ZEOLITE APPLICATION FOR THE ENHANCEMENT OF METHANE PRODUCTION IN LANDFILL LEACHATE

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A thesis submitted in fulfillment of the
requirements for the award of the degree of
Master of Engineering (Environment)

Faculty of Civil Engineering,
Universiti Teknologi Malaysia

JULY 2016

To myself,

Thank you for not giving up

To Mak and Abah,

This is for you

ACKNOWLEDGEMENT

Alhamdulillah, thank you to Allah, the Most Gracious and the Most Merciful for giving me passion and strength to complete this thesis.

I would like to express my sincere appreciation to my supervisor, Dr. Mohd Hafiz bin Puteh, who never fails to guide, help and supervise me since I started my Master's degree. I am grateful and indebted for everything he has taught me and thank you for being patient with me. Thank you also to Prof Dr. Muhammad Ali, Dr. Mohd Hafiz Dzarfan and Dr. Roswanira for their support and knowledge.

Thanks also to Universiti Teknologi Malaysia and Ministry of Higher Education for the financial support. My sincere thanks also go to the Department of Environment, IPASA, SWM, IWK, AMTEC and KULIM for their co-operation in providing data and information needed in my research.

Mak and Abah, thank you for your never-ending love and supports. Sisters, thank you for being my financial backup whenever I really in need and brother for your support. Special gratitude to my colleagues; Irena, Shikin, Syahrul, Anis, Ain, Kak Syakila, Kak Hudai, Abg Hairul, Syida and Yana. Without all of you, I do not think I can make this far. Thanks for all your supports, encouragements and enjoyable memories that we share in Postgrad Room. Faiz and Helmi, even distance separate us, thank you for your helps during my down. Azani, thank you so much for everything you gave and shared. B, thank you for your supports and for always being there, cheering me up. Thank you

ABSTRACT

High concentration of organics, ammonia, and heavy metals in landfill leachate are harmful to the environment as well to human's health. These high toxicity compounds may dampen microorganisms' activity in anaerobic reactor, particularly the methanogens. The aim of this research is to investigate the potential toxicity and biodegradability of landfill leachate under methanogenic conditions using batch microcosm assays, which are anaerobic toxicity assays (ATA) and biochemical methane potential (BMP) methods, and to enhance its biodegradability using natural zeolite (clinoptilolite) and synthetic zeolite (Sigma 96096). Leachate sample was collected from Seelong Sanitary Landfill, Johor. Response Surface Methodology (RSM) was used to determine the adsorption of ammoniacal nitrogen (NH3-N) present in leachate on clinoptilolite and Sigma 96096 based on three variables including dosage, particle size, and percentage of leachate to distilled water. Based on the optimized operational conditions, the maximum removal of NH3-N for clinoptilolite and Sigma 96096 were 90.61% and 56.67%, respectively; with the dosage, particle size, and percentage of leachate to distilled water of 2 g/L, 50 mm and 50% for clinoptilolite, and for Sigma 96096 at 4 g/L, 150 mm and 50%, respectively. Biodegradability assays were conducted on varied concentrations of leachate using two anaerobic biomass from Indah Water Konsortium (IWK), Ulu Tiram, Johor and KULIM Palm Oil Mill Effluent Treatment Plant (KULIM), Kulai, Johor. Based on ATA, no significant inhibition was recorded for 10% leachate concentration supplied with clinoptilolite and seeded with KULIM biomass. Meanwhile, for BMP, the assay contained 5% of leachate with Sigma 96096 and IWK seed recorded the highest conversion efficiency of 43.03%. Hence, the ATA and BMP assays are beneficial to predict the production potential of methane from waste in full scale reactor.

ABSTRAK

Kepekatan bahan organik, ammonia dan logam berat yang tinggi dalam air larut lesap adalah berbahaya kepada alam sekitar dan kesihatan manusia. Sebatian yang sangat toksik ini mengurangkan aktiviti mikroorganisma dalam reaktor anaerobik terutamanya metanogen. Tujuan penyelidikan ini ialah untuk menyiasat potensi ketoksikan dan keupayaan biodegradasi air larut lesap dalam keadaan metanogenik dengan menggunakan assay kumpulan kecil daripada teknik Assay Ketoksikan Anaerobik (ATA) dan Kaedah Potensi Biokimia (BMP) untuk meningkatkan keupayaan biodegradasi air larut lesap daripada tapak pelupusan sampah menggunakan zeolite asli (clinoptilolit) dan zeolit sintetik (Sigma 96096). Sampel air larut lesap diambil dari Tapak Pelupusan Sampah Bersanitari, Seelong, Johor. Kaedah Gerak Balas Permukaan (RSM) digunakan untuk mengkaji penjerapan nitrogen ammonia (NH3-N) ke atas air larut lesap menggunakan clinoptilolit dan Sigma 96096 berdasarkan tiga pembolehubah iaitu dos, saiz partikel dan peratus air larut lesap terhadap air suling. Berdasarkan keadaan operasi yang dioptimumkan, penyingkiran maksimum bagi NH3-N daripada air larut lesap oleh clinoptilolit adalah 90.61% dan 56.67% untuk Sigma 96096. Dos, saiz partikel dan peratusan air larut lesap kepada air suling untuk clinoptilolit adalah masing-masing 2 g/L, 50 mm, dan 50% dan untuk Sigma 96096, 4 g/L, 150 mm, dan 50%. Assay biodegradasi dibuat dengan beberapa kepekatan yang berbeza menggunakan dua sumber benih anaerobik daripada tapak rawatan kumbahan Indah Water Konsortium (IWK), Ulu Tiram, Johor dan Loji Rawatan Efluen Kilang Minyak Sawit KULIM (KULIM), Kulai. Daripada ATA, tiada perencatan ketara yang direkodkan untuk air larut lesap dengan peratusan 10% dibekalkan dengan clinoptilolit dengan pembenihan dari KULIM. Bagi BMP, assay yang mengandungi air larut lesap dengan peratusan 5% dibekalkan dengan Sigma 96096 dengan benih IWK merekodkan peratusan perubahan paling tinggi iaitu 43.03%. Oleh yang demikian, kaedah ATA dan BMP berfaedah untuk meramal keupayaan pengeluaran metana dalam sisa untuk reaktor berskala penuh.

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LIST OF ABBREVIATIONS

APHA	-	American Public Health Association
NH_3	-	Ammonia
ATA	-	Anaerobic Toxicity Assay
BMP	-	Biochemical Methane Potential
Si_4^+	-	Silicon ion
Al_3^+	-	Aluminum ion
CEC	-	Cation Exchange Capacity
Na^+	-	Sodium ion
Mg_2^+	-	Magnesium ion
K^+	-	Potassium ion
NH_3-N	-	Ammoniacal Nitrogen
NH_4^+	-	Ammonium ion
RSM	-	Response Surface Methodology
COD	-	Chemical on Demand
BOD	-	Biochemical on Demand
NO_3^--N	-	Nitrate
NO_2^--N	-	Nitrite
TN	-	Total Nitrogen
TSS	-	Total Suspended Solid
VSS	-	Volatile Suspended Solid
Cu	-	Copper
Zn	-	Zinc
DOC	-	Dissolved Organic Carbon
CH_4	-	Methane
CO_2	-	Carbon Dioxide
H_2S	-	Hydrogen sulphide
AOP	-	Advanced Oxidation Process

CCD	-	Central Composite Design
MRR	-	Maximum Rate Ratio
XRD	-	X-ray Diffraction
XRF	-	X-ray Fluorescence
SEM	-	Scanning Electron Microscope
EDAX	-	Energy Dispersive X-ray
UASB	-	Up-flow Anaerobic Sludge Blanket
$NaHCO_3$	-	Sodium bicarbonate
$C_6H_{12}O_6$	-	Glucose
ANOVA	-	Analysis of Variance

LIST OF SYMBOLS

b	Langmuir constant
B	Langmuir constant
C_0	Concentrations of NH_3-N at initial (mg/L)
C_e	Concentrations of NH_3-N at equilibrium state (mg/L)
C_f	Final concentration of leachate mixed with zeolite after equilibrium(mg/L)
C_i	Initial concentration of the leachate without zeolite (mg/L)
e_i	Error
F-value	Fisher variation ratio
k	Number of factors
k_1	Equilibrium rate constants of pseudo-first-order
k_2	Equilibrium rate constants of pseudo-second-order models
K	Freundlich constant
M	Mass of the zeolite used (g)
N	Freundlich constant
$Prob>F$	Probability value
q_e	Amount of NH_3-N removed at equilibrium (mg/g)
q_t	Amount of NH_3-N removed at time, t
Q	Langmuir constant
R^2	Correlation coefficient
R_L	Dimensionless equilibrium parameter
V	Volume of leachate (L)
Y	Response
x/m	Amount of adsorbate per unit mass of adsorbent (mg/g)
X_i	Variable
X_j	Variable

1/n	Indicator to measure the adsorption intensity or surface heterogeneity
β_0	Constant coefficient
β_{ij}	Interaction coefficients of second-order terms
β_j	Interaction coefficients of linear
β_{jj}	Interaction coefficients of quadratic
p	Probability constant

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Landfilling is currently the world's most popular method of disposing municipal solid waste (MSW) (Rafizul and Alamgir, 2012). Unfortunately, such preference to disposal of wastes comes with the inherent problem associated with the liberation of poisonous liquid called leachate from landfills due to percolation of rainwater through the wastes (Syafalni *et al*., 2012). According to Primo *et al*. (2009), considering the hazardous and harmful effects of leachate may have on the environment and especially on groundwater, the search for new technologies to treat landfill leachate has since become a very intense research area. Proper handling of leachate prior to discharge into water bodies is vital as such many countries have implemented laws to control the quality of discharged leachate (Wiszniowski *et al*., 2007; Turan and Ergun, 2009). This is due to the fact that the composition of leachate varies with landfill age, waste composition and the design or operation of the landfill (Gotvajn *et al*., 2009). Unlike young landfills, where mainly consist of degradable organics in the acidogenic phase (Kargi and Pamukoglu, 2004) is easier to be treated biologically, an old landfill predominantly contains refractory organics in the methanogenic phase that is more difficult to treat (Yusof *et al*., 2009).

Weatherly and Miladinovic (2004) state that another vital parameter monitored in landfill leachate is ammonia (NH_3), such compound can potentially pollute streams and water bodies if not properly treated. Considering that the presence of high concentration of ammonia in water bodies may stimulate excess growth of algae, reduce the efficiency of biological treatment system (Jorgensen and

Weatherly, 2003) as well as toxic to aquatic life (Pinho *et al*., 2011), the removal of such substance by utilizing efficient and economical methods are acquired.

In view of the chemical complexities of landfill leachate and the adverse effects that are associated with poorly treated discharged leachate may have on the environment, concerted efforts in search of alternative technologies to overcome such problem remain a challenge. Studies have reported that treatments using methods of adsorption (Liu and Lo, 2001a,b), membrane bioreactor (Ahmed and Lan, 2012), nitrification and denitrification (Ruiz *et al*., 2006), anaerobic-ammonia removal (Sri Shalini and Joseph, 2012), and ion exchange (Bashir *et al*.,2010) have been employed to degrade or remove ammonia from leachate.

The ultimate anaerobic biodegradation of a specific solute can be ascertained by measuring its disappearance or decrease, and the production of biogas using standard biodegradation assays. According to Surendra *et al*. (2014) anaerobic digestion (AD) of leachate is advantageous since the breakdown of organics under methanogenic condition may produce substantial amount of biogas such as methane gas (CH_4) for energy recovery. Compared to aerobic treatment, anaerobic treatment certainly provides low cost operation where no aeration is required and cost for sludge handling is promisingly lower due to less amount of waste sludge produced (Novak *et al*., 2011). Apart from that, anaerobic degradation also provides a survival environment to the bacteria in habitats where less oxygen is required (Yusof *et al*., 2009).

Nevertheless, refractory nature of the leachate, especially its ammonia toxicity, largely inhibits the most sensitive methanogenic consortia, thereby hampering the methane production. Simple and inexpensive techniques of biochemical methane potential (BMP) and anaerobic toxicity assay (ATA) aiming to evaluate substrate anaerobic biodegradability and substrates toxicity to anaerobes. Respectively, these techniques can be determined by monitoring the cumulative methane production from a sample which is incubated in a chemically defined medium (Owen *et al*., 1979)

According to Montalvo *et al.* (2012), it has been found there is a synergistic interaction between adsorption and biodegradation of substrates on the surface active particles of zeolites, under anaerobic environment. Mainly characterised by its large surface area, zeolite provides high affinity for microbial immobilisation, and high ion exchange capacity for ammonia removal. Nevertheless, the role of zeolite particle to alleviate ammonia toxicity in leachate and the effect of these nanoparticles on methane yield remained unclear.

Interestingly, the use of natural zeolite as sorbent has been reported by Hedstorm (2001). Zeolite can be a naturally occurring or synthetic minerals that consists of a three dimensional framework formed by silica–oxygen tetrahedrals where the Si^{4+} has been replaced by Al^{3+} in a porous lattice work (Zhou and Boyd, 2014). At this juncture, many scientists have suggested the utilization of natural zeolite as sorbent to treat landfill leachate owing to its porous structure containing hydrated aluminosilicate (SiO_4 and AlO_4) minerals (Hedstorm (2001), Halim *et al.* (2010), Bowman (2003), and Karadag *et al*., (2008)). These minerals have been described to have high cation exchange capacities (CECs), molecular sieving, catalysis, and sorption (Pinho *et al*., 2011) properties, which explain the wide use of natural zeolite as an ion exchange to remove ammonia in landfill leachate Halim *et al*. (2010) and Bowman (2003). Moreover, utilization of natural zeolites such as clinoptilolite has been reported by Karadag *et al*., (2008) to be more competitive as compared to other ammonium adsorbents due to its low cost and high ammonium ion selectivity.

It has been suggested by Hedstorm (2001) that clinoptilolite with the size of less than 1 mm can be used to adsorb ammonia. Apart from potassium and sodium enriched natural zeolites (Breck, 2001), utilization of synthetic zeolite such as Sigma 96096 (details in 3.2.4) may be a promising alternative to treat landfill leachate. It is noteworthy to highlight that the utilization of Sigma 96096 as adsorbent may be feasible due to the presence of both inorganic and organic cations such as Na^+, quaternary ammonium ions, and protons (Davis and Lobo, 2002) in its structure as well as it is a readily available commercial adsorbate. To the best of our knowledge, the use of Sigma 96096 as sorbents for the NH_3-N removal has yet to be explored.

The experimental conditions of leachate treatment are also the key concern as the composition of leachate may be influenced by various conditions, as well as the physicochemical properties of the sorbent employed. Owing to the uncertainties, predictions on the effects of independent variables that may affect efficiency of the leachate treatment process become rather complex and are almost unfeasible. In this perspective, response surface methodology would be a technique of choice due to its statistical efficacy to predict the best performance conditions with minimum number of experiments (Chaibakhsh *et al*., 2008). The method of response surface methodology (RSM) utilizes quantitative data in the experimental design to conclude and simultaneously solve multivariate equations in order to optimize the processes or products. Apart from being less expensive, the use of RSM-based optimization experiments is favourable as such experiments may be completed faster than the conventional one-variable-at-a-time or full factorial ones (Wahab, 2014).

Basically, landfill leachate contains high concentration of toxic compounds such as ammonia which if not be treated properly, may cause harm to environment. Anaerobic degradation has been reported to be advantageous in leachate treatment due to its ability to produce substantial amount of biogas specifically methane gas for energy recovery. However, due to high ammonia concentration in leachate, it is hampering the methane production. Owen *et al*. (1979) had proposed method called anaerobic toxicity assay (ATA) and biochemical methane potential (BMP) to provide information on toxicity and biodegradability of landfill leachate. Previous studies have found a collaborative relation between adsorption and biodegradation of leachate. The use of natural and synthetic zeolites as adsorbate in anaerobic biodegradation of leachate has proven comes helpful in reducing high ammonia concentration contained in leachate. Using response surface methodology (RSM), the optimization of few variables was investigated to enhance the biodegradability of leachate.

1.2 Problem Statement

Recently, current treatment of landfill leachate involved the practise of physical, chemical and biological treatment. Of these, biological treatment specifically anaerobic treatment may come in handy. However, methane production from anaerobic degradation in landfill site was not being utilised maximally as it was released without further exploitation especially in Malaysia.

Leachate contains large amount of pollutants such as dissolved organic matter as well as inorganic macro components especially ammonia. High concentration of ammonia contained in leachate causes toxicity not only to the aquatic life and humankind, it also bring toxicity to anaerobic consortia especially methanogens thereby hampering the methane production.

Zeolite on the other hand has found to have variety of criteria which can be used in treating leachate. However, studies on comparison of natural and synthetic zeolite in literature seem not convincing. Plus, no latest study has been found on the use of zeolites added in bioassays to reduce toxicity of ammonia in leachate as well as to improve methane potential production.

1.3 Objective of Study

The specific objectives of this study are as follows:

i. To optimize the adsorption of NH_3-N in landfill leachate using natural and synthetic zeolite which is clinoptilolite and Sigma 96096 respectively; with the used of Response Surface Methodology (RSM).
ii. To investigate the potential toxicity and biodegradability of leachate under methanogenic conditions using batch microcosm assays i.e. anaerobic toxicity assays (ATA) technique and biochemical methane potential (BMP) methods.

iii. To enhance the biodegradability of landfill leachate using natural and synthetic zeolites in a modified batch microcosm assays.

1.4 Scope of Study

In this study, the biodegradability and possible toxicity of landfill leachate are evaluated using simple and inexpensive techniques proposed by Owen *et al*., (1979) called ATA and BMP. A batch microcosm technique is conducted using serum bottle in laboratory scale. ATA is a preliminary study to evaluate samples toxicity, and BMP conveys more flexibility to elucidate samples biodegradation by means of anaerobically in the presence of adsorbate. Prior to biodegradation experiments, the leachate samples was taken from Seelong Sanitary Landfill, Johor and characterised accordingly based on their organic strength (Biochemical on Demand, BOD and Chemical on Demand, COD), nitrogen compounds (Total Nitrogen, TN, Ammonia, NH_3-N, Nitrate, NO_3^--N and Nitrite, NO_2^--N), suspended solid (Total Suspended Solid, TSS and Volatile Suspended Solid, VSS), pH and heavy metals (Copper, Cu and Zinc, Zn). The effects of supplying natural zeolite; clinoptilolite and synthetic zeolite; Sigma 96096 as adsorbate were investigated on readily induced anaerobic bioassays. Later, the leachate was analysed according to few parameters to validate the efficiency and optimized variables of the leachate to work best in adsorption. During the biodegradation study, the biodegradability was evaluated based on the reduction of COD and ammonia, and cumulative methane production in different concentrations of leachate.

1.5 Significance of Study

The capability of leachate to be degraded in anaerobic condition as well as the amount of methane gas production was measured simultaneously to provide information for large scale such as reactor or digester. The outcome from this study will be used for the future design of single reactor unit, capable of treating landfill leachate containing high organic and nitrogen content as well as yields sufficient amount of methane gas to be used as electric generator or incinerator. In addition, the bioassays studies proposed will be used as a tool for accessing the impact of zeolite as adsorbate on anaerobic biodegradation of leachate induced into the system. This will provide an understanding on whether the ion exchange capacity of zeolite and its large surface area for microbial immobilisation; really help in improving anaerobic biodegradation of leachate. The outcome also will evaluate the enhancement of methane production, reduced microbial lag phase, and reduced high organics and ammonia concentrations in landfill leachate using zeolite.

Owen *et al*. (1979) had proposed method called anaerobic toxicity assay (ATA) and biochemical methane potential (BMP) to provide information on toxicity and biodegradability of landfill leachate. A comparison of using two anaerobic biomass from Indah Water Konsortium (IWK), Ulu Tiram, Johor and KULIM Palm Oil Mill Effluent Treatment Plant (KULIM), Kulai, Johor were investigated with the modification of the method was made by adding clinoptilolite and Sigma 96096 to the bioassay with varied of leachate concentrations to defined media. From ATA, concentration of 10% of leachate with the addition of clinoptilolite using KULIM seeds shows the best performance with value of MRR is 0.99 indicates no significant inhibition was recorded. From BMP, the highest percentage of conversion efficiency recorded was by using IWK seed at concentration of 5% of leachate with the addition of Sigma 96096 which is 43.03%.

5.2 Recommendation

The research findings can be used as the basis for conducting the future studies in order to improve the basic knowledge on the anaerobic biodegradability. The following recommendations can be suggested for the use in future researches; such that:

i. The use of another parameter which inhibits and hampering methane production such as hydrogen sulphide (H_2S).
ii. The use of other type of zeolite to improve the performance of biodegradability of leachate.
iii. The use of different type of anaerobic biomass.
iv. Addition of another modification made to the bioassay such as using aerobic-anaerobic to provide information on the effect of adding oxygen to anaerobic consortia.

REFERENCES

Ahmed, F.N., and Lan, C.Q. (2012). Treatment of landfill leachate using membrane bioreactor: A review. *Desalination*. 287: 41-54

Aiyuk, S., Xu, H., and Haandel, A.V. (2010). Removal of ammonium nitrogen from pretreated domestic sewage using a natural ion exchanger. *Environmental Technology*. 25: 37-41.

Alkalay, D., Guerrero, L., Lema, J.M., Mendez R., and Chamy. R. (1998). Review: Anaerobic treatment of municipal sanitary landfill leachates: the problem of refractory and toxic components. *World Journal of Microbiology & Biotechnology*. 14: 309-320.

Alshameri, A., Ibrahim, A., Assabri, A.M., Lei, X.R., Wang, H.Q., and Yan, C.J. (2014). The investigation into the ammonium removal performance of Yemeni natural zeolite: Modification, ion exchange mechanism, and thermodynamics. *Powder Technology*. 258: 20–31.

American Public Health Association (APHA). In: Greenberg, A.E., Eaton, A.D., L.S. Clisceri., Rice, E.W, 2005. (Eds.). Standard methods for examination of water and wastewater, 21^{st} Ed., Washington, DC., USA.

Andreottola, G. and Cannas, P. (1992). Chemical and Biological Characteristics of Landfill Leachate. In: Christensen, T.H., Cossu, R., Stegmann, R. (Eds.), *Landfilling of Waste: Leachate*. Elsevier Applied Science Publishers Ltd.

Angelidaki, I. and Sanders, W. (2004). Assessment of the anaerobic biodegradability of macropollutants. *Reviews in Environmental Science and Bio/Technology*. 3: 117–129.

Angelidaki, I., Alves, M., Bolzonella, D., Borzacconi, L., Campos, J. L., Guwy, A. J., Kalyuzhnyi, S., Jenicek, P., and Lier. J. B. (2009). Task Group for the Anaerobic Biodegradation, Activity and Inhibition of the Anaerobic Digestion Specialist Group of the International Water Association : IWA Publishing.

Angelidaki, I. and Batstone, D.J., (2011). Anaerobic Digestion: Process. In: Christensen, T.H, *Solid Waste Technology & Management*, John Wiley & Sons, Ltd, Chichester.

Appels, L., Baeyens, J., Degreve, J., and Dewil., R. (2008). Principles and potential of the anaerobic digestion of waste-activated sludge. *Progress in Energy and Combustion Science*. 34: 755–781.

Aydin, F., and Kuleyin, A. (2011). The effect of modification and initial concentration on ammonia removal from leachate by zeolite. *World Academy of Science, Engineering and Technology*. 5: 6-28.

Aziz, S.Q., Aziz, H.A., Yusoff, M.S., and Bashir, M.J.K. (2011). Landfill leachate treatment using powdered activated carbon augmented sequencing batch reactor (SBR) process: Optimization by response surface methodology. *Journal of Hazardous Materials*. 189: 404–41.

Baig, S., Coulomb, I., Courant, P., and Liechti, P. (1999). Treatment of landfill leachates: Lapeyrouse and Satrod case studies. *Ozone: Science and Engineering*. 21: 1–22.

Bashir, M.J.K., Aziz, H.A. Yusoff, M.S., and Adlan, M.N. (2010). Application of response surface methodology (RSM) for optimization of ammoniacal nitrogen removal from semi-aerobic landfill leachate using ion exchange resin. *Desalination*. 254: 154-161.

Bezerra, M.A., Santelli, R.E., Oliveira, E.P., Villar, L.S., and Escaleira, L.A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*. 76: 965–977.

Bhargava, D.S., and Sheldarkar, S.B. (1992). Effects of adsorbent dose and size on phosphate-removal from wastewaters. *Environmental Pollution*. 76: 51-60.

Bilgili, M.S., Demir, A., and Varank, G. (2009). Evaluation and modeling of biochemical methane potential (BMP) of landfilled solid waste: A pilot scale study. *Bioresource Technology*. 100: 4976–4980.

Birch, R.R., Biver, C., Campagna, R., Gledhill, W.E., Pagga, U., Steber, J., Reust, H., and Bontinck, W.J. (1989). Screening of chemicals for anaerobic biodegradation. *Chemosphere*. 19: 1527–1550.

Bowman, R.S. (2003). Applications of surfactant-modified zeolites to environmental remediation. *Microporous and Mesoporous Materials*. 61: 43-56.

Breck, D.W. (1971). *Zeolites Molecular Sieves, Structure, Chemistry and Use*. New York: John Wiley and Sons, Inc.

Cavaleiro, A.J., Ferreira, T., Tommaso, G., and Alves, M.M. (2013). Biochemical methane potential of raw and pre-treated meat-processing wastes. *Bioresource Technology*. 129: 519–525.

Chaibakhsh, N., Abdul Rahman, M.B., Basri, M., Salleh, A.B., Raja Abdul Rahman, R.N.Z., and Md. Radzi, S. (2008). Modeling and optimization of lipase-catalyzed synthesis of dilauryl adipate ester by response surface methodology. *Journal of Chemical Technology and Biotechnology*. 83:1534-1540.

Christensen, T., Scharff, H., Hjelmar, O. (2011). Landfilling: Concepts and Challenges. *Solid Waste Technology & Management*. John Wiley & Sons, Ltd, Chichester.

Chen, S., Sun, D., and Chung, J.S. (2008). Simultaneous removal of COD and ammonium from landfill leachate using an anaerobic–aerobic moving-bed biofilm reactor system. *Waste Management*. 28: 339–346.

Chen, Y., Cheng, J.J., and Creamer, K.S. (2008). Inhibition of anaerobic digestion process: A review. *Bioresource Technology*. 99: 4044–4064.

Cho, J.K., Park, S.C., and Chang, H.N. (1995). Biochemical methane potential and solid state anaerobic digestion of Korean food wastes. *Bioresource Technology*. 52(5): 245-253.

Chu, L.M., Cheung, K.C., Wong, M.H., (1994). Variations in the chemical properties of landfill leachate. *Environmental Management*. 1(18): 105–112.

Cotman, M., and Gotvajn, A.Z. (2010). Comparison of different physico-chemical methods for the removal of toxicants from landfill leachate. *Journal of Hazardous Materials*. 178: 298-305.

Cyrus, J.S., and Reddy, G.B. (2011). Sorption and desorption of ammonium by zeolite: Batch and column studies. *Journal of Environmental Science and Health Part A*. 46: 408-414.

Davis, M.E., and Lobo, R.F. (1992). Zeolite and molecular sieve synthesis. *Chemistry of Materials*. 4(4): 756-768.

Elbeshbishy, E., Nakhla, G., and Hafez, H. (2012). Biochemical methane potential (BMP) of food waste and primary sludge: Influence of inoculum pre-incubation and inoculum source. *Bioresource Technology*. 110: 18–25.

Environmental Quality Act 1974. (2009).Environmental Quality (Industrial Effluent) Regulations.

Fernandez, Y., Maranon, E., Castrillon, L., and Vazquez, I. (2005). Removal of Cd and Zn from inorganic industrial waste leachate by ion exchange. *Journal of Hazardous Materials*. 126: 169-175.

Foo, K., and Hameed, B. (2012). Coconut husk derived activated carbonvia microwave induced activation: effects of activation agents, preparation parameters and adsorption performance. *Chemical Engineering Journal*. 184: 57–65.

Fotidis, I.A., Kougias, P.G., Zaganas, I.D., Kotsopoulos, T.A., and Martzopoulos, G.G. (2014). Inoculum and zeolite synergistic effect on anaerobic digestion of poultry manure. *Environmental Technology*. 35(10): 1219-1225.

Gahsimi, S.M.D., Idris, A., Ahmadun, F.R., Beng, T.T., and Teong, G.C. (2008). Batch anaerobic treatment of fresh leachate from transfer station. *Journal of Engineering Science and Technology*. 3: 256 – 264.

Geyikc, F., Kılıc, E., Coruh, S., and Elevli, S. (2012). Modelling of lead adsorption from industrial sludge leachate on red mud by using RSM and ANN. *Chemical Engineering Journal*. 183: 53– 59.

Gotvajn, A.Z., Tisler, T., and Zagorc-Koncan, J. (2009). Comparison of different treatment strategies for industrial landfill leachate. *Journal of Hazardous Materials*. 162: 1446-1456.

Gunaseelan, V.N. (1997). Anaerobic digestion of biomass for methane production: A Review. *Biomass and Bioenergy***.**13: Nos. 83-114.

Gunay, A. (2007). Application of nonlinear regression analysis for ammonium exchange by natural (Bigadic) clinoptilolite. *Journal of Hazardous Materials*. 148: 708-713.

Halim, A.A., Aziz, H.A., Johari, M.A.M., and Ariffin, K.S. (2010). Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment. *Desalination*. 262: 31-35.

Hankins, N.P., Pliankarom, S., and Hilal, N. (2005). An equilibrium ion-exchange study of removal of NH_4^+ ion from aqueous effluent using clinoptilolite. Separation Science and Technology. 39: 3639-3663.

Hansen, T.L., Schmidt, J.E., Angelidaki, I., Marca, E., Jansen, J.C., Mosbæk, H., and Christensen, T.H. (2004). Method for determination of methane potentials of solid organic waste. *Waste Management*. 24: 393–400.

Hedstorm, A. (2001). Ion Exchange of Ammonium in Zeolites: A Literature Review. *Journal of Environmental Engineering*. 127(8): 673-681.

Ho, Y.S., and McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*. 34: 451-465.

Huang, G., Liu, F., Yang, Y., Deng, W., Li, S., Huang, Y., and Kong, X. (2015). Removal of ammonium-nitrogen from groundwater using a fully passive permeable reactive barrier with oxygen-releasing compound and clinoptilolite. *Journal of Environmental Management*. 154: 1-7.

Jokela, J.P.Y., Kettunen, R.H., and Sormunen, K.M. (2002). Biological nitrogen removal from municipal landfill leachate: low-cost nitrification in biofilters and laboratory scale in-situ denitrification. *Water Research*. 36: 4079-4087

Jorgensen, T.C., and Weatherly, L.R. (2003). Ammonia removal from wastewater by ion exchange in the presence of organic contaminants. *Water Research*. 37: 1723-1728.

Karadag, D., Tok, S., Akgul, E., Turan, M., Ozturk, M. and Demir, A. (2008). Ammonium removal from sanitary landfill leachate using natural Gordes clinoptilolite. *Journal of Hazardous Materials*. 153: 60-66.

Kargi, F., and Pamukoglu, M.Y. (2004). Adsorbent supplemented biological treatment of pre-treated landfill leachate by fed-batch operation. *Bioresource Technology*. 94: 285-291.

Khuri, A.I., and Mukhopadhyay, S. (2010). *Response surface methodology*. U.S.A. Vol. 2. WIREs Computational Statistics, John Wiley & Sons, Inc.

Kılıç, M.Y, Kestioglu, K., and Yonar, T. (2007). Landfill leachate treatment by the combination of physicochemical methods with adsorption process. Journal of Biological & Environmental Sciences. 1(1): 37-43.

Kirmizakis, P., Tsamoutsoglou, C., Kayan, B., and Kalderis, D. (2014). Subcritical water treatment of landfill leachate: Application of response surface methodology. *Journal of Environmental Management*. 146: 9-15.

Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A., and Christensen, T.H. (2002). Present and Long-Term Composition of MSW Landfill Leachate: A Review. *Critical Reviews in Environmental Science and Technology*. 32(4): 297–336.

Korbahti, B.K. (2007). Response surface optimization of electrochemical treatment of textile dye wastewater. *Journal of Hazardous Materials*. 145: 277-286.

Korkuna, O., Leboda, R., Skubiszewska-Zieba, J., Vrublevs'ka, T., Gun'ko, V.M., and Ryczkowski, J. (2006). Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite. *Microporous and Mesoporous Materials*. 87: 243–254.

Kulikowska, D., and Klimiuk, E. (2008). The effect of landfill age on municipal leachate composition. *Bioresource Technology*. 99: 5981–5985.

Lee, A.H., Nikraz, H., and Hung, Y.T. (2010). Influence of waste age on landfill leachate quality. *International Journal of Environmental Science and Technology*. 1(4): 347–350.

Labatut, R.A., Angement, L.T., and Scott, N.R. (2011). Biochemical methane potential and biodegradability of complex organic substrates. *Bioresource Technology*. 102: 2255 – 2264.

Lema, J.M., Mendez, R., and Blazquez, R. (1988). Characteristics of landfill leachates and alternatives for their treatment: A Review. *Water, Air, and Soil Pollution*. 40: 223-250.

Lesteur, M., Bellon-Maurel, V., Gonzalez, C., Latrille, E., Roger, J.M., Junqua, G., and Steyer, J.P. (2010). Alternative methods for determining anaerobic biodegradability: A review. Process Biochemistry. 45(4): 431–440.

LeVan, M.D., and Vermeulen, T. (1981). Binary Langmuir and Freundlich isotherms for ideal adsorbed solutions. *The Journal of Physical Chemistry*. 85: 3247-3250.

Leyva-Ramos, R., Jacobo-Azuara, A., Diaz-Flores, P.E., Guerrero-Coronado, R.M., Mendoza-Barron, J., and Berber-Mendoza, M.S. (2008). Adsorption of chromium (VI) from an aqueous solution on a surfactant-modified zeolite. *Colloids and Surfaces A: Physicochem. Eng. Aspects*. 330: 35–41.

Lim, S.J., and Fox, P. (2013). Biochemical Methane Potential (BMP) test for thickened sludge using anaerobic granular sludge at different inoculum/substrate ratios. *Biotechnology and Bioprocess Engineering*. 18: 306-312.

Lisboa, M.S., and Lansing, S. (2013). Characterizing food waste substrates for co-digestion through biochemical methane potential (BMP) experiments. *Waste Management*. 33: 2664–2669.

Lisboa, M.S., and Lansing, S. (2014). Evaluating the toxicity of food processing wastes as co-digestion substrates with dairy manure. *Waste Management*. 34:1299–1305.

Liu, C.H., and Lo, K.V. (2001a). Ammonia removal from composting leachate using zeolite. I. characterization of the zeolite. *Journal of Environmental, Science and Health*. 9: 1671-1688.

Liu, C.H., and Lo, K.V. (2001b). Ammonia removal from compost leachate using zeolite. II. A study using continuous flow packed collumns. *Journal of Environmental, Science and Health*. 36(5): 667-675.

Liu, Z., Dang, Y., Li, C., and Sun, D. (2015). Inhibitory effect of high NH_4^+–N concentration on anaerobic biotreatment of fresh leachate from a municipal solid waste incineration plant. *Waste Management*. 43: 188–195.

Liyana-Pathirana, C., and Shahidi, F. (2005). Optimization of extraction of phenolic compounds from wheat using response surface methodology. *Food Chemistry*. 93: 47–56.

Maranon, E., Castrillon, L., Fernandez-Nava, Y., Fernandez-Menchritdez, A., and Fernandez-Sanchez, A. (2008). Coagulation–flocculation as a pretreatment process at a landfill leachate nitrification–denitrification plant. *Journal of Hazardous Materials*. 156: 538–544.

Mata-Alvarez, J., Mace, S., and Llabres, P. (2000). Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. *Bioresource Technology*. 74: 3-16.

Meylan, W., Boethling, R., Aronson, D., Howard, P. and Tunkel, J. (2007). Chemical structure-based predictive model for methanogenic anaerobic biodegradation potential. *Environmental Toxicology and Chemistry.* 26: 1785 – 1792.

Milan, Z., Sanchez, E., Borja, R., Weiland, P. and Cruz, M. (2001). Synergistic effects of natural and modified zeolites on the methanogenesis of acetate and methanol. *Biotechnology Letters.* 23: 559–562.

Ming, D.W and Dixon, J.B (1987). Quantitative determination of clinoptilolite in soils by a cation-exchange capacity method. *Clays and Clay Minerals*. 35(6) 463-468.

Molino, A., Nanna, F., Ding, Y., Bikson, B., and Braccio, G. (2013) Biomethane production by anaerobic digestion of organic waste. *Fuel*. 103: 1003–1009.

Mondal, P., Majumder, C.B., and Mohanty, B. (2008). Effects of adsorbent dose, its particle size and initial arsenic concentration on the removal of arsenic, iron and manganese from simulated ground water by Fe^{3+} impregnated activated carbon. *Journal of Hazardous Materials*. 150: 695-702.

Montalvo, S., Diaz, F., Guerrero, L., Sánchez, E., and Borja, R. (2005). Effect of particle size and doses of zeolite addition on anaerobic digestion processes of synthetic and piggery wastes. *Process Biochemistry*. 40: 1475–1481.

Montalvo, S., Guerrero, L., Borja, R., Sánchez, E., Milán, Z., Cortés, I., and Rubia, M.A. (2012). Application of natural zeolites in anaerobic digestion processes: A review. *Applied Clay Science*. 58: 125-133.

Myers, R.H., Montgomery, D.C., and Anderson-Cook, C.M. (2009). *Response Surface Methodology: Process and Product Optimization Using Designed Experiments*. U.S.A: 3rd Edition. Wiley Series in Probability and Statistics, John Wiley & Sons, Inc.

Nguyen, M.L., and Tanner, C.C. (1998). Ammonium removal from wastewaters using natural New Zealand zeolites. *New Zealand Journal of Agricultural Research*. 41:427-446.

Novak, J.T., Banjade, S., and Murthy, S.N. (2011). Combined anaerobic and aerobic digestion for increased solids reduction and nitrogen removal. *Water Research*. 45: 618-624.

O'Connor, O.A., Dewan, R., Galuzzi, and Young, L.Y. (1990). Landfill leachate: a study of its anaerobic mineralization and toxicity to methanogenesis. *Archives of Environmental Contamination and Toxicology*. 19: 143 - 147.

Otal, E., Vilches., L.F., Luna, Y., Poblete, R., Garcia-Maya, J.M., and Fernandez-Pereira, C. (2013). Ammonium ion adsorption and settleability improvement achieved in a synthetic zeolite-amended activated sludge. *Chinese Journal of Chemical Engineering*. 21(9): 1062-1068

Owen, W.F., Stuckey, D.C., Healy. Jr., J.B., Young, L.Y., and McCarty, P.L. (1979). Bioassay for monitoring biochemical methane potential and anaerobic toxicity. *Water Research*. 13: 485-492.

Owens, J.M., and Chynoweth, D.P. (1993). Biochemical methane potential of municipal solid waste (MSW) components. *Water, Science and Technology*. 27: 1-14.

Ozacar, M. (2003). Adsorption of phosphate from aqueous solution onto alunite. *Chemosphere*. 51: 321-327.

Pinho, P., Dias, T., Cruz, C., Tang, Y.S., Sutton, M.A., Martins-Loucao, M-A., Maguas, C., and Branquinho, C. (2011). Using lichen functional diversity to assess the effects of atmospheric ammonia in Mediterranean woodlands. *Journal of Applied Ecology*. 148: 1107-1116.

Primo, O., Rivero, M.J., Urtiaga, A.M., and Ortiz, I. (2009). Nitrate removal from electro-oxidized landfill leachate by ion exchange. *Journal of Hazardous Materials*. 164: 389-393.

Rafizul, I.M., and Alamgir, M. (2012). Characterization and tropical seasonal variation of leachate: Result from landfill lysimeter studied. *Waste Management*. 32: 2080-2095.

Raposo, F., De la Rubia, M.A., Fernández-Cegrí, V., and Borja, R. (2011). Anaerobic digestion of solid organic substrates in batch mode: An overview relating to methane yields and experimental procedures. *Renewable and Sustainable Energy Reviews*. 16: 861–877.

Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F., and Moulin, P. (2008). Landfill leachate treatment: Review and opportunity. *Journal of Hazardous Materials*. 150: 468–493.

Rozzi, A., and Remigi, E. (2004). Methods of assessing microbial activity and inhibition under anaerobic conditions: A literature review. *Environmental Science and Bio/Technology*. 3: 93–115.

Ruiz, I., Blázquez, R., and Soto, M. (2009). Methanogenic toxicity in anaerobic digesters treating municipal wastewater. Bioresource Technology. 100: 97–103.

Sabumon, P.C. (2007). Anaerobic ammonia removal in presence of organic matter: A novel route. *Journal of Hazardous Materials*. 149: 49–59.

Shahriari, H., Warith, M., Hamoda, M., and Kennedy, K.J. (2012). Effect of leachate recirculation on mesophilic anaerobic digestion of food waste. *Waste Management*. 32: 400–403.

Shahriari, H., Warith, M., Hamoda, M., and Kennedy, K.J. (2012). Anaerobic digestion of organic fraction of municipal solid waste combining two pretreatment modalities, high temperature microwave and hydrogen peroxide. *Waste Management*. 32: 41–52.

Shehzad, A., Bashir, M.J.K., Sethupathi, S., and Lim, J.W. (2015). An overview of heavily polluted landfill leachatetreatment using food waste as an alternative and renewable source of activated carbon. *Process Safety and Environmental Protection*. 98: 309–318.

Sell, S.T., Burns, R.T., Moody, L.B., and Raman, D.R. (2011). Comparison of methane production from bench and sub pilot-scale anaerobic digesters. *Applied Engineering in Agriculture*. 5: 821-825.

Shelton, D.R., and Tiedje, J.M. (1984). General method for determining anaerobic biodegradation potential. *Applied and Environmental Microbiology*. 47: 850–857.

Silva, A.C., Dezotti, M., and Sant'Anna Jr., G.L. (2004). Treatment and detoxification of a sanitary landfill leachate. *Chemosphere*. 55: 207–214.

Sormunen, K., Einola, J., Ettala, M., and Rintala, J. (2008). Leachate and gaseous emissions from initial phases of landfilling mechanically and mechanically–biologically treated municipal solid waste residuals. *Bioresource Technology*. 99:.2399–2409.

Spiegel, M.R. (1975). Schaum's outline of theory and problems of probability and statistics. NewYork: McGraw-Hill.

Sprynskyy, M., Lebedynets, M., Terzyk, A.P., Kowalczyk, P., Namiesnik, J., and Buszewski, B. (2005). Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studied under dynamic conditions. *Journal of Colloid and Intersface Science*. 284: 408-415.

Sri Shalini, S., and Joseph, K. (2012). Nitrogen management in landfill leachate: Application of SHARON, ANAMMOX and combined SHARON-ANAMMOX process. *Waste Management*. 32: 2385-2400.

Surendra, K.C., Takara, D., Hashimoto, A.G., and Khanal, S.K. (2014). Biogas as a sustainable energy source for developing countries: Opportunities and challenges. *Renewable and Sustainable Energy Reviews*. 31: 846-859.

Syafalni, Lim, H.K., Ismail, N., Abustan, I., Murshed, M.F., and Ahmad, A. (2012). Treatment of landfill leachate by using lateritic soil as a natural coagulant. *Journal of Environmental Management*. 112: 353-359.

Tada, C., Yang, Y., Hanaoka, T., Sonoda, A., Ooi, K., and Sawuayama, S., (2005). Effect of Natural Zeolite on Methane Production for Anaerobic Digestion of Ammonium Rich Organic Sludge. *Bioresource Technology*. 96**:** 459 – 464.

Tsai, W.T., Lai, C.W., and Hsien, K.J. (2003). Effect of particle size of activated clay on the adsorption of paraquat from aqueous solution. *Journal of Colloid and Interface Science*. 263: 29–34.

Turan, N.G., and Ergun, O.N. (2009). Removal of Cu(II) from leachate using natural zeolite as a landfill liner material. *Journal of Hazardous Materials*. 167: 696-700.

Umar, M., Aziz, H.A., and Yusoff, M.S. (2011). Assessing the chlorine disinfection of landfill leachate and optimization by response surface methodology (RSM). *Desalination*. 274: 278-283.

Wahab, R.A., Abdul Rahman, M.B., Basri, M., Raja Abdul Rahman, R.N.Z., and Salleh, A.B. (2014). Enzymatic production of a solvent-free methyl butyrate via response surface methodology catalyzed by a novel thermostable lipase from Geobacillus zalihae. *Biotechnology and Biotechnological Equipment*. 28(6): 1065−1072.

Wang, S. and Peng, Y. (2010). Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal*. 156: 11-24.

Wang, X., and Qin, Y. (2005). Equilibrium sorption isotherms for Cu^{2+} on Rice Bran. *Process Biochemistry*. 40: 677-680.

Weatherly, L.R and Miladinovic, N.D. (2004). Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite. *Water Research*. 38: 4305-4312.

Wei, S., Zankel, A., Lebuhn, M., Petrak, S., Somitsch, W., and Guebitz, G.M. (2011). Investigation of microorganisms colonizing activated zeolites during anaerobic biogas production from grass silage. *Bioresource Technology*. 102**:** 4353 – 4359.

Widiastuti, N., Wu., H., Ang, H.M., and Zhang, D. (2011). Removal of ammonium from greywater using natural zeolite. *Desalination*. 277: 15–23.

Williams, P.T. (2005). *Waste Treatment and Disposal*. Second Edition. U.S.A: John Wiley & Sons, Ltd.

Wiszniowski, J., Robert, D., Surmacz-Gorska, J., Miksch, K., and Weber, J.V. (2006). Landfill leachate treatment methods: A review. *Environmental Chemistry Letters*. 4: 51–61.

Wiszniowski, J., Surmacz-Gorska, J., Robert, D., and Weber, J.-V. (2007). The effect of landfill leachate composition on organics and nitrogen removal in an activated sludge system with bentonite additive. *Journal of Environmental Management*. 85: 59-68.

Wu, Y., Zhou, S., Qin, F., Te, X., and Zheng, K. (2010). Modeling physical and oxidative removal properties of Fenton process for treatment of landfill leachate using response surface methodology (RSM). *Journal of Hazardous Materials*. 180: 456–465.

Xiao, Y., De Araujo, C., Sze, C.C., and Stuckey, D.C. (2015). Toxicity measurement in biological wastewater treatment processes: A review. *Journal of Hazardous Materials*. 286: 15–29.

Yasyerli, S., Ar, I., Dogu, G., and Dogu, T. (2002). Removal of hydrogen sulfide by clinoptilolite in a fixed bed adsorber. *Chemical Engineering and Processing*. 41: 785-792.

Yenigun, O., and Demirel, B. (2013). Ammonia inhibition in anaerobic digestion: A review. *Process Biochemistry*. 48: 901–911.

Yusof, N., Haraguchi, A., Hassan, M.A., Othman, M.R., Wakisaka, M., and Shirai, Y. (2009). Measuring organic carbon, nutrients and heavy metal in rivers receiving leachate from controlled and uncontrolled municipal solid waste (MSW) landfills. *Waste Management*. 29: 2666-2680.

Zhang, Y. and Bi. E. (2012). Effect of dissolved organic matter on ammonium sorption kinetics and equilibrium to Chines clinoptilolite. *Environmental Technology*. 33: 2395-2403.

Zhang, Q.Q., Tian, B.H., Zhang, X., Ghulam, A., Fang, C.R., and He, R. (2013). Investigation on characteristics of leachate and concentrated leachate in three landfill leachate treatment plants. *Waste Management*. 33: 2277–2286.

Zhou, L., and Boyd, C.E. (2014). Total ammonia nitrogen removal from aqueous solutions by the natural zeolite, mordenite: A laboratory test and experimental study. *Aquaculture*. 432: 252-257.