio of basal medium/inoculum/sludge in the BMP test was BM/I/S=0.5/1/1 (v/v). All bottles were purged with 75% N_2 and 25% CO_2 containing gas mixture for 3–4 min to obtain anaerobic conditions. The rubber stoppers and screw caps were used to avoid gas leakage from the bottles. The serum bottles were placed in an incubator at a constant temperature of 37 ± 2ºC. Methane gas production was measured daily by liquid displacement method using 3% NaOH (w/v) containing distilled water (Razo-Flores et al., 1997).

Analytical Procedures

For evaluation of disintegration performance, disintegration degree parameter which is developed by Muller (2000) was considered as the main parameter. The other parameters were done according to the procedure given in Standard Methods (2005).

RESULTS AND DISCUSSION

Optimization of Process Conditions

Box Wilson experimental design is an efficient method that is used to analyze the effects of variables on the objective function. The relationship between objective function (DD) and two variables (hydrogen peroxide and Fe(II) dosage) for sludge disintegration was analyzed with Box Wilson experimental design. **Table 3** shows the analysis of variance (ANOVA) of regression parameters of the predicted response surface quadratic model tested for DD (%). Eleven experiments (**Table 2**) for a complete set of the Box Wilson experimental design were carried out to compare the actual and the model data. The F-value was 31.09 for DD. This indicated that the model is statistically significant for DD. The model for DD was significant also by the F-test at the 5% confidence level (p-value <0.05).

Table 3. ANOVA for Box Wilson experimental design model for DD

Source	DD (%)		
	Mean square	F-Value	p-value
Model	301.59	31.09	0.0001
Residual	13.58		
R^2	0.9569		
Adj.R^2	0.9261		
Adeq. precision	13.111		

The following fitted regression model was used to quantitatively investigate the effects of Fenton process on the disintegration of sludge:

$$DD=-25.64+0.49X_1+14.37X_2-0.004X_1X_2-0.003X_{11}+2.77X_{22} \quad (2)$$

The R^2 coefficient gives the proportion of the total variation in the response variable explained or accounted for by the predictors included in the model. Adjusted R^2, which was found to be 0.93 for DD, indicated that 93% of the variability in the response could be explained by the model. The R^2 coefficient in this study ensured a satisfactory adjustment of the quadratic model to the experimental data. The predicted values of the DD and actual results of DD in the present study are given in **Table 4**.

Disintegration degree permits to evaluate the maximum level of sludge solubilization. Increase of DD

Table 4. Actual and predicted values of DD

Run	Predicted DD, %	Actual DD, %
A_1	11.42	13.6
A_2	1.59	0.8
A_3	5.42	6.2
A_4	3.28	3.9
F_1	8.38	6.6
F_2	1.02	1.4
F_3	9.49	7.6
F_4	2.93	3.2
C_1	13.41	13.5
C_2	13.41	13.6
C_3	13.41	13.5

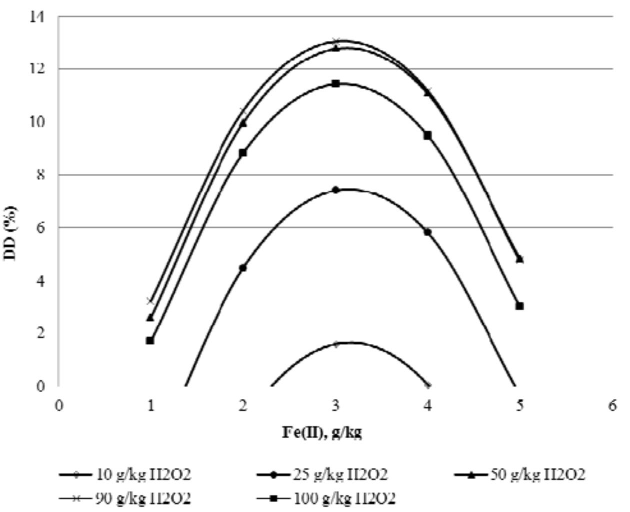

Fig. 1 Variations of DD with Fe(II) concentration at different H_2O_2 concentrations

is determined as the substance that can be readily used to produce methane in the anaerobic digestion [13]. Increase in DD of sludge is a good indicator of floc disintegration. Increasing Fe(II) concentration enhanced the disintegration degree at a certain point (3 g/kg), after which point increasing Fe(II) concentration may have led to loss of some organic matter and started to inhibit disintegration of sludge. The highest DD value was obtained at 90 g/kg H_2O_2 and 3 g/kg Fe(II) application (13%) but 50 g/kg H_2O_2 and 3 g/kg Fe(II) gave the nearest value of 12.8%. So this application was chosen as optimum conditions for Fenton process (Figure 1).

Anaerobic Biodegradability of Fenton Processed Sludge

The BMP assay, in which cumulative methane production was monitored, was applied to both raw sludge and disintegrated sludge for comparison purposes. Different ratio of sludge/inoculum was used in the experiments. Conditions of the experiments and the test code used were given in **Table 5**.

Cumulative methane production in serum bottles was monitored at 40 days (continued until the gas production ceased). The results showed that Fenton process improves the anaerobic biodegradability of industrial oily sludge (Figure 2). Methane gas production was 33% higher in Fenton processed sludge compared with the raw sludge with the application of 1/2 sludge inoculum ratio.

Table 5. BMP test conditions

Test code	Fe(II)/ H_2O_2 (g/ kg DS)	Sludge/ Inoculum Ratio
HI	0/0	1/1
HII	0/0	1/2
FI	3/50	1/1
FII	3/50	1/2

The effects of Fenton Process on Oil Content of Sludge

The main purpose of disintegration is the elimination of the hydrolysis step to accelerate the anaerobic degradation. The first step is the solubilization of complex organics to easy hydrolysis. Fenton process used for the disintegration process was very effective in releasing oil to the liquid phase of meat processing wastewater sludge. While raw sludge's cake oil content was 0.95%, sludge's cake oil content was measured as 0.15%. Oil contents of supernatant was 3 mg/L and 18 mg/L for raw and Fenton processed sludge, respectively (**Table 6**).

The effect of Fenton Process on Dewatering Characteristics of Sludge

CST is a quick test used to evaluate the filterability characteristics of sludge. CST test neglects the shear effect on the sludge and only characterizes the filtration phase of the dewatering process. The bound water content cannot be directly evaluated from the CST test result (Meeten and Smeulders et al., 1995). SRF is a relatively complicated method compared with CST and

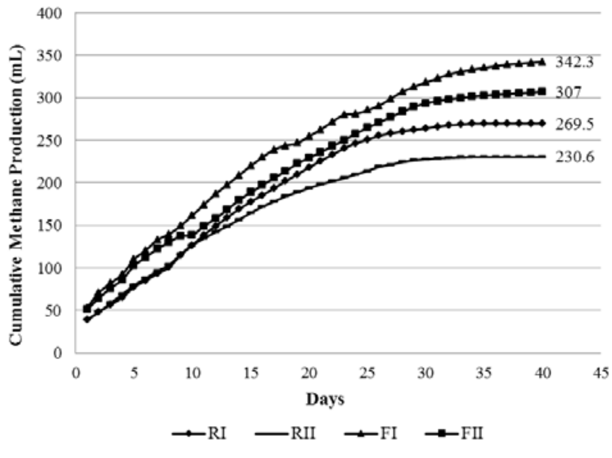

Fig. 2 Results of BMP test

Table 6. The effects of Fenton process on oil content of sludge

Sludge ID	Oil content in sludge's cake, %	Oil content in sludge's supernatant, mg/L
Raw	0.95	3
Fenton processed sludge (3 gFe(II)/kgDS – 50 gH_2O_2 /kgDS)	0.15	18

Table 7. The effect of Fenton Process on dewatering characteristics of sludge

Sludge ID	CST, s	SRF, m/kg
Raw	189.6	1.99×10^{12}
Fenton processed sludge (3 gFe(II)/kgDS – 50 gH_2O_2 /kgDS)	102.4	1.8×10^{11}

gives information about sludge behaviour on mechanical dewatering units. Low values of CST and SRF indicate a good filterability characteristic of sludge. **Table 7** shows CST and SRF values of raw sludge and Fenton processed sludge. CST and SRF values decreased compared with raw and Fenton processed sludge. It can be resulted that Fenton Process increase the sludge dewaterability as shown by the decrease in CST and SRF values. Previous studies carried out with biological sludge support that this positive effect of Fenton Process on dewaterability of sludge (Buyukkamacı, 2004; Erden and Filibeli, 2011).

Conclusions

This investigation deals with disintegration of meat processing wastewater sludge. Fenton process was applied to sludge for this purpose. Optimum conditions were determined as 3 g/kg Fe(II) and 50 g/kg H_2O_2 g/kg application. Fenton methods process increased the anaerobic biodegradability. Methane gas production was 33% higher in disintegrated sludge compared with the raw sludge at the end of the 40 days of incubation. Furthermore, CST and SRF test results showed that Fenton pre-treatment leads to decrease in the biosolids' resistance to dewatering and it can be applied to biological sludge for conditioning purpose before mechanical dewatering units.

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