EFFECT OF THERMAL PRETREATMENT ON THE SOLUBILIZATION OF ORGANIC MATTERS IN A MIXTURE OF PRIMARY AND WASTE ACTIVATED SLUDGE

A.M. Aboulfoth [1*], E.H. El Gohary [1] and O.D. El Monayeri [2]

[1]*Environmental engineering department, Faculty of engineering, Zagazig university, Egypt.*
[2]*Arab Academy for Science, Technology and Marine Transportation, Egypt.*

Abstract: The increased demand for advanced techniques in anaerobic digestion over the last few years has led to the employment of various pre-treatment methods prior to anaerobic digestion to increase gas production. These pre-treatment methods alter the physical and chemical properties of sludge in order to make it more readily degradable by anaerobic digestion. Although the thermal pre-treatment presents high energy consumption, the main part of this energy to heat can be recovered from the biogas produced in the anaerobic process. In this research a mixture of primary and waste activated sludge was thermally pretreated at 100, 125, 150, 175 and 200° C in order to determine the effect of thermal pretreatment on improving the solubilization of sludge by increasing the soluble organic fraction (expressed as soluble COD and VFA). Experimental results proved that the solubilization ratio of sludge is depends on the treatment time and the applied temperature and the optimal temperature ranged between 175 and 200° C. The COD solubilization ratio (at 175° C) increased from 11.2% to 15.1% and 25.1% when the time of treatment increased from 60 min to 120 and 240 min respectively. The experimental data could be fitted to obtain an empirical model (Known as the enzyme-kinetic equation) relating the COD solubilization ratio of sludge and VFA concentration to the applied temperature and the heating time.

* Correspondence to: Aboulfotoh A. M., Tel.: +201111784499.
E-mail: aseaf_1@yahoo.com

INTRODUCTION

The processing and disposal of sewage sludge is one of the most important and complex problems in the operation of municipal wastewater treatment plants (Weemaes et al, 1998). Due to the quantitative and qualitative expansion of wastewater treatment, sludge produced from biological wastewater treatment processes has dramatically increased in recent decades (Kim et al., 2002). The main problem related to sludge treatment is its cost which usually ranges from 20% to 60% of the total operating costs of the wastewater treatment plant (Marcos et al, 2005).

Anaerobic digestion AD is an attractive technology for the treatment of organic waste (Romano et al., 2009). Anaerobic digestion plays an important role in wastewater treatment processes. It includes a series of biochemical processes by different microorganisms to degrade organic matter under anaerobic conditions. Methane, the digestion byproduct, is a rich source of renewable energy, which can help to replace fossil fuel to contribute to environmental conservation and sustainability (Pavlostathis et al, 1991). A major benefit is the large volume reduction of the sludge. Other beneficial features include stabilization of the sludge, inactivation and reduction of pathogens, and improvement of the sludge dewaterability (Apples et al, 2010), which is very important for further handling after AD.

Activated sludge is resistant to anaerobic digestion. The cell contents are very degradable but they are protected by the tough cell walls. Biomass also holds onto water, so it is difficult to dewater (Garg 2009). Anaerobic degradation of particulate materials and macromolecules is considered to occur in four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In sludge digestion, hydrolysis is the rate-limiting step (Tiehm et al, 2001). To use particulates as a substrate, bacteria release extracellular enzymes that break down and solubilize organic particulate matter (Madigan et al, 2005).

To improve digestion efficiency, the most logical approach is to disrupt the microbial cells in the sludge. The disintegration of sludge has therefore been introduced to solubilize and convert slowly biodegradable, particulate organic materials to readily biodegradable low-molecular- weight compounds (Oh, 2006). Different strategies have been studied in order to enhance anaerobic digestion of sludge. Among those wet sludge technologies group various technologies that include physical, chemical, mechanical, thermal, biological, etc.

Thermal pretreatment is considered a promising method to improve the properties of organic solid wastes, which can not only improve the hydrolysis rate of organic solids but also improve the dewaterability (Wang et al., 2010). Heat energy applied during thermal pretreatment acts by disrupting the chemical bonds of the cell wall and membrane, thus releasing the cell components into solution. Moreover, when combined with anaerobic digestion, energy required to perform thermal treatment can be positively balanced by biogas production (Kepp et al, 1999).

Thermal pretreatment has been studied using a wide range of temperatures ranging from 60 to 270 ºC. In practice, the optimum temperature is in range of 160-180ºC and treatment times from 30 to 60min. pressure associated to these temperatures may vary from 600 to 2500 kPa (Weemaes et al, 1998).

Hiraoka et al. (1985) studied the effect of thermal pretreatment of sludge on subsequent anaerobic digestion when the pretreatment temperature is relatively low (below 100 ^{0}C). Waste activated sludge (WAS) was treated at 60, 80 and 100 ^{0}C under pressurized conditions of 3 Kg/cm^2. For 60 and 80 ^{0}C Volatile solids (VS) reduction was not significantly improved. At 100 ^{0}C an improvement between 5 and 10% was observed. However, in terms of gas production, a maximum was reached at 60 ^{0}C. The results obtained above were used to conduct a pilot plant study. WAS was treated at 60 ^{0}C for 120 minutes with a pressure of 3 Kg/cm^2. An increase in VS destruction between 2 and 9% was observed.

Li and Noike (1992) studied the effect of thermal treatment of waste activated sludge by varying the temperature of pretreatment between 62 and 175^{0}C and maintaining a constant treatment time of 30 minutes. Solubilization ratios increased from 25 to 45% as the temperature increased, except a decrease observed at 90^{0}C. To study the effect of thermal pretreatment on anaerobic digestion laboratory-scale chemostat-type experiments were conducted at SRTs of 1.5, 3, 5 and 10 days at 35^{0}C. The pretreatment temperatures used were 120, 150, 170, and 175^{0}C for 30 minutes. Both VSS degradation efficiency and COD removal efficiency were higher in all cases for pretreated sludge. The best results were obtained for a temperature of 170 ºC and SRT of 5 days, an increase of 30% in VSS degradation efficiency over the control was observed.

Zheng et al. (1998) studied rapid thermal conditioning (RTC) of partially digested sludge at three different temperatures: 100, 160 and 220 ^{0}C for 30 seconds. VS reductions of 10, 20, and 40%

were obtained respectively. At 220 ^{0}C a small mineral solids reduction was also achieved. (WAS) was also treated at 220 ^{0}C for 30 seconds achieving a 55% VS reduction.

Bougrier et al. (2006a) compared the thermal pretreatments (130 ºC, pH=10, 150 ºC and 170 ºC during 30min) performance of waste activated sludge collected from urban wastewater plants with untreated sludge samples. The results indicated that there was positive effect on solubilization rates and methanization when thermal pretreatment was added. Particularly, the 170 ºC treatment led to comparable results in anaerobic digestion performance increase: about 80% improvement in removal of matter and in biogas yield.

However, impacts of thermal hydrolyses depend on sludge characteristics and site conditions and systematic tools, mathematical model approaches need to be developed for a more generic process description.

The objective of this study was to investigate the effects of thermal pretreatment on the solubilization of organic matters in a mixture of primary and waste activated sludge under varied temperatures and the time of treatment. Also, gathering the experimental data needed for building of an empirical mathematical model describing the relation between the applied temperature & the time of treatment and the rate of COD solubilization.

MATERIAL AND METHODS

The sludge used in this study was a thickened combined sludge (primary and waste activated sludge) from municipal conventional activated sludge WWTP located at Menia El-Kamh, Sharquiah, Egypt. In order to study the hydrolysis process of the sludge, a series of experiments were performed at different temperatures (100, 125, 150, 175 and 200 ºC). The sludge samples was put in a glass beaker (2 L) and placed in an oven to maintain the desired reaction temperature. Chemical oxygen demand (COD), soluble chemical oxygen demand (sCOD) and Volatile fatty acids (VFA) were measured every (30, 60, 120, and 240 minutes). All measurements were duplicated, and the results given are mean values. Chemical oxygen demand (COD) and soluble Chemical oxygen demand (CODS) was measured according to method (508) of standard methods (Standard Methods, 1985), For soluble COD, samples were first centrifuged at 3000 rpm for 30 minutes and then filtered using 0.45 μm filter before digestion. In this procedure the sample is heated in a COD meter, at 150°C for two hours in vials containing a strong oxidizing agent (potassium dichromate). During the reaction, the oxidizable organic fraction reduces the dichromate ion $(Cr_2O_7^{-2})$ to green chromic ion (Cr^{+3}) then it was measured by titration method against FAS. Volatile fatty acids were measured according to the method proposed by Kapp. (1984), (1992) and modified by Buchauer (1998) as follow

- Before analysis the sample is filtered through a 0.45 μm membrane filter. In the case of online application an ultra-filtration unit is used.
- Filtered sample (20 ml) is put into a titration vessel, the size of which is determined by the basic requirement to guarantee that the tip of the pH electrode is always immersed below the liquid surface.
- Initial pH is recorded.
- The sample is titrated slowly with 0.1 N sulphuric acid until pH 5.0 is reached. The added volume of the titrant is recorded.
- More acid is slowly added until pH 4.3 is reached. The total volume of the added titrant is again recorded.
- The latter step is repeated until pH 4.0 is reached, and the volume of added titrant recorded once more.
- A constant mixing of sample and added titrant is required right from the start to minimize exchange of CO2 with the atmosphere during titration. Depending on the system in use this is done via a small impeller or via a magnetic stirrer.
- Then substitute in the following equation to get VFA concentration
-

$$VFA = \frac{131340 \times N \times V_{4,5}}{V.S.} - \frac{3.08 \times N \times V_{4,3}}{V.S} - 25 \quad (1)$$

where

VFA = the required volatile fatty acid concentration in (p.p.m)

N = the normality of the used acid

$V_{4,5}$ = the volume of acid required to decrease pH from 5 to 4

$V_{4,3}$ = the volume of acid required to decrease pH from initial pH to 4.3

V.S. = volume of sample

Table 1 shows the average concentration of thickened combined sludge used in this study.

Table 1. Raw sludge characteristics

Parameters	Sludge
pH	6.1 – 6.5
tCOD (g/l)	57.80
sCOD (g/l)	3.10
sCOD/tCOD	5.40%
sVFA (g/l)	2.00
Ammonia (p.p.m)	480 - 550
Color	Dark brown

RESULTS AND DISCUSSIONS

Effect of thermal pretreatment on COD solubilization

Table (2) shows the sCOD concentrations for the different tested temperatures (100, 125, 150, 175 and 200 ^{o}C). The total COD concentration almost remains constant at the value of 57.80(g/l), the initial sODs for sludge were 3.10(g/l), which gives a solubilization ratio (sCOD/tCOD) of 5.40%. Results showed that, increasing temperature and heating time increased the sCOD solubilization ratio as it ranged between 14.36% and 28.8% at the end of the thermal pretreatment experiment.

sCOD/tCOD values in the pretreated sludge were clearly higher than that in the raw sludge (see figure 1), thereby indicating that thermal pretreatment had a strong effect on sludge solubilization. The degree of effect depending up on the applied temperature and time of treatment. Results showed that after 120 min of treatment, increasing the temperature from 100 to 150°C led to a slight increase of sludge solubilization ratio (sCOD/tCOD) from 10.8 % to 11.7%. While increasing the temperature to 175 and 200°C led to higher increase on the solubilization ratio of 15.1% and 14.9 % respectively. Theses results coincides with other studies which concluded that the optimal temperature is around 170 -200°C (Neyens et al., 2002, and Bougrier et al., 2006 b).

Figure 1 shows that increasing the time of treatment from 120 min to 240 min, led to increase the solubilization ratio from 15.1% (at 175°C) to 25.1%, and from 14.9% (at 200°C) to 28%. These results confirm that solubilization ratio (sCOD/tCOD) depends on the time of treatment. Results of this study prove that thermal pretreatment would disrupt the complex activated sludge floc structure and release extracellular and intracellular biopolymers such as proteins, carbohydrates, and lipids into the soluble phase, and that it would enhance the solubilization of organic particulate matter. These results comply

with the results of Eskicioglu et al., (2006), Woon et al, (2009) Yuan et al, (2011), Val del rio et al, (2011), and Uma et al, (2013)

Table 2. sCOD concentration in (g/l) for the different tested thermal pretreatment temperatures

Time (min)	Thermal pretreatment temperature (^{0}C)				
	100	125	150	175	200
0	3.10	3.10	3.10	3.10	3.10
30	3.70	4.00	4.20	4.40	4.50
60	4.80	5.00	5.50	6.50	6.80
120	6.20	6.40	6.80	8.70	8.60
240	8.30	10.60	11.20	14.50	16.20

Erro! Vínculo não válido.Fig. 1 Effect of Temperature and Heating time on COD solubilization ratio.

Effect of thermal pretreatment on VFA solubilization

Table (3) shows the VFAs for the different tested temperatures (100, 125, 150, 175and 200 ^{o}C), the initial VFA for sludge were 2.00(g/l). The results show that increasing temperature and heating time increased the VFA concentrations.

Table 3. VFAs concentration in (g/l) for the different tested thermal pretreatment temperatures

Time (min)	Thermal pretreatment temperature (^{0}C)				
	100	125	150	175	200
0	2.00	2.00	2.00	2.00	2.00
30	2.40	2.55	2.70	2.85	2.90
60	3.20	3.40	3.80	4.42	4.70
120	4.55	4.60	5.00	6.40	6.20
240	6.30	8.00	8.00	9.90	11.10

As shown in **Fig. 2** at 120 min of treatment, increasing the temperature from 100 to 150°C led to a slight increase of VFA concentration from 4.55 g/l to 5.0 g/l. While increasing the temperature to 175 and 200°C led to higher increase of VFA concentration to 6.4 and 6.2 g/l respectively.

Erro! Vínculo não válido. Fig.2 Effect of Temperature and Heating time on VFA solubilization.

Results of VFAs also proved that thermal pretreatment would disrupt the complex activated sludge floc structure and that it would enhance the solubilization of organic particulate matter. These results comply with the results of Eskicioglu et al., (2006), Woon et al, (2009) and Val del rio et al, (2011.

Mathematical modeling

Mathematical model is a description of a system using mathematical concepts and language. Mathematical models can take many forms, including but not limited to dynamical systems, statistical or empirical models and differential equations. Empirical models can be used to develop relationships that are useful for forecasting and describing trends in behavior but they are not necessarily mechanistically relevant that is they don't explain the real causes and mechanisms for the relationships. In some cases, empirical models can fit the data more closely than mechanistic models (Saito et al., 2009).

Model fitting is finding a function that is as close as possible to containing all the data points. Such function is also called a regression curve. Most of the technology used (e.g. Excel, graphing calculators, Matlab, and Datafit soft wares) can be used to find regression curves and a variable monitoring the validity of the model, the coefficient of determination usually denoted by R^2. This coefficient takes values in interval [0,1] and indicates how close the data points are to be exactly on the regression curve. If R^2 is close to 1, the model is reliable. If R^2 is close to 0, other model should be considered (Berthouex and Brown, 2002).

Modeling of COD solubilization ratio

In the present study, a new empirical model is built for the determination of COD solubilization ratio (sCOD/tCOD) as a function of the initial solubilization ratio (So), the heating time (Ht); per minute, and Temperature (T); degree Celsius. The experimental data obtained in the present study that presented in figure 1 are used for development of the model (about 25 data point). The model building process is done using different types of model equations (polynomial, power, exponential, and logarithmic). According to the least squares criterion (Berthouex and Brown, 2002), the best estimates of regression parameters (a,b,c, …)'s minimize the sum of the squared residuals. The regression analysis process is done by help of DataFit software version 9.0.59 (Okdale Engineering, 2008).

Results from data fitting process shows that, the model that achieved the best fitting, which gives the highest value of (R^2 = 0.988) and the lowest value of (RMS = 0.677) is known as Enzyme-kinetic equation and expressed as following:

$$(sCOD/tCOD) \% = So + (0.00031*T*Ht)/(1 - 0.00144*T - 0.00024*Ht)$$

Figure 3 shows a plot of the model out put comparing to the experimental results. The Correlation Coefficient R^2 is 0.987, means all values of COD solubilization ratio obtained from the empirical model are very close to values determined experimentally.

Erro! Vínculo não válido.

Fig.3 The agreement between the Empirical model out put and the experimental results for COD solubilization ratio

Modeling of VFA solubilization

Another empirical model is built for the determination of VFA concentration as a function of the initial concentration (VFAo), the heating time (Ht); per minute, and Temperature (T); degree Celsius. The experimental data obtained in the present study that presented in figure 1 are used for development of the model (about 25 data point). The model building process is done using different types of model equations (polynomial, power, exponential, and logarithmic). Results from data fitting process shows that, the model that achieved the best fitting, which gives the highest value of (R^2 = 0.988) and the lowest value of (RMS = 0.27) is known as Enzyme-kinetic equation and expressed as following:

$$VFA \ concentration \ (g/l) = VFAo + (0.00019*T*Ht)/(1 - 0.0002*T)$$

Figure 4 shows a plot of the model out put comparing to the experimental results. The Correlation Coefficient R^2 is 0.987, means all values of VFA concentration obtained from the empirical model are very close to values determined experimentally.

Erro! Vínculo não válido.

Fig.4 The agreement between the Empirical model out put and the experimental results for VFA concentration

CONCLUSION

It has been known for many years that a thermal pretreatment can improve the degradability of sludge. While the carbohydrates and the lipids of the sludge are easily degradable, the proteins are protected from the enzymatic hydrolysis by the cell wall. Heat applied during thermal treatment destroyed the chemical bonds of the cell wall and membrane, thus makes the proteins accessible for biological degradation. In this research a mixture of primary and waste activated sludge was thermally

pretreated at 100, 125, 150, 175 and 200 °C. From the experimental results the following conclusions could be derived:

- Thermal pretreatment of sludge could improve the solubilization ratio of organic particulates and biosolids.
- Increasing the heating temperature increased the COD and VFA solubilization ratios. The optimal temperature range was ranged between 175 and 200° C
- The COD solubilization ratio (at 175° C) increased from 11.2% to 15.1% and 25.1% when the time of treatment increased from 60 min to 120 and 240 min respectively.
- The experimental data could be fitted to obtain an empirical model (Known as the enzyme-kinetic equation) relating the COD solubilization ratio of sludge and VFA concentration to the applied temperature and the heating time.

NOMENCLATURE

AD: Anaerobic digester

COD: Chemical oxygen demand (g/l)

sCOD: Soluble chemical oxygen demand (g/l)

tCOD: Total chemical oxygen demand (g/l)

FAS: Ferrous ammonium Sulphate

VS: Volatile solids (g/l)

VSS: Volatile Suspended Solids (g/l)

VFA: Volatile fatty acids (g-COD/l)

SRT: Solids residence time (d)

WAS: Waste activated sludge

REFERENCES

Appels, L., Degrève, J., Van der Bruggen, B., Van Impe, J., Dewil, R., (2010). Influence of low temperature thermal pretreatment on sludge solubilisation, heavy metal release and anaerobic digestion. Bioresour. Technol. 101, 5743–5748.

Berthouex P., and Brown L., 2002, "Statistics For Environmental Engineers", CRC Press LLC, International Standard Book Number 1-56670-592-4

Bougrier C., Delgene`s J.-P. & Carre`re H. (2006 a). Combination of thermal treatments and anaerobic digestion to reduce sewage sludge quantity and improve biogas yield. Process Safety and Environmental Protection, 84(B4):280-284.

Bougrier C., Delgene`s J.-P. & Carre`re H. (2006 b). Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability. Chemical Engineering and Processing 45 (2006) 711–718

Buchauer K (1998) "A comparison of two simple titration procedures to determine volatile fatty acids in influents to waste-water and sludge" Water SA Vol. 24 No. 1, 49-56.

Eskicioglu, C., Droste, R.L., Kennedy, K.J., 2006. Performance of continuous flow anaerobic sludge digesters after microwave pretreatment. Water Environ. Res. 7, 526–540.

Garg, N.K (2009)"Multi-criteria Assessment of Alternative Sludge Disposal Methods" M.sc. thesis, University of Strathclyde, Scotland.

Hiraoka, M., Takeda, N., Sakai, S., Yasuda, A., (1985) "Highly efficient anaerobic digestion with thermal pretreatment". Wat. Sci. Tech. 17, 529-539.

Kepp U., Machenbach I., Weisz N., Solheim O. E., Enhanced stabilisation of sewage sludge through thermal hydrolysis—three years of experience with full scale plant, in: Proceedings of Specialised Conference on Disposal and Utilisation of Sewage Sludge: Treatment Methods and Application Modalities, October 13–15, Athens, Greece, 1999, pp. 161–168.

Kim, Y.K., Bae, J.H., Oh, B.K., Lee, W.H., Choi, J.W., 2002. Enhancement of proteolytic enzyme activity excreted from Bacillus stearothermophilus for a thermophilic aerobic digestion process. Bioresour. Technol. 82 (2), 157–164.

Li, Y.Y., Noike, T., (1992) "Upgrading of anaerobic digestion of waste activated sludge by thermal pretreatment. Wat. Sci. Tech. 26, 857-866.

Madigan, M. T., Martinko, J. M., Dunlap, P. V., and Clark, D. P., Brock: Biology of microorganisms, 11th ed., Benjamin Cummings (2005).

Marcos von Sperling: Carlos A. Chernicharo, (2005). "Biological wastewater treatment in warm climate regions". IWA Publishing, USA.

Neyens E., Baeyens J., A review of thermal sludge pretreatment processes to improve dewaterability, J. Hazard. Mater. 98 (1–3) (2003) 51–67.

Oh, S. E., "Improvement of anaerobic digestion rate of biosolids in waste activated sludge (WAS) by ultrasonic pretreatment," Environ. Eng. Res., 11(3), 143-148 (2006).

Pavlostathis, S.G. and Giraldo-Gomez, E. (1991) Kinetics of anaerobic treatment: A critical review. Critical Reviews in Environmental Control 21(5-6), 411-490.

Romano, R.T., Zhang, R.H., Teter, S., McGarvey, J.A., 2009. The effect of enzyme addition on anaerobic digestion of Jose Tall Wheat Grass. Bioresour. Technol. 100 (20), 4564–4571.

Saito M., Maksyutov S., Hirata R., and Richardson A. D., ,2009, "An empirical model simulating diurnal and seasonal CO2 flux for diverse vegetation types and climate conditions", Biogeosciences, Vol (6), pa. 585–599

Tiehm, A., Nickel, K., Zellhorn, M., and Neis, U., "Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization," Water Res., 35(8), 2003-2009 (2001).

Uma R., Adish K. S., Kaliappan S., Yeom I., Rajesh B. J., (2013), "Impacts of microwave pretreatments on the semi-continuous anaerobic digestion of dairy waste activated sludge". Waste Management 33, 1119–1127

Val del Ri, N. Morales, E. Isanta, A. Mosquera-Corral ,J.P. Steyer, H. Carrere (2011) "Thermal pre-treatment of aerobic granular sludge: Impact on anaerobic biodegradability" water research 45, 6011-6020.

Wang, W., Hou, H.H., Hu, S., Gao, X.B., 2010. Performance and stability improvements in anaerobic digestion of thermally hydrolyzed municipal biowaste by a biofilm system. Bioresour. Technol. 101, 1715–1721.

Weemaes, M. P. J. and Verstraete, W. H., "Evaluation of current wet sludge disintegration techniques," J. Chem. Technol. Biot., 73(2), 83-92 (1998).

Woon, J. P., Johng H. A., and Chan, K. L., (2009), " Effect of Temperature-increase Rate and Terminal Temperature on the Solubilization of Sewage Sludge using Microwave Irradiation", Environ. Eng. Res. Vol. 14, No. 1, pp. 48~52

Yuan Q., Sparling R., Oleszkiewicz J.A. (2011) "Technical Note: VFA generation from waste activated sludge: Effect of temperature and mixing" Chemosphere 82, 603–607.

Zheng, J., Graff, R.A., Fillos, J., Rinard, I., (1998) "Incorporation of rapid thermal conditioning into a wastewater treatment plant". Fuel Processing Technology 56, 183-200.