# The evaluation of integrated physical and biological system on sludge stabilization of refinery

Ali Almasi<sup>1</sup>, Mitra Mohammadi<sup>1\*</sup>, Abdollah Dargahi<sup>2</sup>, Seyed Alireza Mosavi<sup>3</sup>, Alireza Ejraei<sup>3</sup>, Leila Tabandeh<sup>3</sup>, Somayeh Azemnia<sup>4</sup>

<sup>1</sup>Department of Environmental Health Engineering, School of Public Health, Social Development and Health Promotion Research Center, Kermanshah University of Medical sciences, Kermanshah, Iran. <sup>2</sup>Environmental Health Engineering, Faculty of Health, Hamadan University of Medical Sciences, Hamadan, Iran. <sup>3</sup>Department of Environmental Health Engineering, School of Public Health, Kermanshah University of Medical Sciences, Kermanshah, Iran.

<sup>4</sup>Student Research Committee, Kermanshah University of Medical Sciences, Kermanshah, Iran.

\*Corresponding author: E-Mail: m.mohamadi725@gmail.com ABSTRACT

Industrial wastewater treatment sludge including of organic materials that threated of environment and human. The aim of this study is sludge stabilization of refinery by ultrasonic/ anaerobic stabilization. In this experimental study, evaluate effect of ultrasonic (40 Hz, 100 w) on batch anaerobic digestion with volume of 300 ml in 30 min, 60 min and three stages of 15 min. BOD<sub>5</sub> and COD, measurement according to the Standard methods. Regarding to time of sludge stabilization, hydraulic retention time was 35 day. Data analysis was performed by SPSS 20 and Exell 2010. Efficiency integrated system ultrasonic/ anaerobic digestion on sludge stabilization was high (P value<0.05). The maximum removal of COD was 88.4%. The ratio of BOD<sub>5</sub>/COD effluent increased by integrated system (P value<0.05). Ultrasonic integrated with anaerobic biological process, increased sludge stabilization in refinery treatment. Ultrasonic/ anaerobic system had efficiency better than individual wastewater treatment.

**KEY WORDS:** Ultrasonic, Anaerobic Digestion, Refinery Sludge.

## 1. INTRODUCTION

Wastewaters from exploitation and processing units of oil refinery and resulted sludge have serious dangers by surface and groundwater pollution and therefore threatens human health. Hence, wastewater treatment and refinement in these industrial units has great importance (Chen, 2014). According to previous studies, it was recognized that complicated compounds in industrial wastewaters, high concentrations of organic matter, toxicity and little degradability are common biological barriers for pollutants removal from sludge of oil refinement units (Chen, 2008; Bezerrra Rocha, 2012; El-Naas, 2014). Therefore, nowadays there is great need to developing combined technologies for facilitating sludge fixation and making it safe. Application of ultrasonic waves was considered as advanced oxidation processes in combination with other biological methods for making sludge safe which is updated method in wastewater refinement industry and was considered as a key technology in the world (Cesaro and Belgiorno, 2013). In ultrasonic process, ultrasonic waves by creating very high pressure gradient causes to micron expansion and contraction (sonic cavitation) and consequently makes points with 180 Kpa pressure and 5000°K which in turn causes to formation of H• and OH• free radicals, high hydromechanics shear stress and accelerating chemical reactions (Ruiz-Hernando, 2013; Haddadi, 2007). It should be noted that ultrasonic degradation is a physical process which results to no secondary toxic materials. In addition in high toxic compounds concentration and breaking down of recalcitrant organic pollutant like aromatic compounds, aliphatic chlorinated compounds and surfactants into simpler forms is well operated (Kargar and Mahvi, 2012). Anaerobic digestion process alone cannot meet the contaminant discharge standards and therefore combination of biological digestion methods with above-mentioned technologies will result to increasing sludge treatment efficiency (aerobic and/or anaerobic) (Erden, 2010; Braguglia, 2012). In the present study, combined process of ultrasonic and anaerobic digestion applied in order to overcoming problems in non-refinement of sludge resulted from oil refinement process.

## 2. METHODS AND MATERIALS

Present study was conducted as experimental type in laboratory scale with microbial adaptation period of 100 days and 35 days experiments duration. Sludge samples after concentrating and preparation kept in 2-4 $^{\circ}$ C to conducting experiments. Anaerobic biotic reactor made of Pyrex by 300 ml total volume and 250 mL useful volume with discontinuous flow type. For gas exit from reactor, a tube was installed on reactor cap and its end located into water flask (Fig.1). Mesophyll anaerobic digester established on thermal stirrer (aLFA D500) at 200 rpm and temperature range of 36 to 38 $^{\circ}$ C. It should be noted that for preventing light passage, around the reactor were covered by aluminum foil. In order to creating appropriate growth conditions for microorganisms, pH value of reactor contents maintained at  $7.8\pm0.2$  using  $K_2HPO_4$  buffer.

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Figure.1. schematic of anaerobic digestive

In the present study, three reactors with mixed liquid suspended solids (MLSS) concentration of  $28100\pm282$  mg/L and hydraulic residence time of 35 days applied as follow: reactor No. 1 (control): anaerobic digester, reactor No. 2: pre-refinement by ultrasonic on 60 min and reactor No. 3: combined anaerobic digester by applying ultrasonic during 3 days for 15 min. ultrasonic apparatus (DSA100-SK2) had 40 KHz frequency and 100w intensity. It should be noted that all chemicals and reagents purchased from Merck Co. (Germany) with high purity degree. Whole stages including sampling, maintenance and experiments were conducted according to standard instructions for water and wastewater experiments (APHA, 2005). Means differences of reactors efficiency for CCD removal analyzed using SPSS software in significant level of  $\alpha$ =0.05. Excel 2010 utilized for graphs drawing.

# 3. RESULTS AND DISCUSSION

In concentrated sludge sample from final clarifier in Kermanshah Oil Refinery wastewater treatment plant, COD amount was 46683±675 mg/L. Results showed that reactors which affected by ultrasonic waves, though reached to stable state at final days of anaerobic digestion and didn't show better rate, but had better removal efficiency. COD removal percent in control reactor, 60 min pre-treatment along with anaerobic digestion, and combined reactor was 80.9, 82.3 and 88.4 percent, respectively.

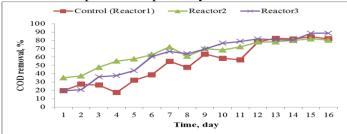


Figure.2. Changes in COD removal by anaerobic digestion reactors

COD decreasing efficiency in 60 min pre-treatment had no significant difference with control reactor. In other words, pre-treatment with ultrasonic waves in reactor No.2 was not able to increase considerably anaerobic reactor efficiency which could be due to presence of chemical pollutants and oils in surplus sludge of oil refinery which their nature were not changed easily by ultrasonic waves in short time period into solution and organic parts. By increasing radiation time from 30 min to 60 min, COD removal reached to 82.3 percent from 80.9 percent. Contact of ultrasonic waves with organic and chemical pollutants causes converting COD easily to soluble form and increases biological degradability. Nosrati (2011) studied disposed activated sludge fixation through discontinuous mesophyll anaerobic digester in which residual COD content decreased from 70000 to 32000 mg/L over 40-day residence time. In other word, COD decreased by 54 percent.

Dilek Sanin (2012), compared SCOD trend in sludge digestion conditions with and without ultrasonic waves and found that soluble organic matter considerably increased due to more rapid hydrolysis than anaerobic digestion without pre-treatment. Cho (2012), found that by increasing ultrasonic waves radiation from 0 to 60 min, SCOD changed from 0 to 10000 mg/L. In other words, longer contact time causes to increasing available soluble and biodegradable matters to microorganisms and fixation would be in better rate. Ultrasound effectively could break down sludge flock and destruction of biological cells. Consequently, bCOD of biodegradable matters resulted from proteins and nucleic acids releases into supernatant (liquid phase) from sludge, therefore degradability will increase. This biodegradable organic part converted into inorganic part (carbon dioxide and methane) through anaerobic digester microorganisms (Agdag, 2007). However there is little information about disposed sludge destruction from industrial wastewater refinery plants, especially from oil refinery. Present study attempted to study a strategy for reducing fixation time, increasing the rate and sludge digestion rate resulted from oil refinery as industrial by-product. COD/BOD5 ratio in anaerobic reactor influent and effluent sludge obtained as 0.21 and 0.30, respectively. According to results of present study, considering to CODe/BOD5 ratio of anaerobic reactor, degradability of sludge after anaerobic digestion via ultrasonic waves partly increased.

Pre-treatment with ultrasonic waves caused to breaking down of organic matter and increasing COD/BOD5 ratio of mixed liquid. This confirms organic matter decomposition during treatment. In the present study, highest COD/BOD5 ration observed in combined reactor. It means that this reactor had better performance in organic matter removal from sludge solution.

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Figure.3. Effect of ultrasonic on effluent COD/BOD ratio

In order to determination of the effect of digestion process on COD removal using one-way analysis of variance at P<0.05 it was recognized that COD removal in just pre-treatment processes at 60 min residence time, there were little difference, so that difference in efficiency with control reactor was not significant (P>0.05). Pre-treatment process alone had no impact on improving anaerobic digestion (P>0.05).

## 4. CONCLUSION

Combined treatment had the best efficiency in sludge fixation parameters removal compared to anaerobic reactors and reactors with pretreatment. However, ultrasound waves caused to accelerating anaerobic digestion duration and showed better efficiency for digestion parameters removal. This could results in decreasing anaerobic digesters volume and consequently could be served as a strategy for preventing of sludge accumulation and disposal of dried sludge in oil refinery and decreasing damages to environment.

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## REFERENCES

Agdag ON, Sponza DT, Co digestion of mixed industrial sludge with municipal solid wastes in anaerobic simulated landfilling bioreactors, J. Hazardous Material, 140, 2007, 75-85.

Bezerrra Rocha JH, Soares Gomes MM, Fernandes NS, Ribeiro de Silva D, Huitle CAM, Application of electrochemical oxidation as alternative treatment of produced water generated by Brazilian petrochemical industry, Fuel Processing Technology, 96, 2012, 80–87.

Braguglia CM, Gianico A, Mininni G, Comparison between ozone and ultrasound disintegration on sludge anaerobic digestion, Environmental Management, 95, 2012, 139-143.

Cesaro A, Belgiorno V, Sonolysis and ozonation as pretreatment for anaerobic digestion of solid organic waste, Ultrasonics Sonochemistry, 20, 2013, 931–936.

Chen C, Wei L, Guo X, Guo S, Yan G, Investigation of heavy oil refinery wastewater treatment by integrated ozone and activated carbon -supported manganese oxides, Fuel Processing Technology, 124, 2014, 165–173.

Chen CM, Yan GX, Guo SH, Yang Y, Pretreatment of super viscous oil wastewater and its application in refinery, Petroleum Science, 5, 2008, 269–274.

Cho S, Shin H, Kim D, Waste activated sludge hydrolysis during ultrasonication: Two-step disintegration, Bioresource Technology, 121, 2012, 480-483.

Dilek Sanin F, Zorba GT, Disintegration of Sludge by Sonication and Improvement of Methane Production Rates in Batch Anaerobic Digesters, Soil Air Water, 41, 2012, 396–402.

El-Naas MH, Alhaija MA, Al-Zuhair S, Evaluation of a three-step process for the treatment of petroleum refinery wastewater, Journal of Environmental Chemical Engineering, 2, 2014, 56–62.

Erden G, Buyukkamaci N, Filibeli A, Effect of low frequency ultrasound on anaerobic biodegradability of meat processing effluent, Desalination, 259, 2010, 223-227.

Haddadi S, Naseri S, Vaezi F, Mahvi AM, Determining the Effects of Various Factors on the Effectiveness of Ultrasonic Treatment of Secondary Effluent, Water and wastewater journal, 63, 2007, 31-38.

Kargar M, Mahvi AH, The survey of ultrasonic on stabilization and dewatering of anaerobic digestive sludge, Environment acknowledge, 38, 2012, 89-94.

Nosrati M, Amani T, Sreekrishnan TR, International Conference on Advances in Biotechnology and Pharmaceutical Sciences, Thermophilic Anaerobic Digestion of Waste Activated Sludge versus Mesophilic Anaerobic Digestion, 2011, 226-229.

Ruiz-Hernando M, Martinez-Elorza G, Labanda J, Llorens J, Dewaterability of sewage sludge by ultrasonic, thermal and chemical treatments, Chemical Engineering Journal, 230, 2013, 102–110.

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