AMMONIACAL NITROGEN REMOVAL FROM AQUEOUS SOLUTION USING ACTIVATED CARBON FROM PAPAYA PEEL AS ADSORBENT

AZUANI BINTI MUSA

UNIVERSITI TEKNOLOGI MALAYSIA

AMMONIACAL NITROGEN REMOVAL FROM AQUEOUS SOLUTION USING ACTIVATED CARBON FROM PAPAYA PEEL AS ADSORBENT

AZUANI BINTI MUSA

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

APRIL 2017

Dedicated specially to my parents, family and friends

ACKNOWLEDGEMENT

I would like to thank Allah for giving me all the means to accomplish this research. My appreciation and greatest gratitude go to my much respected and beloved supervisor, Prof. Ir. Dr. Sharifah Rafidah Wan Alwi, for her guidance throughout my Master's study. Her encouragement and endless support has helped me endure all the difficulties and stresses along this meaningful journey. Without her support, this project would not have seen completion. I would also like to thank my co-supervisor, Dr Norzita Ngadi, for allowing me to access the Pollution Lab (N13) for the majority of my lab work and for her suggestions, comments, and patience through out my study.

My sincere thanks to Sahar Abbaszadeh, a PhD student under the supervision of Prof. Ir. Dr. Sharifah, for guiding me towards realising the path for my experiments. Without her help, I would not have completed my experiments successfully. Also, huge thanks to all PROSPECT staff and my laboratory mates for their cooperation, advice, and suggestions through out my study.

Last but not least, I would like to give special thanks to my family for their patience during my study. There is no word to express how grateful I am for their full support, be it financially or emotionally. Finally, additional thanks goes to all my friends that have lent their help and support. They have been like stars in the sky; I do not always see them, but I know they are there and always there whenever I need them.

ABSTRACT

The presence of ammoniacal nitrogen (NH_3-N) can be detected in industrial, domestic and even treated wastewater. High concentration of this pollutant can cause eutrophication which leads to the growth of excessive algae on the water surface and subsequently affecting the aquatic life due to the lack of oxygen. In recent years, researchers have begun to explore the potential of agro-waste as adsorbent to remove the pollutant from wastewater. Papaya peel has been used due to its abundant availability and cheap cost. There are several successful studies in the removal of dye and heavy metals by using papaya peel. However, no study has been conducted in removal of inorganic pollutant such as NH_3-N. Understanding the capability of papaya peel to adsorb multiple pollutants can help in future studies in evaluating papaya peel adsorption capability in wastewater. In addition, utilization of peel waste also reduces the overall papaya peel waste. In this work, activated papaya peel capability to adsorb NH_3-N was studied. The papaya peel was collected from local market, dried and heated up to 400 ℃ in the furnace and then activated by potassium hydroxide. The surface properties of adsorbents were characterised using Fourier transform infrared spectroscopy, field emission scanning electron microscope, x-ray diffraction, and Brunauer-Emmett-Teller techniques. The adsorption process was carried out in batch mode considering different control parameters of initial pH (4-9), dosage of adsorbent (0.01-0.3 g), contact time (5-120 min), initial ammonium ion (NH_4^+) concentration (10 -150 mg/L) and temperature (25-65 ℃). The final concentrations of NH_3-N were determined using the Nessler method. The best condition with highest removal (42%) was obtained at pH 7, 50 mg dosage of adsorbent, 100 mg/L NH_4^+ concentration at 30 min and 25 ℃. Desorption and regeneration studies were additionally conducted to evaluate the reusability of the adsorbent. The experimental isotherm and kinetics data were evaluated using Langmuir, Freundlich, and Temkin isotherm models and pseudo-first-order and pseudo-second-order kinetic models to relate the mechanism of adsorption ion and the activated carbon papaya peel powder. The data fitted well with the Freundlich model and the pseudo-second-order kinetic model. In addition, thermodynamic parameters such as enthalpy change ($\Delta H°$= -9.627 kJ/mol), free energy changes ($\Delta G°$= -0.851, -1.060, -1.385, -1.593, and -2.355 kJ/mol), and entropy change ($\Delta S°$= 34.812 J/mol K) were also calculated. The result shows that the reaction occurred spontaneously with exothermic reaction under atmospheric condition. High percentage removal of NH_3-N using Carica Papaya Activated Carbon compared to other agricultural waste confirmed that papaya peel potentially can be used as an alternative adsorbent for NH_3-N removal.

ABSTRAK

Kehadiran nitrogen berammonia (NH_3-N) dapat dikesan di dalam industri, domestik dan juga air kumbahan terawat. Kepekatan yang tinggi untuk pencemaran ini boleh menyebabkan eutrofikasi yang membawa kepada pertumbuhan alga yang berlebihan di permukaan air dan seterusnya menjejaskan hidupan akuatik disebabkan oleh kekurangan oksigen. Kebelakangan ini, penyelidik telah mula menerokai potensi sisa agro sebagai bahan penjerap untuk membuang bahan pencemaran daripada air kumbahan. Kulit betik telah digunakan kerana ia mudah di dapati dalam kuantiti yang banyak dan murah. Terdapat beberapa kejayaan kajian dalam penyingkiran warna dan logam berat menggunakan kulit betik. Walau bagaimanapun, tiada kajian dijalankan dalam penyingkiran pencemaran bahan bukan organik seperti NH_3-N. Memahami keupayaan kulit betik untuk menjerap pelbagai bahan pencemaran dapat membantu dalam kajian masa hadapan dalam menilai kebolehan penjerapan kulit betik dalam air kumbahan. Tambahan pula, penggunaan sisa kulit juga dapat mengurangkan jumlah sisa buangan kulit betik. Dalam kajian ini, keupayaan kulit betik teraktif untuk menjerap NH_3-N telah dikaji. Kulit betik dikumpul dari pasar tempatan, dikeringkan dan dipanaskan sehingga suhu 400 ℃ di dalam relau dan kemudian diaktifkan dengan menggunakan kalium hidroksida. Sifat-sifat permukaan bahan penjerap telah dicirikan menggunakan teknik-teknik spektroskopi inframerah transformasi Fourier, mikroskop elektron pengimbas pancaran medan, pembelauan sinar-x, dan Brunauer-Emmett-Teller. Proses penjerapan telah dijalankan dalam mod berkumpulan dengan mempertimbangkan parameter kawalan yang berbeza seperti pH (4-9), berat bahan penjerap (0.01-0.3g), masa tindakbalas (5-120 minit), kepekatan awal ion ammonia (NH_4^+) (10-150 mg/L) dan suhu (25-65 ℃). Kepekatan akhir NH_3-N telah ditentukan dengan menggunakan kaedah Nessler. Keadaan terbaik dengan penyingkiran tertinggi (42%) diperoleh pada pH 7, berat bahan penjerap 50 mg, kepekatan NH_4^+ 100 mg/L selama 30 minit pada suhu 25 ℃. Kajian nyahserapan dan penjanaan semula juga telah dijalankan untuk menilai kebolehan gunapakai bahan penjerap. Ujikaji isoterma dan kinetik telah dinilai menggunakan model isoterma Langmuir, Freundlich dan Temkin dan model kinetik pseudo-kadar- pertama dan pseudo-kadar-kedua untuk mengaitkan mekanisma ion penjerapan dan serbuk bahan aktif kulit betik. Data mematuhi model Freundlich dan model pseudo-kadar-kedua dengan baik. Di samping itu, parameter termodinamik seperti perubahan entalpi ($\Delta H°$=-9.627 kJ/mol), perubahan tenaga bebas ($\Delta G°$= -0.851, -1.060, -1.385, -1.593, dan -2.355 kJ/mol), dan perubahan entropi ($\Delta S°$=34.812 J/mol K) telah dikira. Keputusan menunjukkan tindak balas berlaku secara spontan dengan tindak balas eksotermik di bawah keadaan atmosfera. Peratusan penyingkiran NH_3-N yang tinggi menggunakan karbon teraktif kulit betik berbanding sisa pertanian lain mengesahkan bahawa kulit betik berpotensi untuk digunakan sebagai bahan penjerap alternatif untuk menyingkirkan NH_3-N.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ARE	-	Average Relative Error
BET	-	Brunauer-Emmett-Teller
BILP	-	Boston Ivy Leaf Powder
BOD	-	Biochemical Oxygen Demand
$C_2H_4O_2$	-	Acetic Acid
$CaCl_2$	-	Calcium chloride
CEC	-	Cation Exchange Capacity
COD	-	Chemical Oxygen Demand
CPAC	-	Carica Papaya Activated Carbon
CP-char	-	Carica Papaya charcoal
CP-raw	-	Carica Papaya raw
Cu^{2+}	-	Copper ion
DOE	-	Department of Environment
EAC	-	Extruded Activated Carbon
EDX	-	Energy Dispersive X-ray
Fe^{2+}	-	Iron ion
FESEM	-	Field Emission Scannng Electron Microscope
FTIR	-	Fourier Transform Infrared
GAC	-	Granular Activated Carbon
H	-	Hydrogen
H_2SO_4	-	Sulphuric acid
H_3PO_4	-	Phosphoric acid
HNO_3	-	Nitric acid
IUPAC	-	International Union of Pure and Applied Chemistry
K	-	Potassium

KeTTHA	-	Kementerian Tenaga, Teknologi Hijau dan Air
KOH	-	Potassium hydroxide
Na	-	Sodium
NaOH	-	Sodium hydroxide
NF	-	Nanofiltration
NH_3-N	-	Ammoniacal Nitrogen
NH_3	-	Ammonia
NH_4^+	-	Ammonium ion
NH_4Cl	-	Ammonia Chloride
NSD	-	Normalized Sandard Derivation
Mg	-	Magnesium
MPKj	-	Majlis Perbandaran Kajang
O_2	-	Oxygen
P	-	Phosphorus
PAC	-	Powder Activated Carbon
Pb	-	Lead
Pb^{2+}	-	Lead ion
PP	-	Papaya Peel
RMSE	-	Root Mean Square Eror
RO	-	Reverse Osmosis
SEM	-	Scanning Electron Microscope
UF	-	Ultrafiltration
Uv-Vis	-	Ultraviolet-visible
X-RD	-	X-ray powder Diffraction
Zn^{2+}	-	Zinc Ion
$ZnCl_2$	-	Zinc Chloride

LIST OF SYMBOLS

Δ	-	Delta
℃	-	Degree Celcius
%	-	Percent
Mg	-	Miligram
mg/L	-	Miligram per liter
mg/g	-	Miligram per gram
m^2/g	-	metre square per gram
ha	-	Hectare
ppm	-	Part per million
g	-	Gram
cm^{-1}	-	Reciprocal centimeters
kWh	-	kilo watt hour
cm^3/g	-	Centimeter cubed per gram
g/L	-	Gram per liter
mt	-	Metric tonnes
kV	-	kilovolt
kJ/mol	-	Kilojoule per mol
>	-	More than
<	-	Less than
≤	-	Less and equal to
≥	-	More and equal to
Nm	-	Nanometer
J/mol.K	-	Joule/mol Kelvin
min	-	Minute
Kg	-	Koligram
mm	-	Millimeter
mA	-	milliAmpere

K	-	Kelvin
L/g	-	Liter per gram
ml	-	Mililiter
M	-	Molar
rpm	-	Revolution per minutes
R	-	Universal gas constant
T	-	Temperature
ΔG	-	Gibbs Free Energy
ΔH	-	Enthalphy
ΔS	-	Entrophy

CHAPTER 1

INTRODUCTION

1.1 Research Background

Uncontrolled emission of ammoniacal nitrogen to the environment due to industrialisation and urbanisation has resulted in a major crisis worldwide. Ammoniacal nitrogen is an inorganic chemical that is extremely soluble in water and can exist either in unionised ammonia, NH_3, or ammonium ion NH_4^+. This chemical has been found in various types of agricultural, municipal, domestic, and industrial wastewaters (Copcia *et al.*, 2010). Industries dealing with chemicals such as petrochemicals, textiles, electroplating, and metal finishing contributes to ammoniacal nitrogen pollution and its release to the environment, especially through wastewater discharges. The majority of these industries in Peninsular Malaysia are located in Klang Valley, Melaka, Johor Bahru, and Penang (Liang and Ni, 2009).

Ammonium is one of the main pollutants in municipal sewage and many industrial wastewaters. Naturally, aquatic systems need sufficient amount of ammonium, which is necessary to maintain balance of their biological growth. However, ammonium has been identified as a major toxicant to most organisms if the level of ammonium concentration is higher than the prescribed level which is stated in the Environmental Quality Act 1974, under Environmental Quality (Sewage and Industrial Effluents) Regulations 1979. This poses dangerous effects to living organisms such as harmful effects toward the human respiratory system and irritating the eyes, nose, and skin. It may also change the odour and taste of the polluted water

Despite being harmful to human beings, the higher concentrations of ammonium in lakes and rivers may cause eutrophication which lead to growth of algae on the surface of water stream which push aquatic life to the brink of dangerous situations due to lack of oxygen for them to survive (Genava, 1986). In developed countries, a consensus for the final amount of ammonium in the final effluents needing treatment processes was reached, since ammonium has been identified as a major toxicant. According to Environmental Quality Act 1974, under second schedule of Environmental Quality (Sewage and Industrial Effluents) Regulations 1979, the threshold limit for ammoniacal nitrogen release in sewage discharge is 5mg/Ln. Under fifth schedule of the same regulation, effluent released to the industrial effluent must have a maximum 10mg/L and 20mg/L ammoniacal nitrogen according to standard A and standard B, respectively (EQA 1974).

Nowadays, researchers have developed some reliable methods to remove ammoniacal nitrogen from wastewater such as via biological and physicochemical treatments. However, due to the high concentration of ammoniacal nitrogen, biological treatment results in a lower percentage of removal (Carrerra *et al.*, 2003). Common physicochemical methods used for ammoniacal nitrogen removal are air stripping, reverse osmosis, chemical precipitation, ion-exchange, membrane filtration, and adsorption (Tchobanoglous *et al.*, 2003). The ion exchange technique has received a significant amount of attention recently. However, due to technical constraints such as its complex process and the need for high operational costs, researchers have started searching for new alternatives (Jorgensen and Weatherley, 2003).

The adsorption process has been extensively employed by researchers as an environmentally friendly process to remove organic and inorganic compounds from the wastewater and this process is one of the alternative ways to replace the ion exchange process. Simplicity of process and high percentage removal of compounds has increased the popularity of this method among researchers. From a practical standpoint, adsorption is one of the effective ways to remove colour, odour, and organic and inorganic pollutants from wastewater. In this technique, the adsorbent is able to adsorb a certain mass of components onto its surface selectively (Hegazi, 2013). However, the pollutants are not eliminated but are transferred from the solution to the adsorbent, hence, recovery and regeneration of adsorbents have to be carried out (Jiuhui, 2008). There have been various studies focusing on the removal of ammoniacal nitrogen from wastewater using the adsorption process. Among the adsorbents that are capable of removing ammoniacal nitrogen are mineral materials such as clay and zeolites (Rozic *et al.*, 2000), limestone (Aziz *et al.*, 2004), carbon-zeolite composite (Halim *et al.*, 2010) and organic acid modified activated carbon (Halim *et al.*, 2013).

Recently, adsorption using agro-waste-derived material has been shown to be very promising worldwide. New composite adsorbents using agro-waste material and activated carbon derived from this material has been widely used by researchers. Utilisation of such materials also have advantages such as being inexpensive, readily available, and simple to use (Hossain *et al.*, 2012). The main contents in agricultural waste are hemicellulose, lignin, lipids proteins, simple sugar, water, and hydrocarbon that contains a variety of functional groups, which show potential ion binding capacity (Bailey *et al.*, 1999). Raw agro-waste material and its activated carbon adsorbents are a well-known alternative and effective adsorbent for the removal of various organic and inorganic pollutants in wastewater because of their good adsorption capability. The unique and versatile nature of the activated carbon relates to its extended surface area, micro-porous structure, and high degree of surface reactivity, and therefore makes the activated carbon globally well known (Ismadji and Bhatia, 2001). There are currently only a limited number of studies on the use of agro-waste materials to remove ammoniacal nitrogen. These studies have used bamboo charcoal (Li *et al.*, 2012), pine cones (Demirak *et al.*, 2015), and coconut shells as adsorbents (Boopathy *et al.*, 2013). The limited amount of studies is due to their resulting in a low removal percentage of ammoniacal nitrogen from the aqueous solution i.e. below 30 per cent. Therefore, to overcome this problem, activated carbon surface modification or the production of composite adsorbents is recognised as an attractive approach to improve the activated carbon adsorption properties of the agro-waste materials (Demirak *et al.*, 2015).

Generally, the surface of activated carbon is modified in the activation stage. The modification can be divided into three classes, which are biological, physical, and chemical modification. Among them, chemical modification exhibits higher adsorption capacities (Chen *et al.*, 2003). Chemicals used for modification can be organic acid, oxidising agents, or organic compounds. A modifier can improve the adsorption process of these chemicals due to its higher number of active sites and formation of new functional groups such as hydroxyl, carboxylic acid, carbonyl, phosphate, and amine groups (Yeneneh *et al.*, 2011).

Papaya peel is an agro-waste that is discarded all over the world and considered useless. However, the other parts of the papaya such as its leaves, seed, root, seed, and pulp can bring a lot of medical benefits (Aravind *et al.*, 2013). According to the Department of Agriculture Malaysia (DOA, 2013), the production of papaya is increasing year-by-year. Papaya cultivation is located mostly in the Malaysian States of Johor (853.5 ha), Pahang (186.6 ha), Sarawak (182.0 ha), and Sabah (170.4 ha). Based on the report, Johor had the largest cultivation of papaya in recent years (16,108.9 metric tonnes). However, the high consumption rate of papaya produces high amounts of papaya peel waste, causing waste management problems. Therefore, using it as an alternative adsorbent can reduce solid waste generation. In addition, the other factor that makes papaya peel can be used as adsorbent is due to the chemical composition that consist of cellulose and lignin. This composition contains a variety of functional group such as hydroxyl and carbonyl that can helps in the ammonium ion binding. Recently, papaya peel has been evaluated as a new adsorbent to remove heavy metals such as chromium (IV) (Manjusha *et al.*, 2012) and lead (II) (Abbaszadeh *et al.*, 2014). However, there has been no study that has used papaya peel to remove ammoniacal nitrogen. This study would be the first of its kind, which recognises the potential of papaya peel in the removal of ammoniacal nitrogen.

1.2 Problem Statement

The presence of ammoniacal nitrogen can be detected in industrial and even treated wastewater. Discharge of this pollutant can lead to contamination of surface water. High concentrations of ammoniacal nitrogen in wastewater can cause eutrophication, which promotes excessive growth of algae in the water stream

(Khamidun *et al.*, 2014). According to statistics released by the Department of Environment (DOE, 2014), the number of polluted rivers with ammoniacal nitrogen has increased by 8% from 2013 to 2014 and this number is expected to grow since the water quality caused by NH_3-N can be associated with the discharge of treated and untreated sewage, which is also on the increase. Thus, wastewater, which contains a high concentration of ammoniacal nitrogen, needs to be treated before being discharged into the water stream.

Ion-exchange and adsorption are the common methods used by industries to remove ammoniacal nitrogen. However, ion exchange methods have disadvantages such as their low abundance and high operational costs (Demirak *et al.*,2015). Hence, the use of adsorption has increased in popularity among researchers. In recent years, researchers have begun to explore the use of agro-waste as adsorbents and the activated carbon derivation from this material because of its abundant availability and cheap cost. In addition, agro-waste materials contain lignin and cellulose, which are associated with functional groups such as carbonyl and hydroxyl that are able to participate in the adsorption process (Gonen and Serin, 2012).

The papaya fruit is widely cultivated and typically consumed directly as edible fruit. It can also be used as an ingredient for cosmetics or medical purposes. The papaya peel has thus generated a significant amount of waste from restaurants, pickled manufacturing, and even cosmetics manufacturers. There is now an increased usage of papaya wastes such as utilisation of its leaves and seeds. However the peel still remains as waste. There have been very few publications on the utilisation of the papaya peel. Recently, utilisation of papaya peel as an adsorbent to remove heavy metals and dyes was successfully conducted by Manjusha *et al.* (2012), Teja *et al.* (2013), and Abbaszadeh *et al.* (2016). In their study, chromium (VI), methylene blue, and lead, were respectively removed using the papaya peel. However, no study has been conducted to evaluate papaya peel efficiency in removing inorganic pollutants such as ammoniacal nitrogen. Understanding the capability of the papaya peel to also adsorb inorganic pollutants can help in future studies in evaluating papaya peel adsorption capability in wastewaters, which are contaminated with multiple pollutants. In addition, utilisation of peel waste also reduces overall papaya waste. The major characteristic of papaya peel that contributes in the ammoniacal nitrogen removal is its chemical composition that consists of cellulose and lignin. This composition contains a variety of functional group such as hydroxyl group (O-H), hydrocarbon group (C-H), carbonyl group (C=O), and ether group (-O-) (Rachtanapun, 2009). These groups have the ability to donate the electron which is negative charge and combine with the ammonium ion which is positively charge (Hadi *et al.*, 2011). Due to these characteristics, it is expected that papaya peel may have good potential in adsorbing ammoniacal nitrogen.

In this study, the efficiency of the papaya peel waste and its activated carbon in adsorbing ammoniacal nitrogen from an aqueous solution was studied. The following is the problem statement of this research:

Given the increasing amounts of papaya peel waste, this research aims to develop activated carbon adsorbent from the papaya peel. The suitability of either acid or alkaline modification will be studied. The efficiency of the new adsorbent in ammoniacal nitrogen removal from aqueous solutions and its optimal operating conditions will be determined. The most suitable isotherm, kinetic, and thermodynamic model, which represent the adsorption process, will be evaluated.

1.3 Research Objectives

The main research objective is to study the efficiency of activated carbon adsorbent from the papaya peel in removing ammoniacal nitrogen from aqueous water. In order to achieve the main objective, other objectives for this study are derived, as follows:

i) To characterise the surface properties and area of activated papaya peel before and after adsorption of ammoniacal nitrogen from the aqueous water.
ii) To determine whether acid or alkali is the best chemical activation agent to improve the surface properties and area of the papaya peel.

iii) To investigate the performance of the synthesised activated carbon in the removal of ammoniacal nitrogen via the adsorption parameters of pH, contact time, adsorbent dosage, temperature, and initial concentration of ammoniacal nitrogen in the solution.

iv) To determine the best adsorption equilibrium isotherm, kinetic, and thermodynamic model that can best correlate with the activated carbon papaya peel adsorbent.

1.4 Scope of Work

In order to achieve the objective of this research, the scope of the work is defined, as follows:

i. Characterise the surface morphology of the adsorbent before and after adsorption, the functional groups of papaya peel, papaya peel surface area, the crystallinity of papaya peel, and elemental analysis using Field Emission Scanning Electron Microscope (FESEM), Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), and Energy-dispersive X-ray spectroscopy (EDX), respectively.

ii. Determine the best activating agent to modify the papaya peel surface properties and surface area using a chemical activation method with six chemicals, which are phosphoric acid, nitric acid, acetic acid, sodium hydroxide, potassium hydroxide, and calcium chloride.

iii. Determine the optimal adsorption parameters that maximise the adsorption of ammonium ion using the activated carbon papaya peel in batch experiments such as the effect of initial pH (4–9), contact time (5–120 minutes), adsorbent dosage (0.01–0.3g), temperature (25–65°C) and initial concentration of ion (10–150 mg/L). The concentration of ammonium ion before and after adsorption is evaluated via the Nessler method using a spectrophotometer (DR 6000 Hach).

iv. Analyse ammoniacal nitrogen adsorption parameters in correlation with the existing isotherm models such as the Temkin, Langmuir, and Freundlich kinetics models, in terms of pseudo-first order and pseudo-second order and analyse the spontaneity of the adsorption process, enthalpy, as well as entropy in the thermodynamic part of the study.

v. Evaluate the desorption and regeneration process of the activated carbon papaya peel using hydrochloric acid and sodium hydroxide as desorbing agents.

vi. Perform a batch experimental study using real industrial wastewater in Malaysia to test the efficiency of removal ammonium ion.

vii. Compare the cost between using the new adsorbent and using commercial activated carbon.

1.5 Significance of Study

The significance of study for this work include:

i. Determination of an alternative way to reduce papaya peel waste by converting it into a bio-adsorbent.

ii. Understanding the capability of adsorbent derived from papaya peel for ammoniacal nitrogen removal from wastewater.

iii. The acquisition of optimum operating parameters for using papaya peel-based adsorbent for ammoniacal nitrogen removal from wastewater.

iv. A solution to reduce the concentration of ammoniacal nitrogen released to the water stream and subsequently reduce the pollutants that can harm human health and are hazardous to the environment.

REFERENCES

Abbaszadeh, S., Wan Alwi, S. R., Ghasemi, N., and Muhamad, I. I. (2014). Removal of Pb(II) from Aqueous Solution using Papaya Peel. In *Regional Symposium on Chemical Engineering (RSCE) and Symposium of Malaysian Chemical Engineering (SOMChE)*. 29-30 Oct 2014, Taylor's University,Kuala Lumpur.

Abbaszadeh, S., Wan Alwi, S. R., Webb, C., Ghasemi, N., and Muhamad, I. I. (2016). Treatment of Lead-Contaminated Water using Activated Carbon Adsorbent from Locally Available Papaya Peel Biowaste. *Journal of Cleaner Production*, *118*, 210–222.

Achak, M., Hafidi, A., Ouazzani, N., Sayadi, S., and Mandi, L. (2009). Low Cost Biosorbent "Banana Peel" for the Removal of Phenolic Compounds from Olive Mill Wastewater: Kinetic and Equilibrium Studies. *Journal of Hazardous Materials*, *166*(1), 117–125.

Achmad, A., Kassim, J., Suan, T. K., Amat, R. C., and Seey, T. L. (2012). Equilibrium, Kinetic and Thermodynamic Studies on the Adsorption of Direct Dye onto a Novel Green Adsorbent Developed from Uncaria Gambir Extract. *Journal of Physical Science*, *23*(1), 1–13.

Ademiluyi, F. T., and David-West, E. O. (2012). Effect of Chemical Activation on the Adsorption of Heavy Metals Using Activated Carbons from Waste Materials. *International Scholar Research Network(ISRN) Chemical Engineering*.

Ademiluyi, F. T., and Ujile, A. A. (2013). Kinetics of Batch Adsorption of Iron II Ions from Aqueous Solution using Activated Carbon from Nigerian Bamboo. *International Journal of Engineering and Technology*, *3*(6), 623–631.

Agency(EPA), E. P. (1999). Update of Ambient Water Quality Criteria for Ammonia. Environmental Protection Agency, Washington. Retrieved June 5, 2015, from http://www.epa.gov/caddis/ssr_amm_ref.html

Aguilar, M. I., Saez, J., Lorens, M., Soler, A., and Ortuno, J. F. (2002). Nutrient Removal and Sludge Production in the Coagulation, Flocculation Process. *Water Research*, *36*(11), 2910–2919.

Ahmida, K., Darmoon, M., Al-tohami, F., Erhayem, M., and Zidan, M. (2015). Effect of Physical and Chemical Preparation on Characteristics of Activated Carbon from Agriculture Solid Waste and their Potential Application. In *International Conference on Chemical, Civil and Environmental engineering (CCEE-2015) ,Istanbul,Turkey* (pp. 83–87). Istanbul, Turkey.

Akpomie, K. G., Dawodu, F. A., and Adebowale, K. O. (2015). Mechanism on The Sorption of Heavy Metals from Binary-Solution by a Low Cost Montmorillonite and Its Desorption Potential. *Alexandria Engineering Journal*, *54*, 757–767.

Alturkmani, A. (2013). Industrial Wastewater. Retrieved December 7, 2015, from http://www.4enveng.com

Aravind, G., Bhowmik, D., Duraivel, S., and Harish, G. (2013). Traditional and Medicinal Uses of Carica papaya. *Journal of Medicinal Plants Studies*, *1*(1), 7–15.

Awadalla, F. T., Striez, C., and Lamb, K. (1994). Removal of Ammonium and Nitrate Ions from Mine Effluents by Membrane Technology. *Separation Science and Technology*, *29*(4), 483–495.

Aziz, H. A., Adlan, M. N., Zahari, M. S. M., and Alias, S. (2004). Removal of Ammoniacal Nitrogen (N-NH3) from Municipal Solid Waste Leachate by using Activated Carbon and Limestone. *Waste Management & Research*, *22*(5), 371–375.

Babel, S., and Kurniawan, T. A. (2004). Cr(VI) Removal from Synthetic Wastewater using Coconut Shell Charcoal and Commercial Activated Carbon Modified with Oxidizing Agents and/or Chitosan. *Chemosphere*, *54*(7), 951–967.

Bailey, S. E., Olin, T. J., Bricka, R. M., and Adrian, D. D. (1999). A Review of Potentially Low-Cost Sorbent for Heavy Metals. *Water Resource*, *33*, 2469–2479.

Bansal, R. C., and Goyal, M. (2005a). Activated Carbon Adsorption and Environment: Removal of Inorganic from Water. In *Activated Carbon Adsorption* (pp. 297–364). CRC Pres (Taylor & Francis group).

Bansal, R. C., and Goyal, M. (2005b). Activated Carbon and its Surface Structure. In *Activated Carbon Adsorption* (pp. 1–66). CRC Pres (Taylor & Francis group).

Bansal, R. C., and Goyal, M. (2005c). Adsorption Energetics,Models and Isotherm Equation. In *Activated Carbon Adsorption* (pp. 67–143). CRC Pres (Taylor & Francis group).

Barakat, M. A., and Kumar, R. (2015). Modified and New Adsorbent for Removal of Heavy Metals from Wastewater. In *Heavy Metals in Water; Presence, Removal and Safety* (1st ed., pp. 193–208). Jaipur,India: Royal Society of Chemistry.

Bhat, I. U. H., Mungkar, A. N., Lee, K. E., and Khanam, Z. (2014). Oil Palm Root as Biosorbent for Heavy Metals : Biosorption , Desorption and Isothermal Studies. *International Journal of ChemTech Research*, *6*(1), 163–177.

Boopathy, R., Karthikeyan, S., Mandal, A. B., and Sekaran, G. (2013). Adsorption of Ammonium Ion by Coconut Shell-Activated Carbon from Aqueous Solution: Kinetic, Isotherm, and Thermodynamic Studies. *Environmental Science and Pollution Research*, *20*(1), 533–542.

Boshra, V., and Tajul, A. (2013). Papaya - An Innovative Raw Material for Food and Pharmaceutical Processing Industry. *Health and the Environment Journal*, *4*(1), 68–75.

Brunauer, S., Emmett, P. H., and Teller, E. (1938). *Adsorption of Gases in Multimolecular Layers* (Vol. 407).

Buasri, A., Chaiyut, N., Phattarasirichot, K., Yongbut, P., and Nammueng, L. (2008). Use of Natural Clinoptilolite for the Removal of Lead (II) from Wastewater in Batch Experiment. *Chiang Mai Journal of Science*, *35*(3), 447–456.

Carotenuto, M., Lofrano, G., and Sharma, S. (2015). Arsenic Contamination: An Overview. In *Heavy Metals in Water; Presence, Removal and Safety* (1st ed., pp. 86–117). Jaipur,India: Royal Society of Chemistry.

Carrerra, J., Baeza, J. A., Vincent, T., and Lafuenta, T. (2003). Biological Nitrogen Removal of High Strength Ammonium Industrial Wastewater with Two-Sludge System. *Water Research*, *37*, 4211–4221.

Chen, G. (2004). Electrochemical Technologies in Wastewater Treatment. *Separation and Purification Technology*, *38*, 11–41.

Chen, J. P., Wu, S., and Chong, K. H. (2003). Surface Modification of a Granular Activated Carbon by Citric Acid for Enhancement of Copper Adsorption. *Carbon*, *41*, 1986–1993

Chukwuka, K., Iwuagwu, M., and Uka, U. (2013). Evaluation of Nutritional Components of Carica Papaya L. At Different Stages of Ripening. *Journal of Pharmacy and Biological Sciences (IOSR-JPBS)*, *6*(4), 13–16.

Copcia, V., Hristodor, C., Luchian, C., Bilba, N., and Sandu, I. (2010). Ammonium Nitrogen Removal from Aqueous Solution by Natural Clay. *Academia*, (12), 1192–196.

Dada, A. O., Olalekan, A. P., Olatunya, A. M., and Dada, O. (2012). Langmuir , Freundlich , Temkin and Dubinin – Radushkevich Isotherms Studies of Equilibrium Sorption of Zn(11) onto Phosphoric Acid Modified Rice Husk. *IOSR Journal of Applied Chemistry*, *3*(1), 38–45.

Danish, M., Hashim, R., Ibrahim, M. N. M., Rafatullah, M., Sulaiman, O., Ahmad, T.,and Ahmad, A. (2011). Sorption of Copper (II) and Nickel (II) Ions from Aqueous Solutions Using Calcium Oxide Activated Date (Phoenix dactylifera) Stone Carbon : Equilibrium , Kinetic , and Thermodynamic Studies. *Journal of Chemical & Engineering Data*, *56*, 3607–3619.

Daud, Z., Latif, A. A., and Rui, L. M. (2012). Coagulation-Flocculation in Leachate Treatment by using Ferric Chloride and Alum as Coagulant. *International Journal of Engineering Research and Applications (IJERA)*, *2*(4), 1929–1934.

Demirak, A., Keskin, F., Sahin, Y., and Kalemci, V. (2015). Removal Of Ammonium from Water by Pine Cone Powder as Biosorbent. *Mugla Journal of Science and Technology*, *1*(1), 5–12.

Deng, Y., and Englehardt, J. D. (2007). Electrochemical Oxidation for Landfill Leachate Treatment. *Waste Management*, *27*, 380–8.

Ding, Z., Liu, L., Li, Z., Ma, R., and Yang, Z. (2006). Experimental Study of Ammonia Removal from Water by Membrane Distillation (MD): The Comparison of Three Configurations. *Journal of Membrane Science*, *286*(1–2), 93–103.

DOA. (2013). *Fruit Crop Statistic. Jabatan Pertanian (Department of Agriculture)*. Retrieved from http://www.doa.gov.my

DOA. (2015). Fruit Crop Statistic. Retrieved February 5, 2016, from http://www.doa.gov.my

DOE. (2014). Malaysia Environmental Quality Report 2014. Retrieved August 30, 2015, from https://enviro.doe.gov.m

Du, Q., Liu, S., Cao, Z., and Wang, Y. (2005). Ammonia Removal from Aqueous Solution using Natural Chinese Clinoptilolite. *Separation and Purification Technology*, *44*, 229–234.

El-Ashtoukhy, E.-S. Z., Amina, N. K., and Abdelwahabb, O. (2008). Removal of Lead (II) and Copper (II) from Aqueous Solution using Pomegranate Peel as a New Adsorbent. *Desalination*, *223*, 162–173.

Environmental Protection Agency, E. (1999). Update of Ambient Water Quality Criteria for Ammonia. Retrieved April 10, 2015, from http://www.epa.gov/caddis/ssr_amm_ref.html

EQA. (1974). *Environmental Quality Act. 1974. Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations*. Retrieved from http://www.water-treatment.com.cn/resources/discharge-standards/malaysia.htm

Escudero, A., Blanco, F., Lacalle, A., and Pinto, M. (2015). Struvite Precipitation for Ammonium Removal from Anaerobically Treated Effluents. *Journal of Environmental Chemical Engineering*, *3*, 413–419.

Fang, J., Gao, B., Sun, Y., Zhang, M., and Sharma, S. K. (2015). Use of Industrial and Agricultural Waste in Removal of Heavy Metals Present in Water. In *Heavy metals in water; presence, removal and safety* (1st ed., pp. 281–293). Jaipur,India: Royal Society of Chemistry.

Ferreira do. Nascimento, R., Wagner de Sousa, F., Sousa Neto, V. O., Almeida Fechine, P. B., Pereira Teixeira, R. N., de Tarso C. Freire, P., and Antônio Araujo-Silva, M. (2012). Biomass Adsorbent for Removal of Toxic Metal Ions from Electroplating Industry Wastewater. In *Electroplating* (pp. 101–136). InTech.

Gautam, R. K., Sharma, S. K., and Chattopadhaya. (2015). Functionalized Magnetic Nanoparticles for Heavy Metals Removal from Aqueous Solutions. In *Heavy Metals inWwater; Presence, Removal and Safety* (1st ed., pp. 57–59). Jaipur, India: Royal Society of Chemistry.

Genava. (1986). Environmental Health Criteria. Retrieved March 20, 2015, from http://www.inchem.org/

Gin, W. A., Jimoh, A., Abdulkareem, A. S., and Giwa, A. (2014). Production of Activated Carbon from Watermelon Peel. *International Journal of Scientific and Engineering Research*, *5*(2), 66–71

Gonen, F., and Serin, D. S. (2012). Adsorption Study on Orange Peel: Removal of Ni(II) Ions from Aqueous Solution. *African Journal of Biotechnology*, *11*(5), 1250–1258.

Guaya, D., Valderrama, C., Farran, A., Armijos, C., and Cortina, J. L. (2015). Simultaneous Phosphate and Ammonium Removal from Aqueous Solution by a Hydrated Aluminum Oxide Modified Natural Zeolite. *Chemical Engineering Journal*, *271*, 204–213.

Gueu, S., Yao, B., Adouby, K., and Ado, G. (2007). Kinetics and Thermodynamics Study of Lead Adsorption on to Activated Carbons from Coconut and Seed Hull of the Palm Tree. *International Journal of Environment and Science Technology*, *4*(1), 11–17.

Guo, Y., and Du, E. (2012). The Effects of Thermal Regeneration Conditions and Inorganic Compounds on the Characteristics of Activated Carbon used in Power Plant. *Energy Procedia*, *17*, 444–449.

Gupta, S., and Babu, B. (2008). *Economic Feasibility Analysis of Low cost Adsorbents for the Removal of Cr (VI) from Wastewater. Birla Institute of Technology and Science (BITS).*

Gupta, V. K., Sadegh, H., Yari, M., Shahryari Ghoshekandi, R, Maazinejad, B., and Chahardori, M. (2015). Removal of Ammonium Ions from Wastewater A Short Review In Development of Efficient Methods. *Global Journal of Environmental Science and Management*, 1(2), 149–158.

Hadi, N. B. A., Rohaizar, N. A. B., and Sien, W. C. (2011). Removal of Cu (II) from Water by Adsorption on Papaya Seed. *Asian Transactions on Engineering*, *1*(5), 49–55.

Halim, A. A., Abidin, N. N. Z., Awang, N., Ithnin, A., Othman, M. S., and Wahab, M. I. (2011). Ammonia and COD Removal from Synthetic Leachate using Rice Husk Composite Adsorbent. *Journal of Urban and Environmental Engineering*, *5*(1), 24–31.

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*(1–3), 31–35

Halim, A. A., Aziz, H. A., Johari, M. A. M., Ariffin, K. S., and Adlan, M. N. (2010). Ammoniacal Nitrogen and COD Removal from Semi-Aerobic Landfill Leachate using a Composite Adsorbent: Fixed Bed Column Adsorption Performance. *Journal of Hazardous Materials*, *175*, 960–4.

Halim, A. A., Latif, M. T., and Ithnin, A. (2013). Ammonia Removal from Aqueous Solution using Organic Acid Modified Activated Carbon. *World Applied Sciences Journal*, *24*(1), 1–6.

Hameed, B. H., Krishni, R. R., and Sata, S. A. (2009). A Novel Agricultural Waste Adsorbent for the Removal of Cationic Dye from Aqueous Solutions. *Journal of Hazardous Materials*, *162*(1), 305–311.

Haven, B. (2014). Activated Carbon Market Size, Industry Trends, Regional Outlook, Company Share and Segment Forecasts, 2014 to 2020. Retrieved October 16, 2015, from http://www.grandviewresearch.com/blog/activated-carbon-market

Hegazi, H. A. (2013). Removal of Heavy Metals from Wastewater using Agricultural and Industrial Wastes as Adsorbents. *Housing and Building National Research Center(HBRC)Journal*, *9*, 276–282.

Hesas, R. H., Arami-Niya, A., Wan Daud, W. M. A., and Sahu, J. N. (2013). Preparation and Characterization of Activated Carbon from Apple Waste by Microwave-Assisted Phosphoric Acid Activation: Application in Methylene Blue Adsorption. BioResources, 8(2), 2950–2966.

Ho, Y. S. (2004). Citation Review of Lagergren Kinetic Rate Equation on Adsorption Reactions. *Scientometrics*, *59*(1), 171–177.

Ho, Y. S., and McKay, G. (1998). A comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents. In *Process Safety and Environmental Protection* (pp. 332–340).

Hossain, M. A., Ngo, H. H., Guo, W. S., and Nguyen, T. V. (2012). Removal of Copper from Water by Adsorption onto Banana Peel as Bioadsorbent. *International Journal of GEOMATE*, *2*(2), 227–234.

Huang, H., Liu, J., Zhang, P., Zhang, D., and Gao, F. (2017). Investigation on the Simultaneous Removal of Fluoride, Ammonia Nitrogen and Phosphate from Semiconductor Wastewater using Chemical Precipitation. *Chemical Engineering Journal*, *307*, 696–706

Huang, H., Zhang, P., Zhang, Z., Liu, J., Xiao, J., and Gao, F. (2016). Simultaneous Removal of Ammonia Nitrogen and Recovery of Phosphate from Swine Wastewater by Struvite Electrochemical Precipitation and Recycling Technology. *Journal of Cleaner Production*, *127*, 302–310.

Huiping, Z. (2002). Regeneration of Exhausted Activated Carbon by Electrochemical Method. *Chemical Engineering Journal*, *85*(1), 81–85.

Inglezakis, V. J., and Poulopoulos, S. G. (2006). Adsorption, Ion Exchange and Catalysis. In *Adsorption, Ion Exchange and Catalysis* (pp. 31–56). Elsevier.

Iqbal, M., Saeed, A., and Zafar, S. I. (2009). FTIR Spectrophotometry, Kinetics and Adsorption Isotherms Modeling, Ion Exchange, and EDX Analysis for Understanding the Mechanism of Cd(II) and Pb(II) Removal by Mango Peel Waste. *Journal of Hazardous Materials*, *164*, 161–171.

Ismadji, S., and Bhatia, S. (2001). Characterization of Activated Carbons using Liquid Phase Adsorption. *Carbon*, *39*(8), 1237–1250.

Izanloo, H., and Nasseri, S. (2005). Cadmium Removal from Aqueous Solutions by Ground Pine Cone. *Iranian Journal of Environmental Health Science Engineering*, *2*(1), 33–42.

Jiuhui, Q. (2008). Research Progress of Novel Adsorption Process in Water Purification. *Journal of Environmental Science*, *20*, 1–13.

Jorgensen, T. C., and Weatherley, L. R. (2003). Ammonia Removal from Wastewater by Ion Exchange in the Presence of Organic Contaminants. *Water Research*, *37*, 1723–1728.

Ketcha, J. M., Dina, D. J. D., Ngomo, H. M., and Ndi, N. J. (2012). Preparation and Characterization of Activated Carbons obtained from Maize Cobs by Zinc Chloride Activation. *American Chemical Science Journal*, *2*(4), 136–160.

Khamidun, M. H., Fulazzaky, M. A., Md Din, M. F., and Mohd Yusoff, A. R. (2014). Removal of Ammonium from Domestic Wastewater Treatment Plant Effluent by Adsorbing onto the Coconut Shell Granular Activated Carbon in a Hydrodynamic Column. In *International Conference on Innovative Trends in Multidisciplinary Academic Research (ITMAR)* (pp. 197–206). 20-21 October 2014, Istanbul,Turkey.

Khan, M. A., Alemayehu, A., Duraisamy, R., and Berekete, A. K. (2015). Removal of Lead Ion from Aqueous Solution by Bamboo Activated Carbon. *International Journal of Water Research*, *5*(2), 33–46.

Kizito, S., Wu, S., Kipkemoi Kirui, W., Lei, M., Lu, Q., Bah, H., and Dong, R. (2015). Evaluation of Slow Pyrolyzed Wood and Rice Husks Biochar for Adsorption of Ammonium Nitrogen from Piggery Manure Anaerobic Digestate Slurry. *Science of the Total Environment*, *505*, 102–112.

Koyuncu, I., Topacik, D., Turan, M., Celik, M. S., and Sarikaya, H. Z. (2001). Application of the Membrane Technology to Control Ammonia in Surface Water. *Water Science and Technology: Water Supply*, *1*(1), 117–124.

Kulkarni, S., and Kaware, J. (2014). Regeneration and Recovery in Adsorption- A Review. *International Journal of Innovative Science, Engineering & Technology(IJISET)*, *1*(8), 61–64.

Li, C.-Y., Li, W.-G., and Wei, L. (2012). Research on Absorption of Ammonia by Nitric Acid-Modified Bamboo Charcoal at Low Temperature. *Desalination and Water Treatment*, *47*, 3–10.

Liang, Z., and Ni, J. (2009). Improving the Ammonium Ion Uptake onto Natural Zeolite by using an Integrated Modification Process. *Journal of Hazardous Materials*, *166*, 52–60.

Liew, H. J., Sinha, A. K., Nawata, C. M., Blust, R., Wood, C. M., and De Boeck, G. (2013). Differential Responses in Ammonia Excretion, Sodium Fluxes and Gill Permeability Explain Different Sensitivities to Acute High Environmental Ammonia in Three Freshwater Teleosts. *Aquatic Toxicology*, *126*, 63–76.

Liu, H., Dong, Y., Wang, H., and Liu, Y. (2010). Adsorption Behavior of Ammonium by Bioadsorbent-Boston Ivy Leaf Powder. *Journal of Environmental Sciences*, *22*(10), 1513–1518.

Ma, X., Wang, R., Guo, W., Yang, H., Liang, Z., and Fan, C. (2012). Electrochemical Removal of Ammonia in Coking Wastewater using Ti/SnO \n 2+Sb/PbO \n 2 anode. *International Journal of Electrochemical Science*, *7*, 6012–6024.

Mackenzie, L. D., and David, A. C. (2008). Wastewater Treatment. In *Introduction to Environmental Engineering* (pp. 419–543). New York: Mc Graw Hill.

Mafra, M. R., Igarashi-Mafra, L., Zuim, D. R., Vasques, É. C., and Ferreira, M. A. (2013). Adsorption of Remazol Brilliant Blue on an Orange Peel Adsorbent. *Brazilian Journal of Chemical Engineering*, *30*(3), 657–665.

Manjusha, A., Gandhi, N., and Srisha, D. (2012). Removal of Chromium (VI) from Painting Manufacturing Industry Waste Water using Papaya Peel Powder. *International Journal of Pharma World Research*, *3*(2), 1–9 (ISSN 0976–111X).

Mazloomi, F., and Jalali, M. (2016). Ammonium Removal from Aqueous Solutions by Natural Iranian Zeolite in the Presence of Organic Acids, Cations and Anions. *Journal of Environmental Chemical Engineering*, *4*, 240–249.

Mekonnen, E., Yitbarek, M., and Soreta, T. R. (2015). Kinetic and Thermodynamic Studies of the Adsorption of Cr (VI) onto Some Selected Local Adsorbents. *South African Journal of Chemistry*, *68*, 45–52.

Memon, S. Q., Bhanger, M. I., and Memon, J. U.-R. (2008). Evaluation of Banana Peel for Treatment of Arsenic Contaminated Water. In *Proceeding of the 1st Technical Meeting of Muslim Water Researchers Cooperation* (pp. 104–109). Malaysia.

Mendes, C., Maria, C., Abreu, P. De, Freire, J. M., Queiroz, E. D. R., and Mendonça, M. M. (2014). Chemical Characterization of the Flour of Peel and Seed from Two Papaya Cultivars. *Food Science and Technology*, *34*(2), 353–357.

Mook, W. T., Chakrabarti, M. H., Aroua, M. K., Khan, G. M. a., Ali, B. S., Islam, M. S., and Abu Hassan, M. a. (2012). Removal of Total Ammonia Nitrogen (TAN), Nitrate and Total Organic Carbon (TOC) from Aquaculture Wastewater using Electrochemical Technology: A Review. *Desalination*, *285*, 1–13.

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 Fe3+ Impregnated Activated Carbon. *Journal of Hazardous Materials*, 150(3), 695–702

Ofomaja, A. E., Naidoo, E. B., and Modise, S. J. (2009). Removal of Copper(II) from Aqueous Solution by Pine and Base Modified Pine Cone Powder as Biosorbent. *Journal of Hazardous Materials*, *168*, 909–917.

Okoye, A. I., Ejikeme, P. M., and Onukwuli, O. D. (2010). Lead Removal from Wastewater using Fluted Pumpkin Seed Shell Activated Carbon: Adsorption Modeling and Kinetics. *International Journal of Environmental Science and Technology*, *7*(4), 793–800.

Omar, E. A. S., Neama, A. R., and Maha, M. . (2011). A Study of the Removal Characteristics of Heavy Metals from Wastewater by Low-Cost Adsorbents. *Journal of Advanced Research*, *2*, 297–303.

Padmavathy, K. S., Madhu, G., and Haseena, P. V. (2016). A study on Effects of pH, Adsorbent Dosage, Time, Initial Concentration and Adsorption Isotherm Study for the Removal of Hexavalent Chromium (Cr (VI)) from Wastewater by Magnetite Nanoparticles. *Procedia Technology*, *24*, 585–594.

Paul, A. W. (2016). An Introduction to Chemical Adsorption Analytical Techniques and Methods. Retrieved November 1, 2016, from http://www.micromeritics.com

Pezoti, O., Cazetta, A. L., Bedin, K. C., Souza, L. S., Martins, A. C., Silva, T. L., and Almeida, V. C. (2016). NaOH-Activated Carbon of High Surface Area Produced from Guava Seeds as a High-Efficiency Adsorbent for Amoxicillin Removal: Kinetic, Isotherm and Thermodynamic Studies. *Chemical Engineering Journal*, *288*, 778–788.

Pholosi, A., Ofomaja, A. E., and Naidoo, E. B. (2013). Effect of Chemical Extractants on the Biosorptive Properties of Pine Cone Powder: Influence on lead(II) Removal Mechanism. *Journal of Saudi Chemical Society*, *17*, 77–86.

Prahas, D., Kartika, Y., Indraswati, N., and Ismadji, S. (2008). Activated Carbon from Jackfruit Peel Waste by H3PO4 Chemical Activation: Pore Structure and Surface Chemistry Characterization. *Chemical Engineering Journal*, *140*, 32–42.

Pulkka, S., Martikainen, M., Bhatnagar, A., and Sillanpä, M. (2014). Electrochemical Methods for the Removal of Anionic Contaminants from Water - A Review. *Separation and Purification Technology*, *132*, 252–271.

Rachtanapun, P. (2009). Blended Films of Carboxymethyl Cellulose from Papaya Peel (CMCp) and Corn Starch. *Kasetsart Journal - Natural Science*, *43*(5), 259–266.

Rashed, M. (2013). Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater. In *Organic Pollutants - Monitoring, Risk and Treatment* (p. 238). Intech.

Rozic, M., Cerjan Stefanovic, S., Kurajika, S., Vancina, V., and Hodzic, E. (2000). Ammoniacal Nitrogen Removal from Water Treatment with Clays and Zeolites. *Water Research*, *34*(14), 3675–3681.

Rui, L. M., and Daud, Z. (2011). Efficiency of the Coagulation-Flocculation for the Leachate Treatment. *Internationa; Journal of Sustainable Development*, *2*(10), 85–90.

Sabio, M. M., and Reinoso, F. R. (2004). Role of Chemical Activation in the Development of Carbon Porosity. *Colloids and Surfaces*, *241*, 15–25.

Sahira, J., Mandira, A., Prasad, P. B., and Ram, P. R. (2013). Effects of Activating Agents on the Activated Carbons Prepared from Lapsi Seed Stone. *Research Journal of Chemical Science*, *3*(5), 19–24.

Saltali, K., Sari, A., and Aydin, M. (2007). Removal of Ammonium Ion from Aqueous Solution by Natural Turkish (Yildizeli) Zeolite for Environmental Quality. *Journal of Hazardous Materials*, *141*, 258–263.

Sekar, M., Sakthi, V., and Rengaraj, S. (2004). Kinetics and Equilibrium Adsorption Study of Lead(II) onto Activated Carbon Prepared from Coconut Shell. *Journal of Colloid and Interface Science*, *279*, 307–313.

Sichula, J., Makasa, M. L., Nkonde, G. K., Kefi, A. S., and Katongo, C. (2011). Removal of Ammonia from Aquaculture Water using Maize Cob Activated Carbon. *Malawi Journal of Aquatic Fish*, *1*(2), 10–15.

Slaiman, Q. J. M., Haweel, C. K., and Abdulmajeed, Y. R. (2010). Removal of Heavy Metals Ions from Aqueous Solution using Biosorption onto Bamboo. *Iraqi Journal of Chemical and Petroleum Engineering*, *11*(3), 23–32.

Stuart, B. (2004). Infrared Specroscopy: Fundamentals and Applications. In *Analyrical Techniques in the Sciences* (pp. 21–43). Wiley & Sons, Ltd.

Tangjuank, S., Insuk, N., Udeye, V., and Tontrakoon, J. (2009). Chromium (III) Sorption from Aqueous Solutions using Activated Carbon Prepared from Cashew Nut Shells. *International Journal of Physical Sciences*, *4*(8), 412–417.

Tchobanoglous, G., Burton, F. L., and Stensel, H. D. (2003). Treatment and Reuse. In Metcalf & Eddy (Eds.), *Wastewater Engineering* (p. 4th edition). New York: McGraw Hills.

Teja, D. D., Bhavani, M., Sridevi, V., Snehalatha, P., and Lohita, M. (2013). Biosorption of Methylene Blue Dye from Aqueous Solution using Papaya Peel. *International Journal of Innovative Research in Science, Engineering and Technology*, *2*(8), 4073–4081.

Temkin, M., and Pyzhev, V. (1940). Kinetics of the Synthesis of Ammonia on Promoted Iron Catalyst. *Journal of Physics and Chemical*, *12*, 851–867.

Terme, V. delle. (1985). Wood Carbonisation and the Products Yields. Retrieved July 5, 2015, from http://www.fao.org/docrep/x5555e/x5555e00.htm#Contents

Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquerol, J., and Sing, K. S. W. (2015). *Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report)*. *Pure Applied Chemical* (Vol. 87).

Tosun, I. (2012). Ammonium Removal from Aqueous Solutions by Clinoptilolite: Determination of Isotherm and Thermodynamic Parameters and Comparison of Kinetics by the Double Exponential Model and Conventional Kinetic Models. *International Journal of Environmental Research and Public Health*, *9*, 970–984.

Villegas, V. (1997). "Carica papaya L.", in Verheij,Plant Resources of South-East Asia 2. In *PROSEA Foundation* (pp. 1635–1639).

Vymazal, J. (2014). Constructes Wetlands for Treatment of Industrial Wastewater: A Review. *Ecological Engineering*, *73*, 724–751.

Wang, Z., Guo, H., Shen, F., Yang, G., Zhang, Y., Zeng, Y., and Deng, S. (2015). Biochar Produced from Oak Sawdust by Lanthanum (La)-Involved Pyrolysis for Adsorption of Ammonium (NH4+), Nitrate (NO3-), and Phosphate (PO43-). *Chemosphere*, *119*, 646–653.

Wimalasiri, Y., Mossad, M., and Zou, L. (2015). Thermodynamics and Kinetics of Adsorption of Ammonium Ions by Graphene Laminate Electrodes in Capacitive Deionization. *Desalination*, *357*, 178–188.

Wu, L. na, Liang, D. wei, Xu, Y. ying, Liu, T., Peng, Y. zhen, and Zhang, J. (2016). A Robust and Cost-Effective Integrated Process for Nitrogen and Bio-Refractory Organics Removal from Landfill Leachate via Short-Cut Nitrification, Anaerobic Ammonium Oxidation in Tandem with Electrochemical Oxidation. *Bioresource Technology*, *212*, 296–301.

Yang, X., Guo, M., Wu, Y., Wu, Q., and Zhang, R. (2014). Removal of Emulsified oil From Water by Fruiting Bodies of Macro-Fungus (Auricularia Polytricha). *PLOS ONE*, *9*(4), 1–7.

Yeneneh, A. ., Maitra, S., and Eldemerdash, U. (2011). Study on Biosorption of Heavy Metals by Modified Lignocellulosic Waste. *Journal of Applied Sciences*.

Yuan, H., Xu, C., and Zhu, N. (2014). Disinhibition of the Ammonium Nitrogen in Autothermal Thermophilic Aerobic Digestion for Sewage Sludge by Chemical Precipitation. *Bioresource Technology*, *169*, 686–691.

Zaixing, L., Ren, X., Zuo, J., Liu, Y., Duan, E., Yang, J., and Wang, Y. (2012). Struvite Precipitation for Ammonia Nitrogen Removal in 7-Aminocephalosporanic Acid Wastewater. *Molecules*, *17*, 2126–2139.

Zhang, J., Xie, S., and Ho, Y.-S. (2009). Removal of Fluoride Ions from Aqueous Solution using Modified Attapulgite as Adsorbent. *Journal of Hazardous Materials*, *165*, 218–222.

Zhao, S., Huang, G., Cheng, G., Wang, Y., and Fu, H. (2014). Hardness, COD and Turbidity Removals from Produced Water by Electrocoagulation Pretreatment Prior to Reverse Osmosis Membranes. *Desalination*, *344*, 454–462.

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.

Zhu, Y., Kolar, P., Shah, S. B., Cheng, J. J., and Lim, P. K. (2016). Avocado Seed-Derived Activated Carbon for Mitigation of Aqueous Ammonium. *Industrial Crops and Products*, *92*, 34–41.