RRECOVERY OF LOW CONCENTRATION AMMONIACAL NITROGEN FROM AQUACULTURE WASTEWATER USING OIL PALM FIBER BIOCHAR

TANVEER AHMAD

MASTER OF ENGINEERING SCIENCE

FACULTY OF ENGINEERING AND GREEN TECHNOLOGY
UNIVERSITI TUNKU ABDUL RAHMAN
14 FEBRUARY 2023

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By

TANVEER AHMAD

A dissertation submitted to the Department of Environmental Engineering,
Faculty of Engineering and Green Technology,
Universiti Tunku Abdul Rahman,
In partial fulfilment of the requirements for the degree of
Master of Engineering Sciences
14 February 2023

ABSTRACT

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TANVEER AHMAD

The existence of ammonia-nitrogen (NH_3-N) in water bodies has received much attention due to its toxicity and its impact on human health and the environment. Aquaculture wastewater (AQW) contains NH_3-N, and this can cause tissue damage or even death of fishes. Nevertheless, NH_3-N is also categorized as a nutrient and a source of nitrogen in fertilizer. Adsorption process is considered one of the promising techniques for the adsorption of NH_3-N. Recently, various sorbents have been used for NH_3-N treatment, however limited studies were reported on biochar as a sorbent for NH_3-N recovery in low concentration. Most the studies reported on synthetic wastewater and for the removal of high concentrations of NH_3-N (> 5ppm). In this study, the feasibility of oil palm fiber (OPF) biochar on the recovery of NH_3-N was investigated. The OPF biochar was prepared in the presence of N_2 (pyrolysis) or air (partial oxidation). The preparation was also tested for physically and chemically activated. Design of experiments (DOE) was used to optimize the biochar preparation process. Upon optimization, process study, thermodynamics, kinetics, and mechanism of the removal process was deduced using various parameters and models. Finally, a cost analysis was made to understand the economic viability of the product produced. The OPF biochar preparation was deduced as 300 °C, 150 min, and 100 ml air/min by

DOE. The best biochar prepared with air injection shows a removal efficiency of 71.6 % and capacity of 1.6 mg/g for NH_3-N in synthetic wastewater. Further activation of biochar did not improve the removal efficiency. The process study was further optimized, and the following was achieved; contact time (180 min), shaking speed (150 rpm), dosage (2 g), pH 8~9, and temperature (25 °C). The best removal efficiency adsorption capacity achieved at above conditions are 72.6 % and 0.4 mg/g respectively in actual AQW. The isotherm data of NH_3-N agreed well with Linear and non-Linear Freundlich model (R^2 = 0.9009, 0.9518) compared to Langmuir model (R^2=0.8794, 0.9303) respectively, show heterogenous nature of the OPF biochar. The Langmuir adsorption capacity is 6.42 mg/g for the OPF biochar using non-Linear model. In the kinetics study, the best R^2 values were 0.9988, and 0.9950 for Linear and non-Linear pseudo second order as compared to pseudo first order (R^2 = 0.9861, and 0.9843), respectively, which indicates that chemisorption is the dominant mechanism. The results of the Intra-particle diffusion model indicate that the intraparticle diffusion is not the only rate-limiting step and shows strong initial adsorption as the R_i (0.47) is between $0.5 > R_i > 0.1$. Based on the temperature effect, the values of Gibbs free energy ($\Delta G°$) for OPF biochar were in the range of -13.83 to -15.38 kJ/mol. The negative value of $\Delta G°$ shows that adsorption is spontaneous. The entropy ($\Delta S°$) value (102.72 J/mol) suggests that randomness increases during the adsorption process. The positive value (16.90 kJ/mol) of the enthalpy change ($\Delta H°$) reveals that the process is endothermic and the adsorption efficiency of NH_3-N increases with increasing temperature. In the AQW, OPF biochar exhibits selective

recovery of NH_3-N. The characterization of the OPF biochar shows that the ion exchange process occurs during NH_3-N recovery, however, oxygen surface functional groups also play a key role. The cost analysis of the OPF biochar was investigated using a pilot plant design. The optimize biochar is cost effective and the price is RM 2.17/kg comparable to the ones reported in literature and commercially available. Biochar is an environmentally friendly and biodegradable sorbent. It is suggested in future, the spent OPF biochar can be further utilized as a soil conditioner or fertilizer.

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to my research supervisor Professor Sumathi Sethupathi for the continuous support of my Master study and research, for her patience, motivation, enthusiasm, and immense knowledge. Her guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor than her.
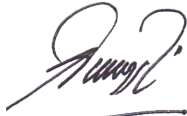
Besides my advisor, I would like to thank my co-supervisor Professor Dr. Mohammed J.K. Bashir, for his encouragement and insightful comments. I would like to thank all the lab-staff for their support in completing this project. I would also like to thank UTAR as a whole for accepting me, financing my research project under the scheme Long Term Research Grant Scheme (LRGS/1/2018/USM/01/1/2) - (UTAR/4411/S01) provided by Ministry of Higher Education Malaysia, and making me a better individual.

I would also like to dedicate this work to every single person, who in their own capacity, tries to protect our planet and environment. Lastly, I would like to dedicate this work to my parents, whose unconditional love has been the inspiration behind all the success in my life.

APPROVAL SHEET

This dissertation entitled **"RECOVERY OF LOW CONCENTRATION AMMONIACAL NITROGEN FROM AQUACULTURE WASTEWATER USING OIL PALM FIBER BIOCHAR"** was prepared by TANVEER AHMAD and submitted as partial fulfillment of the requirements for the degree of Master of Science in Engineering at Universiti Tunku Abdul Rahman.

Approved by:

_____

(Professor Dr. Sumathi Sethupathi)
Date…14/02/2023…….
Supervisor
Department of Environmental Engineering
Faculty of Engineering and Green Technology
Universiti Tunku Abdul Rahman

_____

(Professor Dr. Mohamed J.K. Bashir)
Date..14/02/2023…….
Co-supervisor
Department of Environmental Engineering
Faculty of Engineering and Green Technology
Universiti Tunku Abdul Rahman

FACULTY OF ENGINEERING AND GREEN TECHNOLOGY

UNIVERSITI TUNKU ABDUL RAHMAN

Date: 14/02/2023

SUBMISSION OF DISSERTATION

It is hereby certified that **Tanveer Ahmad** (ID No: *19AGM05256*) has completed this dissertation* entitled " **RECOVERY OF LOW CONCENTRATION AMMONIACAL NITROGEN FROM AQUACULTURE WASTEWATER USING OIL PALM FIBER BIOCHAR"** under the supervision of Prof. Dr. Sumathi Sethupathi (Supervisor) from the Department of Environmental Engineering, Faculty of Engineering and Green Technology, and Prof. Dr. Mohamed J.K. Bashir (Co-Supervisor) from the Department of Environmental Engineering, Faculty of Engineering and Green Technology.

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_____
(Tanveer Ahmad)

DECLARATION

I <u>TANVEER AHMAD</u> hereby declare that the dissertation is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTAR or other institutions.

Signature: _____

Name: Tanveer Ahmad

ID No: 19AGM05256

Date: 14/02/2023

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AQW	Aquaculture wastewater
OPF	Oil palm fiber
FAO	Food and Agriculture Organization of the United Nations
DOF	Department of fisheries
GDP	Gross domestic product
SS	Suspended solid
NH_3	Ammonia
NH_3-N	Ammoniacal-nitrogen
NO_2^-	Nitrite
NO_2^--N	Nitrite-nitrogen
NO_3^-	Nitrate
NO_3^--N	Nitrate-nitrogen
TN	Total nitrogen
PO_4^{3-}-P	Reactive phosphorus
TP	Total phosphorus
BOD	Biological oxygen demand
COD	Chemical oxygen demand
TDS	Total dissolved solid
TSS	Total suspended solid
DO	Dissolved oxygen
Cl^-	Chloride
SO_4^2	Sulphate
$CaCO_3$	Calcium carbonate
EFB	Empty fruit bunches
PKS	Palm kernel shell
POME	Palm oil effluent
RAS	Recirculating aquaculture system
IMTA	Integrated multi-tropic aquaculture
BFT	Biofloc technology
CGS	Calcined gastropod shell
PCFF	Pyrolyzed chicken feathers fiber

DS	Desulfurization slag
IBI	International Biochar Initiative
CO	Carbon monoxide
CO_2	Carbon dioxide
CH_4	Methane
H_2	Hydrogen
HTC	Hydrothermal carbonization
Cu	Copper
Fe	Iron
Zn	Zinc
Mn	Manganese
Ca	Calcium
Mg	Magnesium
Na	Sodium
K	Potassium
NH_4^+	Ammonium
Pb	Lead
RT	Room temperature
CEC	Cation exchange capacity
NaOH	Sodium hydroxide
HNO_3	Nitric acid
HCl	Hydrochloric acid
H_2O_2	Hydrogen peroxide
H_3PO_4	Phosphoric acid
CH_3COOH	Acetic acid
H_2SO_4	Sulfuric acid
$AgNO_3$	Silver nitrate
NaCl	Sodium chloride
N_2	Nitrogen gas
BET	Brunauer-Emmett-Teller
FESEM	Field Emission Scanning Electron Microscope
EDX	Energy Dispersion X-ray
ATR	Attenuated Total Reflectance

RSM	Response surface methodology
CCD	Central composite design
ANOVA	Analysis of variance
F-value	Fisher variance ratio
p-value	Probability value
DOE	Design of experiments
$(NH_4)_2SO_4$	Ammonium sulfate
pHzc	Point zero charge
TGA	Thermogravimetric analysis
Al	Aluminum
Si	Silicon
C	Carbon
O	Oxygen
hr	Hour
min	Minute
PFO	Pseudo first order
PSO	Pseudo second order
Ea	Activation energy
$\Delta S°$	Change in entropy
$\Delta H°$	Change in enthalpy
$\Delta G°$	Change in Gibb's free energy
$	US dollar
RM	Malaysian ringgit

CHAPTER 1

INTRODUCTION

1.1. Background of the study (Aquaculture)

Aquaculture and sea capturing represent 46 % and 54 % of the total fish production (178.5 million tonnes in 2018) respectively. But sea capture has been almost the same since the 1990s, as shown in **Figure 1.1.** The increase in fish consumption increased at a rate of 3.1 % annually from 1961 to 2017.

NOTE: Excludes aquatic mammals, crocodiles, alligators and caimans, seaweeds and other aquatic plants.
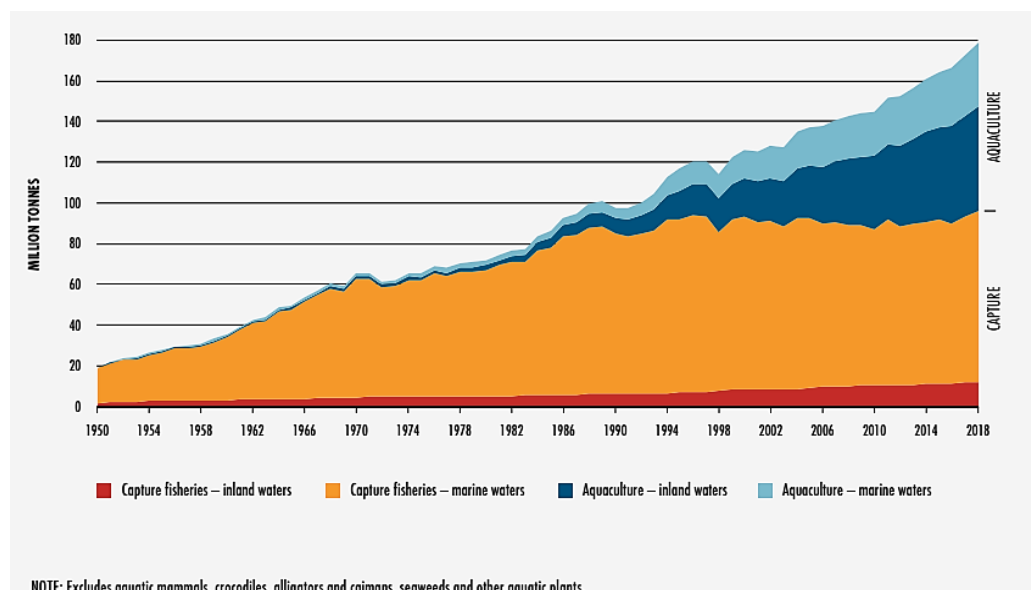
Figure 1.1. World fisheries and aquaculture production. Adapted from report (The state of world fisheries and aquaculture, (FAO, 2020))

To meet the demand, fish farming is required, and aquaculture operation is growing faster than other any other major food sector. The Food and

Agriculture Organization of the United Nations reported an average annual rate of 5.3 % between 2001 – 2018 (FAO, 2020). In the southeast Asian region, Malaysia is the seventh largest contributor to aquaculture production.

Malaysia is ranked fifth in term of total production of fishery and account for 6.9 % (SEAFDEC, 2018). Due to Malaysia long coastline of around 4780 km, the aquaculture industry is dominated by brackish aquaculture. In Malaysia freshwater aquaculture is predominant by pond culture (FAO, 2021). According to the department of fisheries (DOF) of Malaysia, the production of aquaculture is slightly reduced since 2010 to 2019 from 0.58 to 0.39 million tonne as shown in **Figure 1.2**, (DOF, 2020). The aquaculture industry contributes to about 12 % of the total GDP of Malaysia in 2020 (Department of Statistics Malaysia, 2020). Although aquaculture production is necessary to ensure world food security, it produces a large amount of wastewater that has repercussions on the environment.
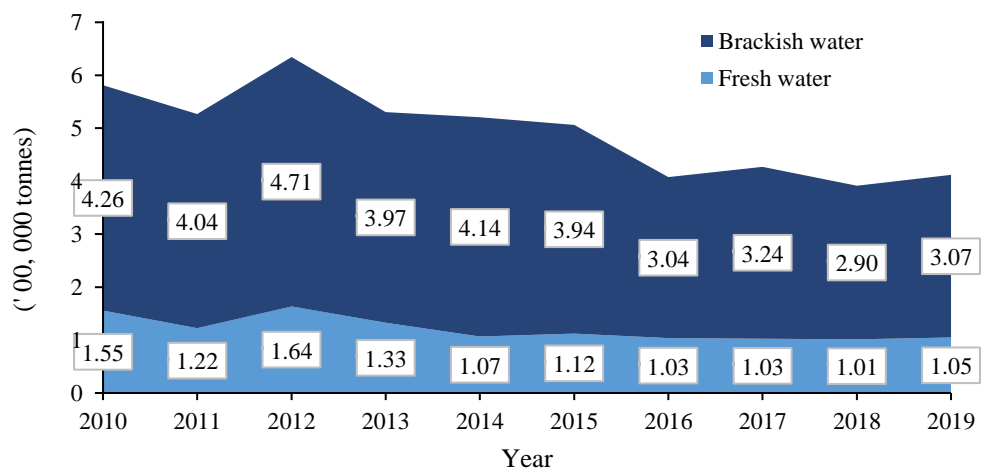
Figure 1.2. Aquaculture production in Malaysia (DOF, 2020)

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1.2. Aquaculture wastewater

Aquaculture wastewater (AQW) consists mainly of suspended solids (SS), dissolved organic matter, and nutrients (i.e. nitrogen and phosphorus compounds) (Turcios and Papenbrock, 2014). The total solid in AQW is mainly composed of uneaten food and fish feces (Akinwole, Dauda and Ololade, 2016). Dissolved organic matter in AQW is the decomposition of uneaten feed or food metabolism in fish (Dauda *et al.*, 2019) and mainly contains nitrogen and phosphorus (Boyd and Massaut, 1999). Nitrogen and phosphorus retention varies in fish, with average nitrogen and phosphorus retained between 10 – 49 % and 17 – 40 %, respectively, from the utilized feed. Additionally, nitrogen (3.6 – 35 %) and phosphorus (15 – 70 %) in feces and excretory products (37 – 72 % nitrogen and 1 – 62 % phosphorus) are released (Dauda *et al.*, 2019). Phosphorus is excreted in the form of particulate matter (fecal) (Sugiura *et al.*, 1999). Although nitrogen is excreted in the form of ammonia (NH_3) (Lazzari and Baldisserotto, 2008) and is typically suggested to be less than 1 ppm in the culture tank, as it is toxic to fish (Dauda *et al.*, 2019). Also, NH_3 occurs in AQW in unionized and ionized form (NH_3 and NH_4^+) and the equilibrium ratio depends on the pH and water temperature (Ebeling and Timmons, 2012). Further, NH_3 is converted into nitrite (NO_2^-) and nitrate (NO_3^-) (Dauda, Akinwole and Olatinwo, 2014). High concentration of NO_2^- significantly reduce the growth of fish (Romano and Zeng, 2013). Although NO_3^- is the final product of NH_3 oxidation and is known to be non-toxic to fish species at low concentrations

(Dauda and Akinwole, 2015) and can accumulate to a level as high as 300 – 400 ppm over time (Dauda *et al.*, 2019).

Nitrogen and phosphorus are the main final product of the fish farming which make aquaculture high risk for environmental pollution (Lazzari and Baldisserotto, 2008) and further cause eutrophication (Dauda *et al.*, 2019). In addition to this, the effluent of fish farm is rich in nutrients (Ahmad *et al.*, 2022) and can be recovered (Zhou *et al.*, 2019; Beckinghausen, Odlare, *et al.*, 2020). Further, the circular economy of the AQW industry could be improve through recovery (Beckinghausen, Reynders, *et al.*, 2020). Therefore, there is need to treat the AQW wastewater before it is released into the environment. Moreover, ammonia is a form of nutrient, and it will be useful if it can be recovered.

1.3. Oil palm industry waste

Malaysia is the world's second largest producer of palm oil and accounts for 28 % (19.92 million ton) of the world's production (FAO, 2018). The palm industry causes various type of wastes including empty fruit bunches (EFB), palm kernel shell (PKS), mesocarp fiber or oil palm fiber (OPF), and palm oil effluent (POME). The generation of solid biomass waste about 40,072.17 million tonnes per annum, while POME was produced at 136,328 million tonnes per year, been projected by 2030 (Jafri *et al.*, 2021). Among the waste, 15.73 million tons of OPF were produced annually (Wafti *et al.*, 2017). OPF were produced from different types of biomasses waste

such oil palm trunk, empty fruit bunches, and oil palm frond. The OPF contains of cellulose (25.0 %), hemicellulose (25.7 %), lignin (25.5 %), and ash (5.8 %) on dry weight basis and having the heating value of 17.15 MJ/kg dry wt (Kaniapan *et al.*, 2021). Having the 2nd highest heating value of OPF compared to other biomass waste from the palm industry (Kaniapan *et al.*, 2021). At present 98.4± 1.0 % of OPF is used to produce electricity and steam for palm oil extraction, while the rest is sold on the market (Kong *et al.*, 2014).

The growth in the waste generation poses great challenges to the environmental sustainability in relation to waste management, and greenhouse gas emission from waste biomass. Reutilization of waste biomasses has gained many interests among the researchers. Biochar, value-added product, can be formed from OPF using slow pyrolysis. The biomass conversion to biochar results in the sequestration of around 50 % of the initial carbon compared to the less amount preserved after biological degradation (less than 10-20 % after 5-10 years) and burning (3 %) (Kong *et al.*, 2014).

The NH_3-N occurs in wastewater in dissolved formed and can be removed via coagulation and flocculation, biofloc technology, and adsorption process. In flocculation and coagulation process when the chemicals are added to the wastewater the NH_3 in the wastewater react with the chemical and removed (Rishel and Ebeling, 2006). However, in the biofloc technology, the microorganism discomposes the NH_3 into nitrogen and hydrogen (Fatimah et al., 2019). In the adsorption process the NH_3-N

molecules are interact with the adsorbent surface via surface functional groups, or ion exchange process or physically adsorbed in the pore of the adsorbent (El-sherbiny, El-chaghaby and El-Shafea, 2019).

1.4. Problem statement

The prime sources of NH_3-N in AQW are the excretion of fish, organic matter produced by the algae and decomposition of fecal. (Hargreaves and Tucker, 2004). NH_3-N is toxic to aquatic species and recommended to be less than 1 ppm in fish culture tank (Dauda *et al.*, 2019). Moreover, direct discharge of AQW to the river will pollute the water, affecting the growth of aquatic species in the receiving water bodies, as well as the loss of the nutrients. Therefore, it is necessary to treat the AQW to recover the nutrients prior to discharge.

Most of the latest studies in the literature, focuses on high initial concentrations of NH_3-N (>10ppm) and reported using synthetic wastewater. (Aghoghovwia, Hardie and Rozanov, 2020; Xu *et al.*, 2022). The synthetic wastewater did not represent the actual wastewater scenario as it contains other various pollutants which inhibit the performance of the adsorbent (Yao *et al.*, 2022). Low concentration of NH_3-N in AQW, further worsen the removal as low concentration shall have very little interaction between the adsorbent and the adsorbate molecule. Therefore, in this study, the recovery potential OPF biochar for low concentration condition of NH_3-N in actual AQW was investigated. Different preparation methods for biochar

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production were evaluated to understand the removal mechanism of the NH3-N in lower concentration. Among the methods, partially oxidized biochar (with injection of air) shows the best performance.

Malaysia is one of the major producers of the palm oil and generates biomass wastes. The growth of palm industry waste poses a great challenge to the environment (Khatun *et al.*, 2017). Direct incineration of OPF is illegal in Malaysia (Kaniapan *et al.*, 2021), and because of the poor utilization and abundant availability of OPF in Malaysia, there is an urgent need for reutilization of this waste. Not only to be reutilized but also to enhance it to a value-added commercial product. Many has reported converting to biochar and AC for dyes, pesticides, heavy metals, and analyte (Marsin *et al.*, 2018). But very limited on nutrients removal especially NH_3N (Ricky *et al.*, 2016; Zahrim *et al.*, 2017; Ismail *et al.*, 2018; Nasir *et al.*, 2018). So far only four studies have been reported on OPF and cost analysis was not done. In this study, the cost of analysis on the pilot scale was calculated for commercialization of the product.

1.5. Objectives of the study

The aim of this study is to investigate the feasibility of oil palm fiber biochar to recover NH_3-N from AQW via adsorption. The objectives of this study are as follows:

- To optimize the preparation conditions of OPF biochar for low concentration NH_3-N adsorption.
- To optimize the adsorption parameters, and to evaluate the kinetics, mechanism, isotherms, and thermodynamics.
- To analyze the costing of OPF biochar production.

1.6. Novelty

Limited studies on carbon-based adsorbent have been found for the removal of low concentrations of NH_3-N from wastewater, especially AQW. Biochar and activated carbon produced from different raw materials have been tested for NH_3-N (<15 ppm). Limited studies have been done on concentration of less than 5 ppm (Sichula *et al.*, 2011; Zahrim *et al.*, 2017; Karia *et al.*, 2022). However, most studies have been done on synthetic wastewater (Hussain *et al.*, 2007; Shi, Wang and Zheng, 2013; Khalil, Sergeevich and Borisova, 2018). Three studies using different types of activated carbon, that is commercial activated carbon, chicken feather, and maize cob, were tested for the adsorption of NH_3-N from AQW by Karia *et al.*, (2021) , Moon *et al.*, (2017), and Sichula *et al.*, (2011), respectively. The

performance of the adsorbents was poor and could only achieve less than 60% removal of NH_3-N. Moreover, the initial concentration of NH_3-N was reported to be higher than 15 ppm. In addition to this, the economic feasibility and the cost of the biochar production at a pilot plant scale was evaluated.

Thus, in this study, OPF biochar shall be prepared and tested for its recovery efficiency for low concentration NH_3-N in AQW. Also, to the best of our knowledge, studies have not been reported applying OPF biochar for low concentration recovery of NH_3-N from AQW.

1.7. Scope of study

This research is narrow down to the scope low initial concentration of NH_3-N as reported highly to fish as well as other aquatic species. The bio-adsorbent raw material that was focusing on in this study was oil palm waste (OPF). The physical, chemical, and morphological structures of the OPF biochars were studied while their adsorption uptake adsorption efficiency/capacity were examined. The best-performing biochar for NH_3-N was further use for the effect of various operating parameters such as shaking speed, contact time, temperature, pH and dosage. The results were also compared with those of the biochars in the literature.

1.8. Organization of dissertation

Chapter 1: Introduction start with overview of aquaculture production as well as the AQW including the presence of nutrients and pollutants has been discussed. The waste of the oil palm industry and its application in various fields are described. The toxicity of the NH_3-N on aquaculture species and the recovery with biochar has been outlined. The objective of palm waste is also mentioned, while the novelty and scope of the study explain how deeply the adsorption research and operating factors parameters will be studied in the work.

In Chapter 2: Literature review, the concentration of nutrients in the AQW has been reported with the addition of various treatment methods to remove pollutants and nutrients from the AQW. On other hand, a brief study on biochar, production method of biochar, pollutant removal by biochar, and adsorption mechanism has been discussed. Furthermore, a literature study on activated carbon and biochar prepared from OPF and its application is described for different pollutants and nutrients. Moreover, a detail study of the adsorption isotherms, kinetics, and thermodynamic is reviewed in the end of the chapter.

In Chapter 3: Methodology, besides laboratory testing and characterization studies, materials (chemicals and reagents,), and equipment used, are explained. Along with the production of biochar and activated

biochar, adsorption study and its parameters are discussed in detailed with collection of real AQW collection with its initial readings.

In Chapter 4: Results and discussion, all the collected results are shown in graphical and images form, in consecutive order from batch adsorption tests in preliminary screening stage, all characterizations, parameter evaluation, thermodynamics, adsorption isotherm, and kinetics. The analysis and discussion of the mechanism are carried out based on the experimental findings. Also, cost analysis of the biochar is also calculated using optimized OFP biochar preparation conditions from the lab to a pilot scale.

Lastly, in Chapter 5: Conclusion, the deductive reasoning is stated based on the results explained in Chapter 4. For future references and advancements in the research, recommendations are also made on the relevant areas of the research.

CHAPTER 2

LITERATURE REVIEW

2.1. Characteristics of AQW

Based on the literature, the characteristics of the AQW are shown in **Table 2.1**. These pollutants and nutrients need to be removed from AQW before being discharge to the environment. NH_3-N is highly toxic and is recommended less than 1 ppm in the fish tank (Dauda *et al.*, 2019). Otherwise, it can decrease the growth and the immune response system (hemolymph THC) of fishes (Romano and Zeng, 2013). NO_2^--N is the intermediate product of ammonia oxidation and generally recommended to be less than 0.5 ppm. However, NO_2^--N is not stable and convert to NO_3^--N. Further, NO_3^--N is considered safe as it not harmful most of fish at concentration as high 200 ppm. Phosphorus causes eutrophication (Dauda *et al.*, 2019). A higher concentration of COD will cause less DO in the water. This may disturb live stability of the aquatic environment. TSS are considered extremely harmful since they can block fish gills and cause death, while TDS increase nitrogenous compound and stress cultured fish (Dauda *et al.*, 2019). Salts are using for reducing stress in fish, and lime is used for the treatment of ponds for acidity during the preparation of the pond (Dauda *et al.*, 2019). The pH range 6 – 9 is necessary for optimal growth, however, an acidic pH ~ 4 or less is lethal to fish (Ndubuisi *et al.*, 2015). In general high concentrations of the nutrients (phosphorus and nitrogen) can also cause

the eutrophication and promote the growth of floating macrophyte hence reduced the sunlight penetration disrupts the underwater photosynthesis of phytoplankton hence decreasing the DO in aquatic environment (Kurniawan *et al.*, 2021). So, it is required to treat the AQW and recover the valuable nutrients before it is being release to the receiving water bodies.

Table 2.1. Characteristics of AQW

Temp. (ºC)	DO (ppm)	pH	TSS (ppm)	TDS (ppm)	NH_3-N (ppm)	NO_2-N (ppm)	NO_3-N (ppm)	TN (ppm)	PO_4^{3-}-P (ppm)	BOD (ppm)	COD (ppm)	Cl^- (g/l)	SO_4^{2-} (ppm)	$CaCO_3$ (ppm)	Ref.
-	1.9-16.8	6-9.3	0.7-3.3	-	0.0 -7.7	0.0-1.4	0.2-16.8	0.6-14.0	0.0	-	-	-	-	-	Boyd *et al.*, 2000
-	6.2	7.7	-	-	0.8	0.2	19 ± 10	-	20 ± 12	5.3	-	5	85	-	Kioussis, Wheaton and Kofinas, 2000
27.4 ± 0.8	5.0 ± 0.9	7.3±0.1	-	-	0.5 ± 0.1	0.1 ± 0.1	7.2 ± 12.8		-	-	-	-	-	-	Dauda and Akinwole, 2014
27	4.9	7.2	1125	2275	3.0	0.3	5.0	-	-	-	-	-	-	-	Akinwole, Dauda and Ololade, 2016
-	-	7.8	-	-	0.3 ± 0.1	2.4 ± 0.7	51.8 ± 0.2	-	-	-	17 ± 3.4	-	-	-	Zou *et al.*, 2018
23.4 ± 2.6	7.2 ± 1.0	6.2 ± 0.6	-	-	0.6 ± 0.2	0.5 ± 0.1	26.6 ± 3.2	27.7 ± 2.3	-	-	-	-	-	-	Chunjie Li *et al.*, 2019
28	-	8.1	254 ± 29	-	1.6 ± 0.2	1.5 ± 0.0	35.8 ± 0.4	-	3.9 ± 0.1	-	-			148.9 ± 2.3	W. Liu *et al.*, 2019
-	-	7.5	-	-	≤ 0.1	0.3	152.8	-	16.1	-	38.4	147.3	420.6	-	Tejido-nuñez *et al.*, 2019s

Table 2.1. Continued

Temp. (ºC)	DO (ppm)	pH	TSS (ppm)	TDS (ppm)	NH$_3$-N (ppm)	NO$_2$-N (ppm)	NO$_3$-N (ppm)	TN (ppm)	PO$_4^{3-}$-P (ppm)	BOD (ppm)	COD (ppm)	Cl$^-$ (g/l)	SO$_4^{2-}$ (ppm)	CaCO$_3$ (ppm)	Ref.
30 ± 2	6.7 ± 0.7	7.8 ± 0.2	-	-	1.1 ± 0.3	0.3 ± 0.2	0.4 ± 1.0	-		-	-	-	-	-	John, Krishnapriya and Sankar, 2020
-	-	7.8 ± 0.0	83 ± 4	-	24.8 ± 1.4	<0.01	<0.3	-	0.7 ± 0.1	-	-	-	-	-	Ng and Chan, 2021
-	3.1	7.9	-	-	3.5			-		-	-	-	-	-	Karia et al., 2022
-	-	7.2	-	-	0.0	0.0	21.82	-	0.7	-	-	-	-	-	Stamenković, Steinwall and Wulff, 2021
-	-	-	-	-	0.2 ± 0.0	0.1 ± 0.1	0.5 ± 0.4	-	0.2 ± 0.1	-	-	-	-	-	Iber and Kasan, 2021
-	-	7.5	492	-	50.1	-	-	-	2.8	-	139	-	-	-	Kurniawan et al., 2022
33.4	2.1	8.9	-	734	1.3	0.8	-	-	0.1	2.2	1184	-	-	-	Saxena et al., 2022s

2.2. Treatment technologies for AQW pollutants

Figure 2.1 illustrates types of wastewater treatment processes used to improve the AQW, quality. Physical, chemical, and biological methods have been applied to aquaculture systems to reduce the concentration of nutrients and other pollutants in effluent before disposing to the environment.
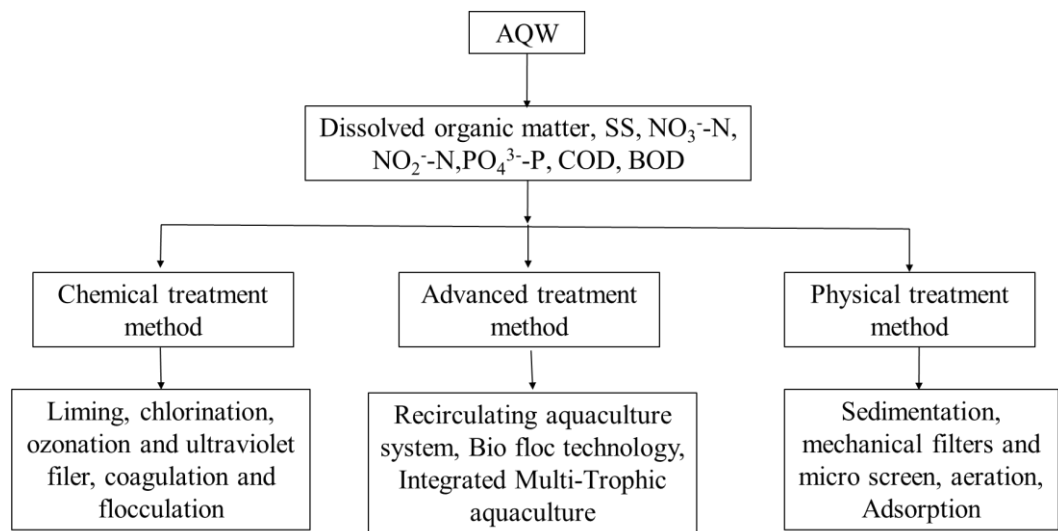
Figure 2.1. AQW treatment methods

In aquaculture systems, wastewater can be treated chemically by various methods. In liming, the pH of the water was increased by passing water from lime filter as a result reduced the soluble phosphorus and free CO_2. Chlorination is a very common method used for disinfectant (Metcalf and Eddy, 2003; Crittenden, Trussell and Hand, 2012). It has been reported, that deactivation rate of bacteria increases from 0.19 to 0.3 s⁻ with the chlorine concentration from 2 to 4 ppm in AQW (Liltved and Landfald, 1995).

Ultraviolet or ozone treatment for AQW is a common method specifically used in recirculating aquaculture system (RAS) (Ling and Weimin, 2010). This method successfully eliminates parasites, pathogens, and bacteria, etc., that can harm fish (Davis, 2010). Ozonation is, very advantageous in the RAS, and it not only decreases the organic load but also sterilizes the system to make it more helpful for fish growth (Ling and Weimin, 2010). In the AQW system, ozone nearly decomposed all NO_2^--N while reduced total ammonia (TAN) concentration to 0.1 ppm (Chen *et al.*, 2015). The combination of ultraviolet irradiation and ozonation (20 ppb) remove all bacteria as well as 66.67 – 83.33 % of NO_2^--N and 37.5 – 47.5 % of TSS from AQW as shown in **Table 2.2** and **2.3** (Summerfelt *et al.*, 2009).

Table 2.2. Particles removal efficiency of various techniques for AQW treatment

Technique	Modification	Removal efficiency (%)	Particle size (µm)	Remarks	Ref.
Sedimentation (centrifugal separation)	Swirl separator	37.1 ± 3.3	-	Used as a primary settler nutrient recovery	Davidson and Summerfelt, 2005
		60–63 (feed waste), 59–71 (fecal solid)	-	-	Lee, 2015
		46	-	-	Lee, 2014
		> 90	> 250	-	Pfeiffer, Osborn and Davis, 2008
	Radial separator	77.9 ± 1.6	-	-	Davidson & Summerfelt, 2005
Filtration	Fluidized sand filtration	> 65	23 – 55	Final filtration component in RAS	Pfeiffer, Osborn and Davis, 2008
	Micro-screen drum filter	~ 50 (filter aperture size 100 µm) 100 (filter aperture size 18 µm)	-	-	Dolan, Murphy and Hehir, 2013
	Drum screen filter	34.22 ± 8.85 (Powder feed), 52.41 ± 16.77 (Pellet feed)	-	-	Ali, 2013
	Inclined belt filter + coagulant / flocculent	95	-	-	Ebeling, Welsh and Rishel, 2006
	Granular filter	100 40 - 50	> 50 < 10	- -	Malone and Beecher, 2000

Table 2.2. Continued

Technique	Modification	Removal efficiency (%)	Particle size (μm)	Remarks	Ref.
Filtration	Polystyrene floating filter or sand medium filter	60	-	-	Steicke, Jegatheesan and Zeng, 2007
RAS wastewater management	-	85 – 98	-	-	Martins *et al.*, 2010
Ozonation	Ozonation + UV irradiation	37.5 – 47.5	-	-	Summerfelt *et al.*, 2009
Coagulation and flocculation	Addition of chemicals	99	-	Polymer	Ebeling, Rishel and Sibrell, 2005
		99	-	Alum + polymer	Rishel and Ebeling, 2006
		95.1	-	FeCl + polymer	Sharrer, Rishel and Summerfelt, 2009
		> 90	-	FeCl$_3$, PAS	Zhang *et al.*, 2014

Table 2.3. Nutrient recovery from AQW using different treatment methods

Method	Process	Removal efficiency (%)						System	Ref.
		NO_2^--N	NO_3^--N	NH_3	TN	PO_4^{3-}	TP		
RAS and wastewater management	-	-	-	-	-	-	65 – 96	-	Martins et al., 2010
	Denitrification	-	49 – 71	-	-	-	-	Woodchip bioreactor	Lepine et al., 2018
	Denitrification	78.3	-	-	-	93.5	-	Suspended growth bioreactors	Liu et al., 2019
Ozonation	Injection of ozone	55.5	-	-	-	-	-	Ozone + TiO_2/Al_2O_3 membrane	Chen et al., 2015
		66.7– 83.3	-	-	-	-	-	Ozonation + UV irradiation	Summerfelt et al., 2009
Coagulation and flocculation	Generally, used addition of chemicals	-	-	-	-	92 – 95	-	Optimum polymer doses	Ebeling, Rishel and Sibrell, 2005
		50	68	64	-	92 – 99	-	Alum + polymer	Rishel and Ebeling, 2006
		-	-	99.1	-	99.1	-	Chitosan	Chung, Li and Chen, 2005

Table 1.3. Continued

Method	Process	Removal efficiency (%)								System	Ref.
		NO_2^--N	NO_3^--N	NH_3	Dissolved Nitrogen	Sedimentary Nitrogen	TN	PO_4^{3-}	TP		
IMTA	Different tropic species are grown together	-	-	-	-	-	49.4		99	Tetraselmis suecica	Michels et al., 2014
BFT	Using carbon as a source for microorganism growth	99.3	45.5	-	-	-	-		47	FeCl + Polymer	Sharrer, Rishel and Summerfelt, 2009
		-	-	-	-	-	-	-	> 80	$FeCl_3$, PAS	Zhang et al., 2014
		-	-	-	36.4	89.8	-	-	-	Biofloc + continuous aeration	Liu *et al.*, 2019
		-	-	-	-	-	92.2	-	-	Biofloc + denitrification + LED light	Changwei Li *et al.*, 2019
		-	-	52.3	-	-	-	-	-	Biofloc + quorum sensing	Fatimah et al., 2019

In coagulation and flocculation, chemicals are added to wastewater to increase particle size and convert the dissolved or colloidal substance into insoluble SS (Metcalf and Eddy, 2003; Stechemesser and Dobiás, 2005). Generally, aluminum and iron-based coagulants such as aluminum sulfate, aluminum chloride, ferric sulfate, ferrous sulfate, etc. are used. Other chemicals like hydrated lime and magnesium carbonate also used as a coagulant (Bratby, 2006). Various coagulants and flocculants have been studied for the removal of TSS and nutrients from AQW. According to the literature, the removal efficiency of TSS and PO_4^{3-} is greater than 90 %, however, NO_2^--N (50 – 99.3 %), NO_3^--N (45.5 – 68 %), NH_3 (64 – 99.1 %), and total phosphorus (TP, 47 – > 80 %), as shown in **Table 2.2** and **Table 2.3**. Moreover BOD, and COD were reduced to 97.3 % and 96.4 %, respectively (Rishel and Ebeling, 2006).

In RAS, nutrients are controlled by using a biological method and the treated water is recycled. Due to recycling, the RAS process has advantages including, little water usage, a lower environmental impact because of nutrient recovery (Martins *et al.*, 2010) and having improved hygienic conditions (Summerfelt *et al.*, 2009; Tal *et al.*, 2009). The nitrification process has been reported to convert NH_3 (toxic) to NO_3^- (less toxic) in RAS (Crab, Avnimelech and Defoirdt, 2007; Dauda, Akinwole and Olatinwo, 2014). Recently, different biofilters are used in the nitrification process for AQW (Martins *et al.*, 2010). Such as, emerge fixed-film filters and submerged fixed-film filters (Malone and Pfeiffer, 2006; Dauda, Akinwole and Olatinwo, 2014). Organic matter and SS removal efficiencies were found

to be 85 – 98 % while for phosphorus removal efficiency was 65 – 96 % in RAS (Martins *et al.*, 2010). Research on the nitrification and denitrification process shows a different tendency for the removal of nutrients. The NH_3 removal rate in the denitrification tank (using pumice stone) with the addition of methanol is, 116.9 g-N/m^3 packing volume per day, which is higher than the nitrification process (Pungrasmi et al. 2016). Also, the efficiency removal of NO_3^--N for denitrifying wood bioreactor (Lepine *et al.*, 2018) is lower than suspended growth bioreactors (SGBRs) shown in **Table 2.3** however, SGBRs also removes 93.48 % of PO_4^{3-} (W. Liu *et al.*, 2019).

For sustainable aquaculture, biofloc technology (BFT) is now receiving more attention in the fish culture system (Bossier and Ekasari, 2017; Dauda *et al.*, 2018). In BFT, water is treated inside the pond and no need for extra equipment as compared to RAS in which the treatment is performed outside of the culture (Vinatea *et al.*, 2018). In this method, carbon is used as a source material for bacteria growth to convert NH_3 into nitrogen gas (Ekasari, Crab and Verstraete, 2010; Luo *et al.*, 2014; Dauda and Akinwole, 2015; Sgnaulin *et al.*, 2018). It was found that at in the C/N ratio of 15, the concentration of NH_3-N and NO_3^--N were < 1 ppm while the NO_2^--N was less than 50 ppm (Dauda *et al.*, 2018). Also, similar results were observed by Sgnaulin et al., (2018) for NO_2^- (0.1 ppm), total NH_3 (0.96 ppm) and NO_3^- (0.9 ppm). Formation of biofloc with addition of continuous aeration has lower removal of dissolved nitrogen compounds (Liu *et al.*, 2019) compared to combine BFT with denitrification and blue LED light (Changwei Li *et al.*, 2019) and addition of the quorum sensing signal (C6-

HSL) (Fatimah *et al.*, 2019) as shown in **Table 2.3**. However, research is needed to improve the oxidation or removal efficiency of NH_3 and NO_2^- in the biofloc system because small bioflocs are less efficient for NH_3 and NO_2^- oxidation (Souza *et al.*, 2019). Besides, RAS and BFT, integrated multi-trophic aquaculture (IMTA) also one of the advanced methods for fish farming.

Various trophic species are grown together in IMTA (Martan, 2008), and waste of one species is used as a feed for others by providing collective interaction between the species (Chopin *et al.*, 2001; Troell *et al.*, 2003; Neori *et al.*, 2004; Turcios and Papenbrock, 2014; Buck *et al.*, 2018). Michels et al., (2014) found that tetraselmis suecica significantly convert the nitrogen and phosphorus into algal biomass as a primary nutrient for fish. Similar outcomes were found by Abreu et al., (2011) using G. Vermiculophylla as shown in **Table 2.3**. On the contrary, seabream and grey mullet reduced total sludge by 85 % and nitrogen in sludge by 98 % (Shpigel *et al.*, 2016) as well as tilapia, shrimp, and Sarcocornia ambigua reduced the total sludge production by 48.57 % and have no effect on the recovery of nitrogen and phosphorus (Poli *et al.*, 2019) when these species were grown together. Also, sea urchin and cucumber consumed 3.8 – 16.3 % and 11.7 – 45.9 % of fish waste respectively, when injected to the culture as a feed (Israel, Lupatsch and Angel, 2019).

Various physical methods have been also adopted for the treatment AQW. These methods were originally developed for conventional

wastewater treatment plants. In AQW, visible and large particles were separated mechanically by various inexpensive methods alike sedimentation, physical straining, and sand filtration, etc. The smaller particles were removed using coagulation and flocculation, flotation, and membrane filtration (Lekang, 2007).

For AQW with a low overflow rate of 1 m/h, 85 – 90 % of the solid is generally removed by sedimentation (Cripps and Bergheim, 2000). Recently, many modifications have been adopted in the sedimentation for AQW in order to achieve higher efficiency, as shown in **Table 2.2**. The swirl and radial separator remove 37.1 ± 3.3 % and 77.9 ± 1.6 % solid particles from AQW respectively (Davidson and Summerfelt, 2005). However, greater than 90 % of the suspended particle larger than 250 µm was removed through swirl separator in a recirculating aquaculture system (RAS) (Pfeiffer, Osborn and Davis, 2008). In addition to this, hydrocyclones remove solid particles based on centrifugal force inside the free vertex flow of wastewater and were used by Lee, (2014, 2015) for AQW. However, study shows that raw fish sludge (not suitable) has significantly lower plant biomass (82.6 % less) compared to commercial fertilizer and anaerobic digested sludge (Yogev *et al.*, 2020). Besides sedimentation, filtration has been used for AQW.

For larger particles (> 15 mm) bar filter racks are employed and specially designed screens are used for smaller particles (< 6 µm) (Lekang, 2007). Some studies reported that the sand filter removes more than 65 % of

the SS particle (23 – 55 µm) when used as a final filtration component in RAS (Pfeiffer, Osborn and Davis, 2008). Higher removal efficiency was observed for larger particles (Malone and Beecher, 2000; Ali, 2013) and smaller aperture size of filter media (Dolan, Murphy and Hehir, 2013) as shown in **Table 2.2**. Furthermore, an inclined belt filter with the addition of alum ($Al_2(SO_4))_3.18H_2O$) and polymer (Hychem, CE 1950) removed 95% SS and 80 % PO_4^{3-}. The PO_4^{3-} was recovered by chemical reaction with alum and polymer (Ebeling, Welsh and Rishel, 2006).

Aeration is used to remove dissolved gases by providing oxygen to the wastewater pond through water surface or using mechanical equipment at the bottom of the pond. A sufficient amount of oxygen is also necessary for aquatic life and to prohibit the natural aging of pond soil (Rogers, 1989). During aeration, the CO_2 degassing occurs while meeting the oxygen deficiency in the pond system and increasing the production of fish (Brune *et al.*, 2003). Further, with continuous aeration and organic carbon, heterotrophic bacteria decrease dissolve nitrogen from 22 – 14 % and sedimentary nitrogen from 49 – 5 % and are converted to bacterial biomass (Liu *et al.*, 2019).

Many techniques and methods have been highlighted, however the usage of this very much dependent to the types of fish cultured system (Turcios and Papenbrock, 2014). Also, there is need to investigate the pros and cons of the methods and techniques suggested.

2.3. Advantages and disadvantages of current treatment methods

Various methods have been used for AQW treatment as discussed in the above section. Each method has their own pros and cons. Sedimentation can be used as secondary treatment for thickness of the sludge however it's difficult to recover the nutrient as a primary treatment because of low concentration (Cripps and Bergheim, 2000). Aeration and liming is used for DO and pH of the pond water, respectively, hence improved the pond productivity (Rogers, 1989; Wurts and Masser, 2013). Chlorination generally oxidized the organic compound and kills the microorganism, but higher than 0.05 ppm in water makes it lethal to fish (Wedemeyer, 1996; Stickney, 2000). The advantages and disadvantages of AQW treatment method are shown briefly in the **Table 2.4**.

Furthermore, the conventional technique is not sufficient to reduce phosphorus, nitrogen, and toxic heavy metals etc. There is no advanced technology available for the treatment of wastewater to treat most of the pollutant in a single step. Various factor can be take into account for the selection of particular treatment i.e. required level of clean up, waste type and concentration, effluent heterogeneity, as well as economic factors (Rajasulochana and Preethy, 2016). The recovery of nutrients from wastewater is difficult to remove using primary and secondary treatment. However, adsorption is one of the methods used in the final treatment for the organic and inorganic pollutants removal even at low concentrations of adsorbate molecule.

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Table 2.4. Advantage and disadvantages AQW treatment methods

Method	Description	Advantage	Drawbacks	Ref.
Sedimentation	Particle settled due to gravity and effect on retention time in settling tank	Used for secondary thickness of sludge in aquaculture system	Cannot be used as primary nutrient recovery due to low concentration of the nutrient Require very low velocity	Cripps and Bergheim, 2000
Mechanical filters and micro screen	-	Inexpensive and simple -	- Smaller suspended solid accumulation	Lekang, 2007 Ling and Weimin, 2010
Aeration and circulation	Addition and redistribution of oxygen	Improve pond water and soil quality Uniform DO and temperature Higher quality product	-	Rogers, 1989
Adsorption	Using solid material as adsorbent	Cost effective, simple design, excellent approach for removal of pollutants	Required regeneration of adsorbent	Sukmana *et al.*, 2021
Liming	Addition of lime	Increasing pH and hardness Increasing pond production	-	Wurts and Masser, 2013
Chlorination	Using chlorine compound as disinfectant	Oxidized organic compound -	Dichlorination should be done > 0.05 ppm dosage is lethal for fish	Stickney, 2000 Wedemeyer, 1996
BFT	Using carbon for the growth of bacteria	Productivity improvement, less environmental impact, Almost no need for water exchange -	- Constant accumulation of suspended solid	Bossier and Ekasari, 2017 Ekasari, Crab and Verstraete, 2010; Luo *et al.*, 2014; Sgnaulin *et al.*, 2018s

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Adsorption has advantage because of simple design and involved low investment (initial cost and required land) compared to other methods (Rashed, 2013; Crini and Lichtfouse, 2019; Sukmana et al., 2021)

2.4. Nitrogen compound removal or recovery from AQW by adsorption

In adsorption process, the liquid or gas molecules accumulates on the surface of solid and is classified into physical and chemical adsorption, based on the type of attraction between the solute and adsorbent. Physical adsorption is a reversible process and caused by Van der Waals force between the adsorbate molecule and adsorbent however, chemisorption is irreversible and occur between solute and solid surface (adsorbent) through of chemical reaction (Lehr and Keeley, 2005; Ahmad *et al.*, 2019). Various sorbents and adsorption mechanisms (pore diffusion, electrostatic attraction, hydrogen bonding, ion exchange, memory effect, ion complexation, and chemical reaction) had reported to remove nitrogen compounds from wastewater (Dai *et al.*, 2020).

Several types of sorbents including zeolite-based, gastropod shells, carbon-based, clay-based, and biopolymer-based, etc. had been reported for the removal of nitrogen compounds from AQW and the adsorption capacity/efficiencies of numerous adsorbents have been summarized in **Table 2.5** for better clarity. However, a brief review has been done here based on adsorbents type.

Table 2.5. Adsorption capacity / efficiency of adsorbents for AQW nitrogen compound removal

Adsorbents	Adsorption capacity / efficiency					Operational parameters	Model	Study	Ref.
	NH_4^+	NH_3	NH_3-N	NO_3^-	NO_2^-				
Zeolite-based adsorbents									
Zeolite 13X	8.6 mg/g	-	-	-	-	25 °C, 0.67 hr	Langmuir	Batch	Zheng *et al.*, 2008
NCLP	7.3 mg/g	-	-	-	-	25 °C, 20 g/L, 48 hr	Langmuir	Batch	Yin *et al.*, 2018
Commercial zeolite 13X	17.6 mg/g	-	-	-	-	2 hr, 100 g/L	Freundlich	Batch	Ahmadiannamini *et al.*, 2017
Z3	15.2 mg/g	-	-	-	-	0.5 g/L, 48 hr	Langmuir	Batch	Bernal and Lopez-Real, 1993
Z2	-	14.2 mg/g	-	-	-		Langmuir	Batch	
CCZBs	-	-	0.18 mg/g	-	-	25 °C, 9.2 hr	Langmuir	Batch	Tian *et al.*, 2016
Commercial zeolite	18.5 %	-	-	58.3 %	12.1 %	10 g/L, RT, overnight	-	Batch	El-sherbiny, El-chaghaby and El-Shafea, 2019
Natural zeolite	32 %	-	-	-	-	18 °C, 10 g/L, 3.75 hr	-	Batch	Şahin *et al.*, 2018)
Zeolite + bentonite	38 %	-	-	-	-		-	Batch	
Natural zeolite	-	-	76.6 %	-	-	26.5 °C, 5 week, 5×10^{-9} g/L	-	Fish rearing tank	Aly *et al.*, 2017
Mordenite sample 1&2	8.7 mg/g	-	-	-	-	22 – 26 °C, 24 hr, 0.05 g/L	Langmuir	Batch	Zhou and Boyd, 2014
Gastropod shell-based adsorbent									
Calcined gastropod shell (CGS)	-	-	-	9.8 mg/g		2 g/L, 6 hr	Pseudo 2nd order	Batch	Saliu *et al.*, 2019s

Table 2.5. Continued

Adsorbents	Adsorption capacity / efficiency					Operational parameters	Model	Study	Ref.
	NH$_4^+$	NH$_3$	NH$_3$-N	NO$_3^-$	NO$_2^-$				
Carbon-based adsorbents									
Activated carbon	-	65.3 %	-	-	-	22 °C, 0.33 g/L, 9 hr	-	Fish rearing tank	Sichula *et al.*, 2011
Pyrolyzed chicken feathers fiber (PCFF)	-	-	39.13 %	-	-	11.7 g/L, RT, 1.25 hr	Langmuir	Batch	Moon *et al.*, 2017
Biochar (RSII)	4.5 mg/g	-	-	-	-	45 °C, 1.5 hr	Freundlich	Batch	Khalil, Sergeevich and Borisova, 2018
Activated carbon filter	17.8 %	-	-	89.3 %	89.6 %	23.2 °C, 0.9-1.8 hr	-	Continuous	Jegatheesan *et al.*, 2007
98% DD chitosan	-	89 %	-	-		0.02 g/L, 25 °C, 0.5 hr	-	Batch	Chung, 2006
Chitosan foam 0.10 % (m/v)	-	32.8 %	-	-	57.2 %	25 °C, 25 hr	-	Batch	Zadinelo *et al.*, 2018
Chitosan (Q2)	-	94.3 %	-	-		25 °C, 3 hr	-	-	Bernardi *et al.*, 2018
Clay-based adsorbents									
Bentonite hydrochar composite	23.7 mg/g ~ 100 %	- -	- -	- -	- -	1- 10 g/L, 30 °C, 6 hr -	Langmuir	Batch Continuous	Ismadji *et al.*, 2016
Bentonite	0.5 mg/g	-	-	-	-	18 °C, 10 g/L, 3.75 hr	-	Batch	Şahin *et al.*, 2018
Clay 1	97.8 %	-	-	-	-	20 ppm, 75 g/L, 27 °C, 3 hr	-	Batch	Zadinelo *et al.*, 2015

Table 2.5. Continued

Adsorbents	Adsorption capacity / efficiency					Operational parameters	Model	Study	Ref.
	NH_4^+	NH_3	NH_3-N	NO_3^-	NO_2^-				
Other adsorbents									
PAA.HCl hydrogel	-	-	-	> 53 %	> 85 %	0.1 g/L, 3 hr	-	Batch	Kioussis, Wheaton and Kofinas, 2000
Aged refuse	1.4 mg/g	-	-	-	-	20 g/L, 0.67 hr, 250 rpm and at ambient temperature	Freundlich	Batch	Anijiofor *et al.*, 2018
Fe_3O_4@CNT	-	-	-	55 %	-	-	-	Batch	Nezhadheydari *et al.*, 2019
Desulfurization slag (DS)	0.1 mg/g / 45.1 %	-	-	-	-	30 ppm, 40 g/L, 2 hr, and 30 °C	Pseudo 2nd order	Batch	Yang *et al.*, 2017

Few studies have been found in the literature that worked on the recovery of the nutrient from the spent sorbent. The NH_4^+ was recovered from the spent zeolite (clinoptilolite) by injection of NaOH to the continuous column process following the stripping and scrubber in the regeneration process and convert to $(NH_4)_2SO_4$ as a final product (Lubensky and Ellersdorfer, 2021). Similar method has been used for the recovery of NH_4^+ by injection of NaCl/NaOH to the zeolite (clinoptilolite) bed for the regeneration. The material balanced showed that with addition of the air stripping at total of 1267 mg of NH_4^+ is recovered in the solution (Ellersdorfer, 2018). Also, 95 % of NH_3 is recovered from the spent zeolite during the regeneration (NaCl/NaOH) subsequently air stripping and scrubber process (Deng, Elbeshbishy and Lee, 2016). Addition of the regeneration process could increase the cost of the process however, it would be economical feasible to direct used the spent sorbent as a nutrient-rich zeolite fertilizer (Wu and Vaneeckhaute, 2022).

2.5. Biochar

According to the International Biochar Initiative (IBI), biochar is standardized "as a solid material obtained from the thermochemical conversion of biomass in a limited oxygen environment". The biochar and charcoal preparation method (pyrolysis) is the same as both are obtained from carbonaceous raw materials (Aller, 2016). The main characteristics that distinguish the two materials, however, are their starting materials and their final application. Biochar is applied as a soil amelioration or an adsorbent

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(having high porosity, nutrient content) whereas charcoal is used for heat generation. It has been reported the biochar term is not applied for the charred materials, which are obtained from coal and petroleum etc. (non-renewable source). Also, having the sorption properties, biochar can used for the purification of gases and wastewater. Research has been conducted on the biochar which shows the immobilization of heavy metals, sulfamethoxazole, antibiotics etc from the pharmaceutical residue and industrial wastewater (Saletnik *et al.*, 2019). Furthermore, having large application in agronomic sector, and environmental management, the biochar market increasing faster, with a global market price of $80–13,480/oven-dried metric tonne. Additionally, the biochar market is expected to reach up to $3.14 billion by 2025, with an annual growing rate of 13.1 % (Rashidi and Yusup, 2020).

2.5.1. Preparation of biochar

Currently, various methods are used to produce biochar. However, depending on the feedstock and the required characteristics of the biochar for its application, the selection of pretreatment methods is very limited. According to the definition, biochar is normally prepared by heating the biomass at high temperatures in the absence or limited supply of oxygen (Kambo and Dutta, 2015). The various physical and chemical characteristics of biochar is based on technology used, such as pyrolysis, hydrothermal carbonization, and torrefaction.

Pyrolysis is the thermochemical decomposition of biomass in an inert atmosphere at high temperature (300 – 650 °C). The main product of pyrolysis is carbon rich solid material (biochar), volatile matters (condense to liquid as a bio-oil), and the remaining is "non condensable" gases, such as CH_4, CO_2, CO, and H_2. Pyrolysis can be further divide in fast, and slow pyrolysis depends on the heating rate, and reaction time (Mohan, Pittman and Steele, 2006).

Slow pyrolysis is generally used for the production of biochar as it gives high yield of solid (25 – 30 %)   than other pyrolysis process (Brownsort, 2009). In this process, the biomass is heated to a temperature range of 300 – 650 °C using long residence time (few minutes to several hours), and a low heating rates (10 – 30 °C/min) (Onay and Kockar, 2003). The slow heating rate and low operating temperatures favor high solid product yield (Kambo and Dutta, 2015).

Fast pyrolysis yield more bio-oil than other products such as gases and solid because the bio-oil could be directly used as source of energy for many processes (Czernik and Bridgwater, 2004). In fast pyrolysis the biomass is rapidly heated with the heating rates (> 120 °C/min), short residence times (< 2 sec), and at temperature range of 500 – 1000 °C. High amount of bio-oil (75 %) is obtain in fast pyrolysis process while small quantity of biochar (12 %) and non-condensable (13%) gases is produced. The produce bio-oil during fast pyrolysis t could be use a source of energy (Shakoor *et al.*, 2020).

Carbonization is a thermochemical process that convert biomass into charcoal. The carbonization process occurs when the biomass or carbonaceous material is slowly heated to temperature > 300 °C in the presence of limited oxygen and to obtain maximum fixed carbon. During carbonization 300 – 400 °C, the cellulose and hemicellulose completely decompose and produce richer fixed carbon biochar. If heating continues over 400 °C, a high rich carbon material (charcoal) is achieved (Amer and Elwardany, 2020).

Hydrothermal carbonization (HTC), also called wet torrefaction, in which the organic feedstock is converted into a carbon rich solid product via thermochemical process. During HTC, the biomass is heated in a confined system under pressure (2 - 6 MPa) for 5 to 240 minutes while being immersed in water at a temperature between 180 and 260 °C. (Mumme *et al.*, 2011). Typically, there is no control over the reaction pressure throughout the process in which the water saturation vapor pressure is corresponding to the reaction temperature (autogenic process). Liquid (bio-oil mixed with water), hydrochar, and small fraction of gases (mainly CO_2) are the main products of HTC process. Hydrochar is the desired product in the HTC process, having the mass yield of around 40 – 70 % (Yan *et al.*, 2010). After hydrochar preparation before being used as adsorbent or fuel, it must go through a number of processes such as mechanical dewatering, filtering, and drying (Kambo and Dutta, 2015).

Torrefaction is a thermochemical process in which the sample is heated to temperature range of 200 – 300 °C in the absence of oxygen with a residence time of 30 min to several of hours (Kambo and Dutta, 2015). During this process, the slowly decomposition of biomass or waste material releases CO_2, H_2O and increases the carbon content in the material which possesses high energy density, hydrophobic behavior, homogenous, etc. and has high quality (equal to coal). The quality of rich carbon material depends on the torrefaction temperature and holding time because the depolymerization of biomass occurred in this process. The torrefaction process has been reported to increase the carbon content to 92.6 % of the Leucaena leucocephala woody biomass, suitable for the combustion. Biochar prepared from coffee residue through torrefaction exhibits a higher calorific value (31.12 MJ/Kg) and energy yield (48.08 %) (Jeyasubramanian *et al.*, 2021).

2.5.2 Nutrients removal/recovery by biochar

Biochar has been used to remove various pollutants from wastewater, such as organic pollutants, heavy metals, nitrogen and phosphorus, etc. (Deng, Zhang and Wang, 2017) which cause harm to the environment. Deng, Zhang and Wang, (2017), reported that biochar has been employed for the removal of different types of pollutants in wastewater and the percentage of biochar usage for the adsorption of nutrients *i.e.* nitrogen and phosphorus is about 13 % from other studies such as organic matter, heavy metals, etc. (Deng, Zhang and Wang, 2017).

Table 2.6 summarizes studies reported in the literature on biochar adsorption nutrients. Some wastewaters such as livestock contains abundant of nutrients, especially nitrogen and phosphorus.

Table 2.6. Nutrient removal by biochar from wastewater

Type of nutrients	Raw material	Pyrolysis temperature (°C)	Pyrolysis time (hr)	Adsorption temperature (°C)	Adsorption capacity/ efficiency	Model fitted	Ref.
NH_4^+	Bamboo waste	400	1	RT	3.9 mg/g	Redlich-Peterson / Elovich	Chen *et al.*, 2017
	Sugarcane harvest residue	550	1	22.5	22 mg/g	Langmuir / PSO	Li *et al.*, 2017
	Pine sawdust	550	2	RT	3.4 mg/g	Redlich-Peterson / PSO	Yang *et al.*, 2018
	Pine sawdust	300	-	20	5.38 mg/g		
	Fruit pericarp	300	4	25	4.1 mg/g	Langmuir / PSO	Xue *et al.*, 2019
	Rice straw	600	4	-	0.4 mg/g	-	Meng *et al.*, 2019
	Rice straw	600	0.17	25	1.4 mg/g	PSO	Song *et al.*, 2019
	Wood chips	700	-	-	6.7 mg/g	Langmuir	Hailegnaw *et al.*, 2019
	Rice straw	300	0.33	25	7.5 mg/g	PSO	Gong *et al.*, 2019
	Pineapple peel	300	2	-	4.4 mg/g	Langmuir / PSO	Hu *et al.*, 2020

Table 2.6. Continued

Types of nutrients	Raw material	Pyrolysis temperature (°C)	Pyrolysis time (hr)	Adsorption temperature (°C)	Adsorption capacity/ efficiency	Model fitted	Ref.
NH_4^+	Grape skin	-	-	RT	38 %	Freundlich	Aghoghovwia, Hardie and Rozanov, 2020
	Coffee husk	350	1	RT	1.6 mg/g	Langmuir / PFO	Vu and Do, 2021
	Peanut shell	500	2	30	3.8 mg/g	Langmuir / PSO	An *et al.*, 2021
	Wood chips	700	-	RT	0.96 mg/g	Langmuir	Begum *et al.*, 2021
	Corn straw	500	2	RT	4.4 mg/g	Langmuir / PSO	Li *et al.*, 2021
	Rice husk	550	3	28	0.1 mg/g	Freundlich	Thao *et al.*, 2021
	Pineapple peel	400	4	-	13.4 mg/g	Dubinin-Radushkevich	Otieno *et al.*, 2021
	Rice straw	550	-	25	24.3 mg/g	Langmuir	Lv *et al.*, 2021
	Sorghum straw	300	0.5	25	3.5 mg/g	Langmuir / PSO	Xu et al., 2022

Table 2.6. Continued

Types of nutrients	Raw material	Pyrolysis temperature (°C)	Pyrolysis time (hr)	Adsorption temperature (°C)	Adsorption capacity/ efficiency	Model fitted	Ref.
NO_3^-	Soybean straw	500	2	25	42 mg/g	PSO	Yin, Wang and Zhao, 2018
	Corncob	600	2	30	3.3 mg/g	Langmuir / PSO	Zhao *et al.*, 2018
	Bamboo wastes	460	2	25	~5 mg/g	Langmuir	Viglašová *et al.*, 2018
	Rice straw	300	0.33	25	~10.7 mg/g	PSO	Gong *et al.*, 2019
	Rice straw	600	4	10	0.80 mg/g	-	Meng *et al.*, 2019
	Wood chips	700	-	-	11.3 mg/g	Langmuir	Hailegnaw *et al.*, 2019
	Rice straw	300	2	30	< 0 mg/g	-	Zhou *et al.*, 2019
	Wood biochar	900 - 1000	-	23	0.3 mg/g	-	Rahman, Nachabe and Ergas, 2020
	Rubber tyre	-	-	RT	87 %	-	Aghoghovwia, Hardie and Rozanov, 2020
	Grape skin	-	-	RT	85.6 %	-	

Table 2.6. Continued

Types of nutrients	Raw material	Pyrolysis temperature (°C)	Pyrolysis time (hr)	Adsorption temperature (°C)	Adsorption capacity/ efficiency	Model fitted	Ref.
NO_3^-	Pinewood wastes	600	2	22	4.2 mg/g	Langmuir / PFO	Vijayaraghavan and Balasubramanian, 2021
	Rice straw	550	-	25	2.3 mg/g	Langmuir	Lv *et al.*, 2021
	Rice husk	550	3	28	0.13 mg/g	Freundlich	Thao *et al.*, 2021
PO_4^{3-}	Wood	600	10	25	7.67 mg/g	Langmuir / PSO	Kizito *et al.*, 2017
	Soybean stover	700	3	40	~ 65 mg/g	Freundlich / Elovich	Karunanithi *et al.*, 2017
	Raw sludge	650	0.5	25	92.86 %	Langmuir	Xu, Zhang and Deng, 2018
	Soybean straw	500	2	25	77 mg/g	PFO	Yin, Wang and Zhao, 2018
	Crawfish waste	800	2	25	70.9 mg/g	Langmuir / PSO	Park *et al.*, 2018
	Sesame straw	700	2	25	34.17 mg/g	Freundlich / PSO	Yin *et al.*, 2018
	Wood waste	600	-	25	116.4 mg/g	Redlich-Peterson / PSO	Xu *et al.*, 2018

Table 2.6. Continued

Types of nutrients	Raw material	Pyrolysis temperature (°C)	Pyrolysis time (hr)	Adsorption temperature (°C)	Adsorption capacity/ efficiency	Model fitted	Ref.
PO_4^{3-}	Sewage sludge	600	3	RT	49.95 mg/g	Langmuir / PSO	Yin, Liu and Ren, 2019
	Broussonetia papyrifera leaves	500	2	25	~7.5 mg/g	Freundlich / PSO	Qiu *et al.*, 2019
	Egg shell and rice straw (1:1)	800	2	25	~225 mg/g	Langmuir / PSO	Liu, Shen and Qi, 2019
	Hickory wood chips	600	1	25	8.34 mg/g	Langmuir / PSO	Zheng *et al.*, 2019
	Pinewood wastes	600	2	22	18.4 mg/g	Langmuir /PFO	Vijayaraghavan and Balasubramanian, 2021

Using biochar as adsorbent is not only reducing the eutrophication but can be also recycled for the enhancing the soil fertility, and nutrient resources. A maximum adsorption capacity (9.67 mg/g) for NH_3-N was observed onto biochar when corn cob was pyrolyzed at 600 °C for 2 hr (Deng, Zhang and Wang, 2017). Also, biochar prepared from cow dung represent a remarkable adsorption capacity (25.84 mg/g at 25 °C) of NH_3-N (Deng, Zhang and Wang, 2017). Modification of corn cob biochar with calcium and magnesium significantly improved the adsorption capacity of PO_4^{3-} and a highest adsorption capacity of 319.63 mg/g was achieved (Fang *et al.*, 2015). The result indicating that increasing the anion exchange capacity of biochar by using of calcium and magnesium improve its phosphate adsorption efficiency. Also, two studies have been found in which the ammonia spent biochar was used for the growth of ryegrass (Taghizadeh-Toosi *et al.*, 2012)and water spinach (Shang *et al.*, 2018). From the discussion above, it can be concluded that biochar can be used to adsorb the nitrogen and phosphorus from wastewater and can be further applied as a fertilizer if the biochar is made from green material.

Biochar prepared from various feedstocks using different conditions such as gas flow, heating rate, temperature, heating rate, and time etc. shows various characteristics. it has been reported that using rice husk and empty fruit bunch biochar has different CEC, surface area, and pore volume using same preparation condition (Yavari *et al.*, 2017). In addition to this, biochar from peanut shell, wheat straw, and corn straw have different functional groups, pH, surface area, and electrical conductivity (Gai *et al.*, 2014).

Biochar made from different feedstocks and various conditions involve in various adsorption mechanisms for inorganic and organic pollutants, including physical and chemical interaction such as Vander Waals forces, surface complexation, ion exchange, electrostatic interaction, and pore filling (Barquilha and Braga, 2021). Van der Waals forces occurs when the molecules aligned having opposite charge (Roy, Kar and Das, 2015). Electrostatic interactions occur between the surface of biochar and ionizable species and strongly influenced by pH of the solution (Li *et al.*, 2019). Surface complexation is another adsorption mechanism in which the ionic species forms complexes on the surface of biochar. A complex is formed when a central atoms are surrounded by ligands (Barquilha and Braga, 2021). In ion exchange process, the biochar could be impregnated with the ions such as K^+, Na^+, Mg^{2+}, and Ca^{2+} and further exchanged for the target atom or molecule in the adsorption process. During ion exchange process, the solid phase must be insoluble in the medium (Barquilha and Braga, 2021). Pore-filling is a physical adsorption method and occurs in adsorbent materials, such as activated carbon and biochar, due to high surface area and large volumes of micro and mesopore (Barquilha and Braga, 2021).

2.6. OPF biochar

Table 2.7 shows the adsorption efficiency/capacity of biochar and activated carbon for various pollutants from wastewater. Few studies have been found on the removal of nutrients.

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Table 2.7. OPF based adsorbent for removal of different pollutants from wastewater

Pollutants	Preparation conditions	Operation parameters	Adsorption Capacity/ efficiency	Model fitted	Ref.
Pb^{2+}	Powder oil palm empty fruit bunces	10 g/L, 2 hr, RT	94.3 %	PSO	Daneshfozoun, Abdullah and Abdullah, 2016
	Fine sized of oil palm EFB fiber + Fe_2O_3 solution, sonicated for 5 min followed by shaking for 10	10 g/L, 25 °C, 2.5 hr	48.7 mg/g	-	Daneshfozoun, Abdullah and Abdullah, 2017
	EFB fiber + 10mM NaOH for 12 hr at RT, washed with DI water, dried (60 °C, 48 hr)	14 g/L, 2 hr	0.19 – 0.6 mg/g	-	Ricky et al., 2016
	EFB fiber + 10mM NaOH for 12 hr at RT	15.7 g/L, 0.67 hr, 27 °C	0.53 – 10.89 mg/g	-	Zahrim et al., 2017
NH$_3$-N	Pyrolysis (450 °C, 2 hr) Activation (600 – 900 °C, 0.25 – 4 hr)	6.67 g/L, 2 hr	16 – 32 %	-	Ismail et al., 2018
	0.6 M citric acid + EFB, dried at 50 °C for 24 hr followed by raising temperature to 120 °C for 90 min, washed, dried (50 °C, 24 hr)	35 g/L,2 hr	79.5 %	Langmuir	Nasir et al., 2018
Methylene blue	Carbonization (450 °C, 15 °C/min, 0.5 hr), Activation (Biochar + 1 M HNO$_3$, 132 °C, 1 hr, 35 psi)	2 g/L, 30 °C, 24 HR	62.52 mg/g	Langmuir / PSO	Ibrahim et al., 2021

The best removal efficiency of 79.5 % was observed using citric acid activated EFB (Nasir *et al.*, 2018). Also, the NaOH modified EFB represents 0.83 mg/g and 10.89 mg/g of NH_3-N at a concentrations of 50 and 4000 ppm, respectively (Zahrim *et al.*, 2017). Moreover, one study has done adsorption isotherm study on NH_3-N removal using modified citric acid EFB and its follow Langmuir model which mean the adsorption is monolayer but have not conducted the kinetics or thermodynamic to understand the adsorption mechanism (Nasir *et al.*, 2018). Also, biochar or activated carbon from OPF has not been investigated for the adsorption mechanism of NH_3-N removal using OPF based biochar. In addition to this, OPF biochar is also used for other pollutant such as heavy metals and dye (Marsin *et al.*, 2018). In case of Pb^{2+} the powder EFB follows pseudo- second order (PSO) model shows chemisorption (Daneshfozoun, Abdullah and Abdullah, 2016). However, methylene blue adsorption onto activated biochar exhibit monolayer chemisorption (Ibrahim *et al.*, 2021).

2.7. Cost analysis of biochar

The production cost of biochar is a significant factor in its application and marketing. In cases where biochar is the prime product, the cost must cover operating expenses such as the costs of feedstock, transport, labor, maintenance, production, distribution, and others to ensure the long-term business feasibility. The price of biochar varies depending on the product sites countries. The price arranges from $0.09/kg in the Philippines to as high as $8.85/kg in the UK (Ahmed *et al.*, 2016). The cost of biochar production

appears to be lower than that of synthetic fertilizer. According to the World Bank (April 2022) the price of phosphorus fertilizers is as high as 954 US $/ton and nitrogen fertilizers (Urea) 925 US $/ton (Marcińczyk, Ok and Oleszczuk, 2022). By applying a high biochar rate, ranging from 2.5 – 20 ton/ha, significant changes in crop productivity are achieved (Joseph *et al.*, 2013). Nutrient enriched biochar can decrease this dosage level and providing the fertilization for long time hence reducing agricultural cost (Marcińczyk, Ok and Oleszczuk, 2022). The high wastewater production has not only adverse effect on environment, although requires large financial outlays (Jones *et al.*, 2021). Moreover, in Europe the average price for biowaste landfilling is 30 €/ton (Marcińczyk, Ok and Oleszczuk, 2022). Biochar-based fertilizer could be a profitable sector if wastes has been used for biochar preparation, waste heat is used for pyrolysis process, nutrient rich obtained biochar is further targeted for fertilization (Stávková and Maroušek, 2021).

CHAPTER 3

RESEARCH METHODOLOGY

3.1. Introduction

This chapter consist of the research methodology adopted for this research work. The research work was divided into three phases. The first phase is to produce biochar and further activate the biochar via activating agents. In the second phase, the process parameter study has been evaluated using OPF biochar. In third phase, the adsorption isotherms, kinetics, and thermodynamic study was investigated for adsorption mechanism as well as cost analysis of the biochar. At each stage, the adsorption efficiency/capacity was evaluated. The schematic flow chart of the whole research is presented in **Figure 3.1**.
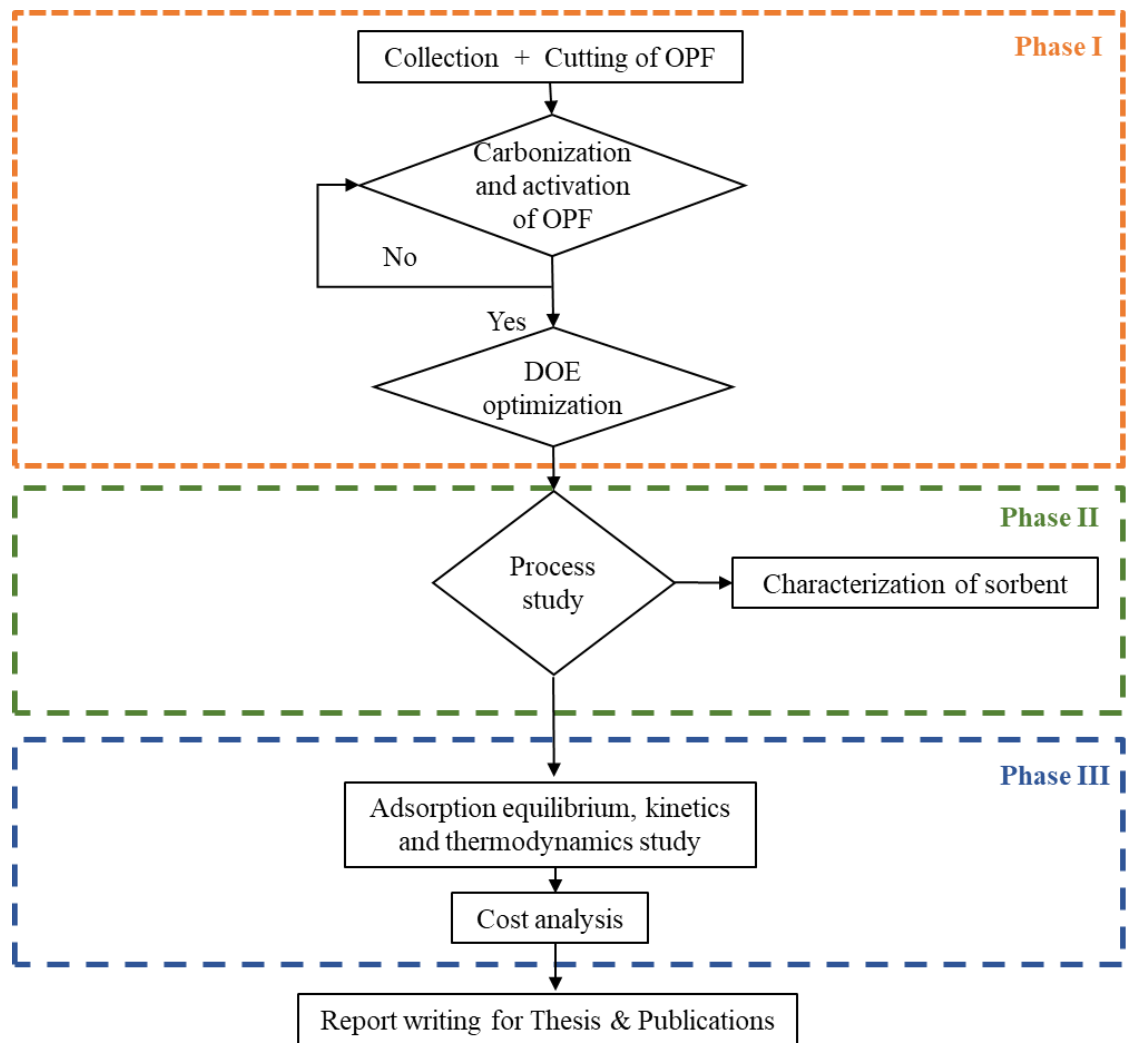
Figure 3.1. Schematic flow chart of the research study

3.2. Materials

The materials and chemicals used in this study are listed in **Table 3.1**.

Table 3.1. List of materials and chemicals

Materials	Manufacturer/supplier	Purity (%)
Oil palm fiber	Tian Siang Oil Mill (Air kuning) Sdn. Bhd	-
Ammonium sulfate $((NH_4)_2SO_4)$	Merck Chemicals Germany	≥ 99
65 % HNO_3	R&M chemical Malaysia	65
37 % HCl	R&M chemical Malaysia	37
85 % H_3PO_4	R&M chemical Malaysia	85
98 % H_2SO_4	R&M chemical Malaysia	98
Glacial CH_3COOH	R&M chemical Malaysia	99.8
30 % H_2O_2	R&M chemical Malaysia	30
Silver nitrate $(AgNO_3)$	GENE chemicals	99
Barium acetate	SYNERLAB	99
Sodium hydroxide (NaOH)	R&M chemical Malaysia	99
Sodium chloride (NaCl)	R&M chemical Malaysia	99
Test 'N TubeTM Vials, 0.4 – 50.0 ppm NH_3-N (HR)	Hach company USA	-
Nitrogen gas	Linde Malaysia Sdn. Bhd.	99
Compressed air	Linde Malaysia Sdn. Bhd.	99

3.3. Apparatus

The equipment's use in this study is listed in **Table 3.2**.

Table 3.2. List of apparatus

Apparatus	Purpose	Model	Manufacturer/Supplier& Country
Grinder	Biochar grinding	ZM 200	Retsch /Germany
Sieve analysis	Sieving as per the required particle size	-	Fisher Scientific (M) Sdn. Bhd/USA
Oven	Drying	UF110	Memmert/Germany
pH meter	Checking the pH of solution	HQ30d	Hach USA
Vis-spectrophotometer	NH_3-N measurement	DR3900	Hach USA
BET surface area	To measure the surface area of the sorbet	Autosorb 1	Quantachrome instruments ASIC/USA
FESEM and EDX	Image analysis and elemental content	JSM-6701F	JEOL /Japan
ATR-IR	To identify the functional group	Perkin Elmer spectrum 2	Perkin Elmer/USA
Heating mental	Activation of biochar	MS ES302	Lab Medical Science Sdn.BhD/UK
Thermo gravimetric analyzer	Proximate analysis of biochar	TGA/DSC 3^+	Mettler Toledo/USA
Orbital shaker	For shaking of the solution	KS 4000 i	IKA

3.4. Preparation of OPF

The raw OPF was provided by Tian Siang Oil Mill (Air Kuning) Sdn.
Bhd. Located in Kampar, Perak, Malaysia. Raw OPF was collected from the
bedding processing mill within the palm oil factory, which was pre-cleaned

and polished. The collected OPF were then cut into small pieces in a range of 1 – 2 cm and stored in the plastic bag at room temperature prior to use. The raw and cut OPF is shown in **Figure 3.2.**
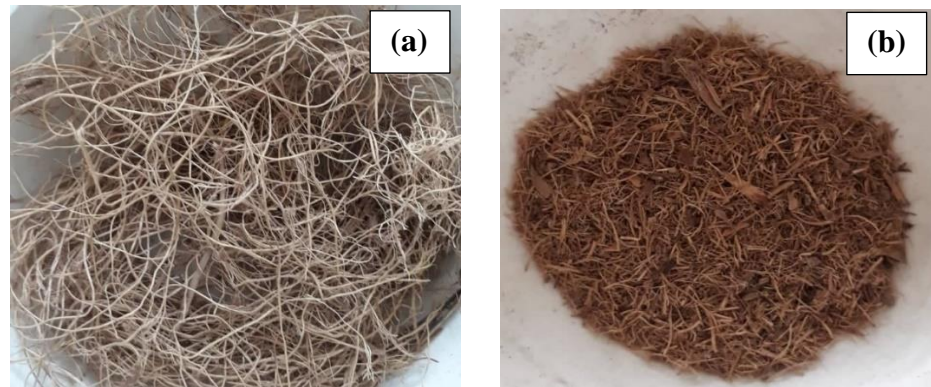
Figure 3.2 Raw (**a**) and Cut (**b**) OPF

3.4.1. Preliminary preparation of biochar with and without Air

10 g of OPF was put into the vertical fixed bed carbonization unit and carbonized at different temperature (200 °C – 500 °C) keeping holding time (1 hr), and heating rate (15 °C/min) constant. For the samples prepared without air, nitrogen gas (N_2) was flowed at a rate of 300 ml/min. For the sample prepared with air, 100 ml/min of air was flown into the carbonization unit. The injection of air was strictly controlled through mass flow controller to avoid combustion. A preliminary study was conducted on using different air flow before choosing the actual range for DOE. In preliminary study it was found that the flow more than 150 ml/min will be an oversupply of oxygen and the biochar tend to form ash. Also, at higher temperature more

than 400 °C can burn the biochar and convert to ashes. Further, the air was injected to partially oxide the biochar and improve the surface functional group. After the carbonization process, the biochar samples were cooled in N_2 and air environment, respectively. The conditions were based on the adsorption efficiency of NH_3-N by increasing the carbonization temperature the adsorption efficiency decreases by Gai *et al.* (2014). After, cooling, the biochar samples were crushed and sieved to a particle size of less than 250 µm. The prepared samples were thoroughly washed with distilled water until the filtrate was clear for removing the contaminants and till neutral pH because the biochar surface contains some organic compounds which can readily leached into the water. These organic compounds condensed on the surface of biochar during cooling process. The biochar samples were then oven dried at 105 °C for 2 to 4 hr until no changes in weight were observed and sealed in a container and stored in a desiccator for further use.

3.4.2. Preliminary preparation of activated biochar

The best biochar prepared from Section 3.4.1 were further activated via chemical and physical activation. This is to test whether this could further improve the adsorption efficiency/capacity of the adsorbent. 5 g of the OPF biochar added to a 1M solution (100 ml) of HNO_3, HCl, H_3PO_4, H_2SO_4, CH_3COOH or H_2O_2 and heated to 100 °C for 2 hr with a continuous stirring of 200 rpm (Shim, Park and Ryu, 2001; Tan *et al.*, 2014; Kim *et al.*, 2020; Niyousha *et al.*, 2020). The modified biochar samples are labeled BC-HNO_3, BC-HCl, BC-H_3PO_4, BC-H_2SO_4, BC-CH_3COOH, and BC-H_2O_2. For

physical activation, CO_2 activation was tested. The OPF biochar is activated at various holding time (0.5 – 2 hr) keeping activation temperature (300 °C) and CO_2 injection (300 ml/min) constant (Iberahim *et al.*, 2022). After, activation the activated samples were cooled down in the presence of N_2. After cooling, samples were prepared as described in Section 3.4.1 prior to usage.

3.4.3. Optimization via DOE

Design Expert 13.0 software was used to optimize the preparation OPF biochar. The experimental design suggested by the software is given in **Table 3.3.**

In optimization study, a standard response surface methodology (RSM) design has been applied using central composite design (CCD). CCD is a suitable statistical approach for sequential testing that can readily fit the quadratic surface. The RSM technique not only determines the best optimum conditions for the minimum number of experimental tests but also gives the information to estimate results in order to design a process. RSM is a systematic and efficient procedure for studying interaction effect of various parameters (Iberahim *et al.*, 2019). On the other hand, the factorial design gives many experimental runs with a modest number of parameters. For examples for 3 factors, the RSM design calculate 10 experimental runs while factorial design gives 27 runs.

The adsorption efficiency for NH_3-N in the current study was chosen as a response. Variance analysis (ANOVA) was applied using the statistical model. Only significant coded term was obtained for NH_3-N in the final empirical model. The model significance can be calculated by probability value (p-value) and Fisher variance ratio (F-value), which quantifies how effectively the model explain the variance in the data around its mean value. Larger the F-value is, the more significant that term is, while for the p-value, the term is only significant if the value Is less than 0.05 and not significant if its value exceeds 0.1. (Iberahim *et al.*, 2022).

Based on preliminary study, the carbonization parameters were varied as factors and adsorption capacity/efficiency as the response. **Table 3.3.** shows the details. Upon input to the software the software generated a series of runs as per **Table 3.4.** The alpha value was 0.5. t was fixed as 0.5 to obtain the inscribe designed as the limits are specified.

Table 3.3. Input parameter range for DOE design

Temperature (°C)	200 – 400
Holding time (min)	30 – 270
Air injection (ml/min)	50 – 250

Table 3.4. Design of experiments

Run	Temperature (°C)	Holding time (min)	Air flowrate (ml/min)
1	200	30	50
2	400	30	50
3	200	270	50
4	400	270	50
5	200	30	250
6	400	30	250
7	200	270	250
8	400	270	250
9	250	150	150
10	350	150	150
11	300	90	150
12	300	210	150
13	300	150	100
14	300	150	200
15	300	150	150
16	300	150	150
17	300	150	150
18	300	150	150
19	300	150	150
20	300	150	150

3.5. Synthetic NH_3-N solution preparation

The synthetic wastewater for NH_3-N was prepared based on the measured averaged value of NH_3-N from two actual aquaculture farm wastewater (Air Kuning) Kampar (4°13'25.3"N, 101°09'02.4"E), and Kampar (4°18'58.2"N, 101°05'27.8"E), Perak. Between the two farms the one having the higher concentration of NH_3-N was chosen. The initial concentration of 10 ppm NH_3-N was prepared by dissolving 0.0472 g the ammonium sulfate (($NH_4)_2SO_4$) in 1L of distilled water.

3.6. Collection and characterization of actual AQW

For collection of AQW sample, a commercial hyphen fishpond in Air Kunning, Kampar (4°13'25.3"N, 101°09'02.4"E), Perak, Malaysia was chosen in this study. Also, the concentration of the pond changes and it mostly depends on the weather (rainy or dry season). In rainy season the concentration reduces. The pond produced approximately 16.67 metric tonnes of wastewater and the discharge after 3-4 months of harvesting into the river. Currently, there is no treatment for the wastewater in the fish farm and directly discharge to the river. Three different samples from the same pond were taken at various locations as shown in the **Figure 3.2** and combined as a mixed sample. **Table 3.5** shows the parameters measured and its methods.

Figure 3.3. Sampling of AQW from fishpond

Table 3.5. AQW parameters and its measurement methods

Parameters	Measurement methods
pH	Multimeter (HQd30, Hach)
Salinity	Multimeter (HQd30, Hach)
DO	Multimeter (HQd30, Hach)
NH_3-N	Salicylate Method (Test 'N TubeTM Vials, 0.4 – 50.0 ppm NH_3-N (HR), Hach method 10031
PO_4^{3-}-P	Ascorbic acid method (TNT plus 845, Hach method 10209/10210)
Total phosphorus (TP)	Ascorbic acid method (TNT plus 845, Hach method 10209/10210)
NO_3^- -N	Cadmium reduction method (Reagent powder pillows, NitraVer ®5)
NO_2-N	Ferrous sulfate (reagent powder pillows, NitriVer®2)
COD	Digestion method (COD HR vial 20 – 1500 ppm)
Turbidity	Turbidity meter (HI 98703, Hanna instrument USA)

3.7. NH_3-N adsorption

For both synthetic and actual AQW, the concentration of NH_3-N was determined by Salicylate Method using a vis spectrometer. The adsorption efficiency/capacity of NH_3-N was measured by following equations:

$$Adsorption\ efficiency\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (3.1)$$

$$Adsorption\ capacity\ (mg/g) = \frac{C_i - C_f}{W} \times V \qquad (3.2)$$

Where C_i and C_f is the initial and final concentrations (ppm) of the solution respectively. V is the volume of the solution in liters (L), and W is the mass (g) of adsorbent used.

For the preliminary adsorption study, 200 ml of 10.0 ± 1 ppm of synthetic NH_3-N was tested using 1.0 g of biochar. The solution was shaken at 150 rpm, for 90 min at RT. For actual AQW, 200 ml of the wastewater was used for each run in the process parameter study. All the experimental work was repeated twice for accuracy and an averaged data was reported.

3.7.1. Process study

The identified optimized adsorbent was further used for adsorption process study of actual AQW. This was carried out by changing, one parameter at a time, while holding the others fixed. The following are the evaluated parameters: temperature (25 °C – 40 °C), contact time (15 – 240 min), shaking speed (50 rpm – 250 rpm), pH (3 – 11), and dosage (0.5 – 4 g) using 200 ml of actual AQW.

3.7.2. Adsorption kinetics, isotherms, and thermodynamics study

The measurement of adsorption isotherm was done by using different dosage of the OPF biochar. The results were fitted to Freundlich and Langmuir isotherms models. The Freundlich and Langmuir isotherms assume heterogeneous adsorptive energies on the adsorbent surface and homogeneous monolayer surface sorption, respectively (Goh *et al.*, 2019). Equation 3.3 and 3.4 are Langmuir, while equation 3.5 and 3.6 are Freundlich, which are non-Linear and Linear isotherm models, respectively (Tran *et al.*, 2017).

$$q_e = \frac{Q_{max}^0 K_L C_e}{1 + K_L C_e} \tag{3.3}$$

$$\frac{1}{q_e} = \left(\frac{1}{Q_{max}^0 K_L}\right)\frac{1}{C_e} + \frac{1}{Q_{max}^0} \tag{3.4}$$

$$q_e = K_F C_e^n \tag{3.5}$$

$$\log q_e = n \log C_e + \log K_F \tag{3.6}$$

Where q_e (mg/g) is the amount uptake at equilibrium, C_e (ppm) is the equilibrium concentration of the adsorbate, Q_{max}^0 (mg/g) is the maximum saturated monolayer adsorption capacity of an adsorbent, and K_L (L/mg) is the constant related to the affinity between the adsorbent and adsorbate, K_F is the Freundlich constant, and n (dimensionless) is the Freundlich intensity

parameter and shows the magnitude of the adsorption driving force or surface heterogeneity. If n = 0 the process is irreversible, Linear if n = 1, unfavorable if n > 1, favorable if n < 1. An intercept of $1/Q^0_{max}$ and a straight line with a slope of $(1/Q^0_{max} K_L)$ is obtained when $1/q_e$ is plotted against $1/C_e$. Hall separation factor was used for the adsorption favorability, where R_L is dimensionless, favorable if $0 < R_L < 1$, If $R_L = 0$ the process is irreversible, Linear if $R_L = 1$ and unfavorable if $R_L > 1$ (Hall *et al.*, 1966).

The kinetic models of pseudo first order (PFO) and pseudo second order (PSO) were used for the analysis of adsorption kinetics. The experimental findings, from various contact times, were applied to the models. The following equations represent the non-Linear and Linear PFO model, respectively, (Tran *et al.*, 2017).

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (3.7)$$

$$\ln(q_e - q_t) = -k_1 t + \ln(q_e) \qquad (3.8)$$

Where k_1 is the rate constant (1/min), and q_t and q_e of the amount of adsorbate uptake at per mass of adsorbent at time t and at equilibrium of PFO equation. The PSO kinetic model is significantly influenced by the amount of adsorbate on the adsorbent surface and the equilibrium amount adsorbed. The rate is proportional to the number of the active sites on the adsorbent

surface. The following equation represent the non-Linear and Linear model of PSO (Tran *et al.*, 2017).

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \tag{3.9}$$

$$\frac{t}{q_t} = \left(\frac{1}{q_e}\right) t + \frac{1}{k_2 q_e^2} \tag{3.10}$$

Where k_2 is the PSO adsorption rate constant (g/mg min).

The linearized intra-particle diffusion model is stated as (Weber and Morris, 1963):

$$q_t = k_p \sqrt{t} + C \tag{3.11}$$

Where k_p (mg/g $\times$ min$^{1/2}$) is the rate constant and C (mg/g) is the constant related to boundary layer thickness, a higher value of C is related to a higher value in the limiting boundary layer. However, from the intra-particle diffusion model, the initial adsorption behavior (R_i) was measured. If $R_i = 1$ shows no initial adsorption behavior, weakly initial adsorption behavior if $1 > R_i > 0.9$, intermediately initial adsorption when $0.9 > R_i > 0.5$, the value of Ri at $0.5 > Ri > 0.1$ shows strong initial adsorption, if $R < 0.1$ shows approaching completely initial adsorption (Wu, Tseng and Juang, 2009).

For the investigation of thermodynamics parameters, at various temperatures (25 °C – 40 °C) the OPF biochar was shaken while holding the other process condition fixed. The Gibbs free energy was calculated from the following equation (Tran *et al.*, 2017).

$$\Delta G° = -RT ln K_C \qquad (3.12)$$

The relationship between the ΔG°, ΔH°, and ΔS° is describe as follow:

$$\Delta G° = \Delta H° - T\Delta S° \qquad (3.13)$$

$$\ln K_C = -\frac{\Delta H°}{R} \times \frac{1}{T} + \frac{\Delta S°}{R} \qquad (3.14)$$

Where ΔG° is the standard free energy change for ion exchange (J/mol), T is the absolute temperature (K), and R is the universal gas constant (8.314 J/mol K), K_C is the equilibrium constant, and must be dimensionless (Zhou, 2017), ΔH° represents the enthalpy, while ΔS° indicates the entropy (J/mol K). From the Linear plot of lnK_C and 1/T, the slope and intercept were used for measuring the value of ΔH°, and ΔS°.

3.8. Characterization

Different adsorbent samples having the lowest and the highest adsorption were characterized via various techniques to justify the results.

These methods include Attenuated Total Reflectance (ATR), Field Emission Scanning Electron Microscope (FESEM), Energy Dispersion X-ray (EDX), Brunauer-Emmett-Teller (BET), Cation Exchange Capacity (CEC), Point Zero Charge (pHzc), Zeta potential, and Thermogravimetric analysis (TGA). Brief description of each technique is given below.

3.8.1. Attenuated Total Reflectance (ATR-FTIR)

ATR is popular sampling technique for Fourier transform infrared (FTIR) spectroscopy. ATR-FTIR easily and quickly examines a wide range of sample types such as, solids, semisolids, powders, liquids, and pastes. The ATR-FTIR is used to investigate the information about functional groups of the samples. This method of spectroscopy is mostly used to produces qualitative analysis of a sample, and from the peaks, we can determine the functional groups of the material. ATR-FTIR machine measures the infrared frequencies in a very short period. In this study, the ATR-IR was conducted on the machine Perkin Elmer ATR-IR spectrum 2. The crystal of the ATR-FTIR was cleaned and the sample was placed directly on the plate in order to cover the crystal. The arm is then lock to the position over the crystal and turned clockwise until the metal tip is close to the plate. Click on the scan, for acquiring the preview of spectrum and pressure gauge. To obtain a uniform disc of the sample, handle is continuously twisted until the force gauge reads between 60 – 80. Click on the scan to get the final spectrum and then further analyzed the spectrum.

3.8.2. Field Emission Electron Microscopy (FESEM)

To investigate the surface morphology of the adsorbent samples, FESEM was performed using the machine model JEOL JSM-6701F. A small quantity of the sample was pasted onto the sample plates and then coated with the beam very finer layer of gold metal for 60 seconds to avoid charging during the electron emissions. The sample was placed in high vacuum environment to develop a good quality of image scanning. The images of the FESEM image of the adsorbents were observed at different magnification such as 350X, 500X, 1000X, and 2000X.

3.8.3. Energy Dispersion X-ray (EDX)

The EDX detector installed with the FESEM apparatus determines the presence of elements on the surface of the material. The sample preparation is similar to that of the FESEM, and the examination can be performed on the FESEM machine.

3.8.4. Brunauer-Emmett-Teller (BET)

The pore properties of the adsorbent, such as specific surface area, pore volume, and pore size distribution were determine using by Quantachrome Instruments ASIC by nitrogen adsorption-desorption isotherms. Before the BET analysis the samples were degassed first at 110 °C for 5 hr on the sample of 0.5 g inside the analysis tube, to remove the

unwanted pre-adsorbed matter on the sample surface. After the degassing process, the sample was put in liquid nitrogen at 77 K. The software that was attached to the analyzer automatically collected the data for the nitrogen adsorption and desorption process. Further, the BET equation was used to determine the specific surface area from the adsorption isotherm.

3.8.5. Cation Exchange Capacity (CEC)

To determine the cation exchange capacity (CEC) of the samples, a similar protocol from AOAC method 973.09 was used (Rippy and Nelson, 2007; Huff and Lee, 2016). Briefly, 0.5 g of the samples were taken and was placed in 100 ml of conical flask with the addition of 50 ml of 0.5M HCl. The samples were shaken for 2 hr at 120 rpm. The mixture was filtered and rinsed through Whatman cellulose filter paper with a 100 ml portion of New Human Up 900 deionized water until no sign of precipitation was observed by adding few drops of dilute (0.028M) $AgNO_3$. The washed samples with the filter paper were added to 50 mL of with 0.5M $Ba(OAc)_2$ solution. After then, the samples were shaken for another 2 hr, filtered, and washed New Human Up 900 deionized water. The sample residue was thrown away and the filtrate were titrated with 0.025 M NaOH solution until the pink color appeared as phenolphthalein is used an indicator. Each test was repeated twice. The CEC was measured using the following equation:

$$\frac{cmol}{Kg\ biochar} = \frac{ml \times molarity\ of\ NaOH \times 100}{gram\ sample} \qquad (3.15)$$

3.8.6. Point Zero charge (PHzc) and Zeta Potential

The pH drift technique was used for the determination of the point zero charge (pH_{PZC}) of the biochar samples. 0.1M NaCl solution (50 ml) was added to a 100 ml conical flask. The solution initial pH (pH_i) was adjusted between 3 and 11 by addition of 0.1M HCl or NaOH. After fixing the pH, 0.2 g of biochar was put into the flask and shaken it at room temperature for 24 hr. The solution was filtered after 24 hr using Whatman filter paper, and the final pH (pH_f) of the filtrate was determined using pH meter (PHC201, Hach). The difference between the initial and final pH values ($\Delta pH = pH_i - pH_f$) were plotted against pH_i. The pH at which the $\Delta pH = 0$ is a pH value at the point of zero charge (Hafshejani *et al.*, 2016). The zeta potential was measured using Litesizer™ 500, (Anton Paar, Austria) using the same pH range.

3.8.7. Thermogravimetric analysis (TGA)

Proximate analysis of the adsorbent samples was determined using TGA analyzer (Mettler Toledo, USA). The adsorbent sample was kept in the presence of nitrogen and the temperature was increased at a rate of 20 °C/min to 110 °C and kept constant at 110 °C for 6 min to measure the water content in the sample. Then the temperature was raised to 900 °C at a heating rate of 20 °C/min and kept constant for 10 min at 900 °C to calculate the volatile matter content of the sample. At 900 °C air was injected for 25 min to

determine the fixed carbon content of the sample (Min, Ahmad and Lee, 2017).

3.8.8. Ultimate analysis

The ultimate analysis of the adsorbent was performed using an elemental CHN analyzer (LECO CHN628S, USA). This examination determined the percentage of carbon, nitrogen, and hydrogen in the adsorbent. The technique used in the ultimate analysis to determine the composition of combustion element is pyrolyzed a sample of 100 mg at 950 °C with excess oxygen in a helium atmosphere. The test is referred to ASTM D5291 standard, and this is one of the best quantitative measurements of elemental composition.

3.9. Cost analysis

Economic analysis of the biochar is necessary to evaluate the cost benefit of the current research project. The cost calculation was done based on the production of 1000 kg biochar/day, 320 days/year of production, two men per shift (3 shifts) for 24 hr/day at RM 18/hr. The respective power of the machines was converted into kilowatt-hour (kWh) unit, as given in **Equation 3.16**, and electricity prices are taken form Tenaga National, Malaysia for commercial consumers which is 0.38/kWh (Tenaga, 2022).

$$Cost\ per\ kg = time\ (hr) \times electricity\ consumption\ of\ device\ (kW)$$

$$\times\ electricity\ cost\ per\ kWh \qquad\qquad (3.16)$$

The total fixed capital investment was calculated by the summation of the total equipment cost and the total capital cost. The annual operating cost and capital cost, shown in **Table 3.6,** are based on the percentage given by Peters and Timmerhaus, (1991).

Table 3.6. Estimated cost measurement method for pilot plant based on the percentage in Peters and Timmerhaus, (1991).

Services	Cost measurement
Equipment installation	25 % of purchased equipment
Instrumentation	6 % of purchased equipment
Piping and material transport	80 % of purchased equipment
Electrical installation	10 % of purchased equipment
Building	12 % of fixed capital investment
Yard improvement	10 % of purchased equipment
Service facility	30 % of purchased equipment
Land	8 % of purchased equipment
Engineering and supervision	30 % of purchased equipment
Construction expenses	1.5 % of fixed capital investment
Contractor fee	1.5 % of fixed capital investment
Contingency	5 % of purchased equipment
Maintenance labor	15 % of operating labor
Supervision	15 % of operating labor
Fringe and benefits	16 % of operating labor
Maintenance supplies	2 % of purchased equipment
Operating supplies	15 % of Maintenance supplies
General and administrative	2 % of operating labor
Property insurance and tax	20 % fixed capital investment
Depreciation	3 % of building + 10 % purchased equipment

The annual production and cost of biochar was calculated from equation 3.17 and 3.18 respectively.

$$Annual\ production = \frac{biochar\ (kg)}{day} \times \frac{320\ days}{year} \qquad (3.17)$$

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$$Cost\left(\frac{per}{kg}\right) = \frac{Total\ operating\ cost\ (RM)}{Total\ annual\ biochar\ production\ (kg)} \quad (3.18)$$

Malaysia produces large quantity of OPF as a waste from palm industry, so the raw material was provided free of cost. The pilot scale plant for biochar was designed based on laboratory work. First the OPF was received from the palm oil company and stored for further used. In laboratory scale, the OPF was cut into smaller particle so in the pilot plant a shredder is needed covert the OPF to smaller size. Further, in our work the vertical carbonization unit has been used for the conversion of OPF into biochar however for bigger scale a horizontal rotary kiln is necessary for biochar production. The constant rotation of the rotary kiln will provide a constant homogenize heat to all the OPF particles. In laboratory scale the biochar cool down easily while having large amount of biochar in pilot scale a rotary cooler is essential for the cooling process as the process is continuous. After cooling process, the biochar is directly stored and then packages. All the prices of the equipment's were taken from the Alibaba online website (Alibaba, 2022).

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Preliminary carbonization

Biochar was prepared by injecting of two different types of gases *i.e.* N_2 and air. Various temperatures have been evaluated keeping the holding time constant and testing the removal capacity and efficiency of NH_3-N removal. After the carbonization process, the optimized OPF biochar was physically and chemically activated and further tested for NH_3-N adsorption.

4.1.1. N_2 and air carbonization of OPF

In N_2 and air injection, the prepared biochar was tested for the removal of NH_3-N as given in **Figure 4.1**. At a holding time of 1 hr, and 300 ml/min injection of N_2, when the pyrolysis temperature was increased from 200 °C to 350 °C the adsorption efficiency increased from 4.4 % to 48.4 %. The adsorption efficiency decreases further increase in temperature and reach to 5.3 % at 500 °C. However, in the case of air injection, the highest adsorption efficiency of 65.8 % was noticed at 300 °C. Further increase in carbonization temperature decreases the performance. The higher adsorption efficiency in injection of air is expected due to the addition of oxygen functional groups. The best performance was noticed at 300 °C, 1 hr, 100 ml

air/min. The decrease in the adsorption efficiency at high pyrolysis temperature is caused by the loss of oxygen functional groups (Gai *et al.*, 2014). Because at higher pyrolysis temperature, the loss of volatile matter diminishes the oxygen functional groups which decrease the negative surface charge on the carbon surface and hence decrease the NH_3-N removal. Next, activation was tried to further improve the performance of the adsorption.
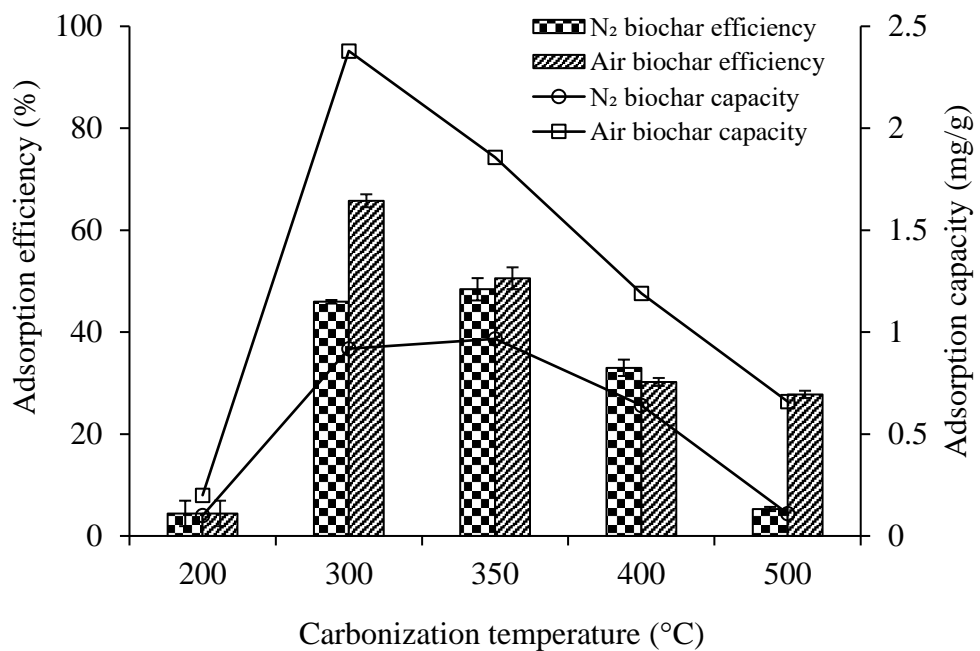
Figure 4.1: Adsorption efficiency/capacity of NH_3-N (10 ppm) onto carbonized biochar

4.1.2. Activation of carbonized OPF

The biochar prepared at 300 °C, 1 hr, 100 ml air/min from the above section was further physically activated with the injection of CO_2 (300 ml/min) at 300 °C at different activation times. This method is chosen for

physical activation because CO_2 activation could improve the BET surface area and porosity of the sorbents (Iberahim *et al.*, 2022). The adsorption efficiency/capacity of NH_3-N onto activated carbon is shown in **Figure 4.2**.
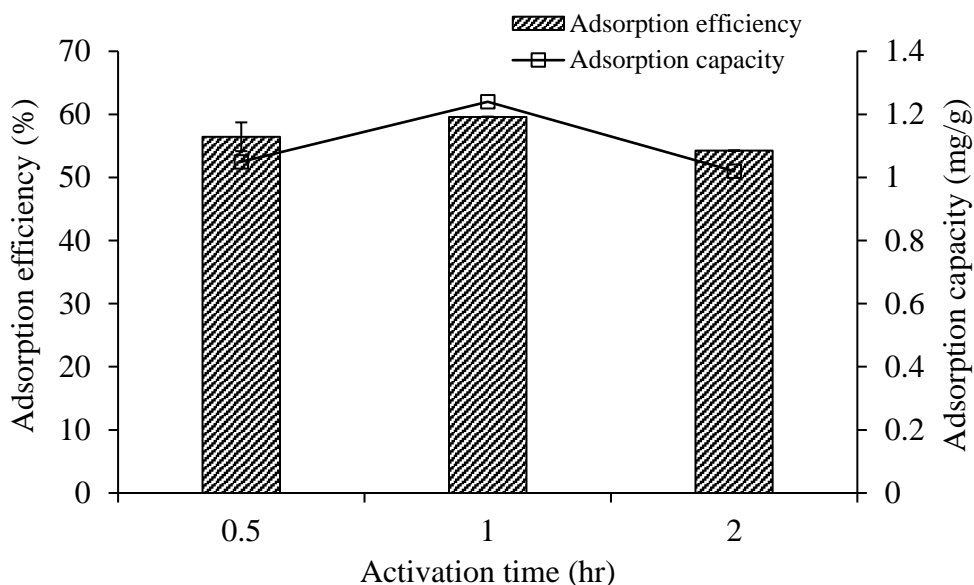
Figure 4.2: Adsorption efficiency/capacity of NH_3-N (10 ppm) onto CO_2 activated biochar

The adsorption efficiency of activated biochar decreases from 59.6 % to 54.3 % when the activation time was increase from 0.5 hr to 2 hr. The physical activation process did not improve the adsorption efficiency of air carbonized biochar. Because during physical activation, the injection of CO_2 burn off the biochar sample at higher holding time which decreases the oxygen functional groups and hence reduced the adsorption efficiency. Also, in our study it has been found that oxygen functional groups play an important role in NH_3-N adsorption. Next, the best biochar prepared at 300 °C, 1 hr, 100 ml air/min was activated using chemical activation with various types of oxidation agents. The performance of chemically activated biochar and its adsorption efficiency/capacity are given in **Figure 4.3.** In the oxidized

samples, only BC-HNO$_3$ represents the highest adsorption efficiency of 41

% but still lower compared to biochar (65.8 %). The remaining modified

sample exhibits leaching. Form these results, it can be concluded that in this

study the adsorption efficiency of the NH$_3$-N did not improve even by

applying various oxidizing agents.
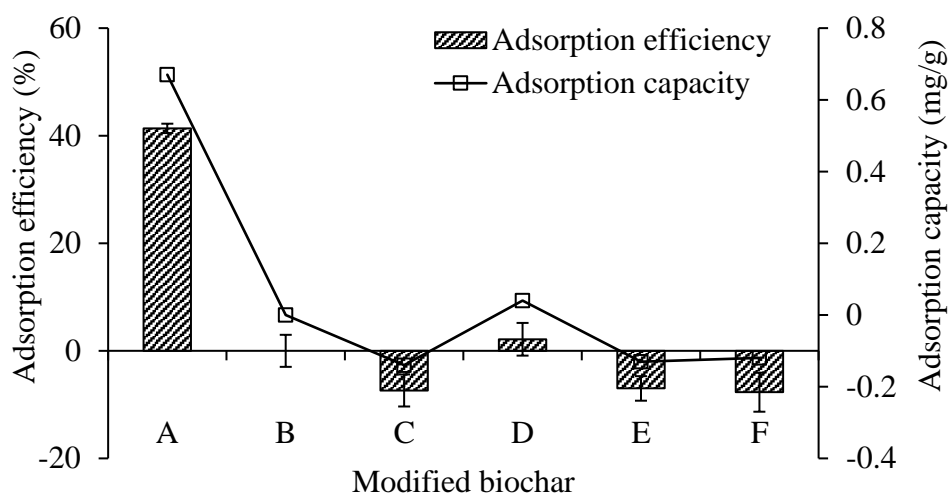
Figure 4.3: NH$_3$-N (10 ppm) adsorption efficiency/capacity onto modified
biochar. (A = BC-HNO$_3$, B = BC-CH$_3$COOH, C = BC-HCl, D = BC-H$_2$O$_2$, E =
BC-H$_2$SO$_4$, F = BC-H$_3$PO$_4$)

Activation temperature (50, 80, 100, and 150 °C) effect was also

evaluated to confirm that chemical activation did not improve the adsorption

properties of the biochar prepared by keeping HNO$_3$ concentration (1M) and

activation time 2 hr constant. **Figure 4.4** represents the adsorption

efficiency/capacity of NH$_3$-N onto activated biochar. HNO$_3$ activation

reduced the adsorption efficiency of NH$_3$-N. Also, at activation temperature

50 °C, the biochar shows leaching however at 80 °C and 100 °C the biochar

shows positive results of 24 % and 41 % removal efficiency of NH_3-N respectively. Overall, the efficiency has not shown any increment.
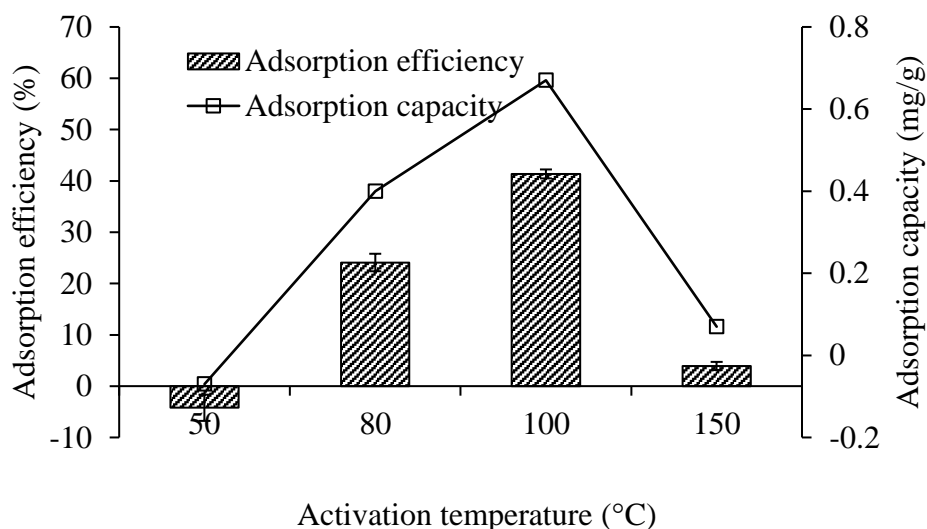
Figure 4.4: NH_3-N (10 ppm) adsorption efficiency/capacity on HNO_3 activated biochar at different temperature

In addition to this, the effect of HNO_3 concentration was evaluated on the activation of biochar (300 °C, 1 hr, 100 ml air/min) keeping temperature (100 °C), and time (2 hr) constant. As the molarity of HNO_3 is increased from 0.1 to 1 M, the adsorption capacity of activated biochar increases from 7 % to 41 % as given in **Figure 4.5**. Further increase in HNO_3 concentration *i.e*. 2 M dissolved the biochar in the solution. Thus, only up to 1M can be tested. Although HNO_3 is a very high oxidizing agent, it did not enhance the adsorption efficiency of NH_3-N as the final pH of the

solution (after adsorption test) was acidic (around 4) which cause the competitive adsorption between NH^{4+} and H^+.
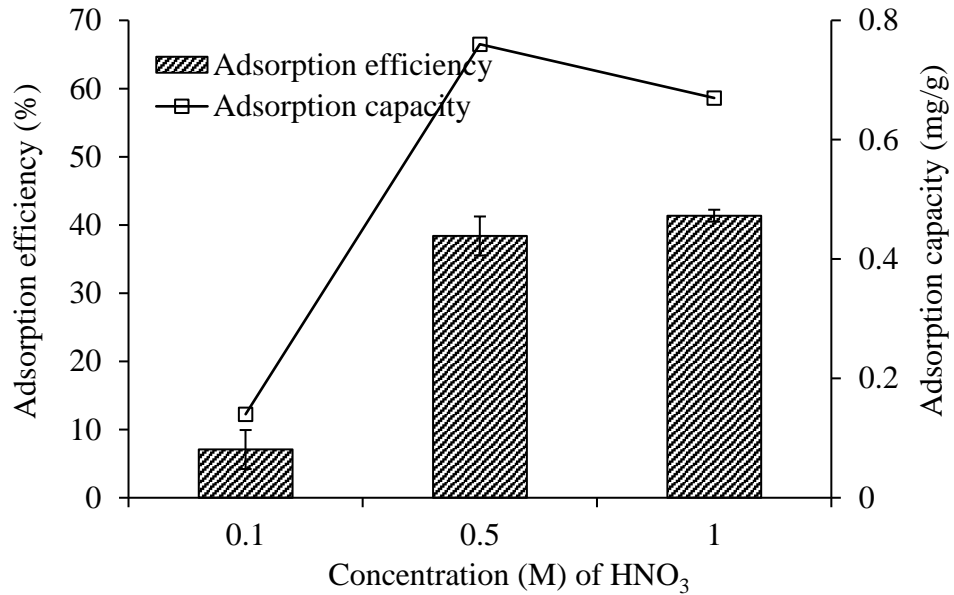
Figure 4.5: NH_3-N (10 ppm) removal efficiency/capacity onto HNO_3 modified biochar at different molarity

Based on the preliminary results presented above, it can be concluded that the performance of carbonized OPF biochar did not improve with any type of activation for the removal of NH_3-N. It is expected that during chemical activation the value-added metals such as Mg, K, and Ca have been completely removed from the sorbent. Same goes to other metals such as Cu and Zn as shown in **Table 4.1.** Value-added metal could help in adsorption of NH_3-N via the ion exchange process (Yu *et al.*, 2016). In addition to this, the functional groups of the activated biochar did not improve using chemical activation, as shown in **Figure 4.6**. Moreover, adsorbent treated with acid washing reduces the common and useful active surface functional groups such as C=O, C=C, and -OH (Gai *et al.*, 2014). Nonetheless, the functional

group (C=O) drastically enhanced in BC-HNO₃, which is responsible for NH₃-N adsorption (Ibrahim *et al.*, 2021). However, the biochar produce in the presence of air which contains limited oxygen. The oxygen enriched the oxygen functional groups such as carboxyl and carbonyl which play a key role in the adsorption of NH₃-N.
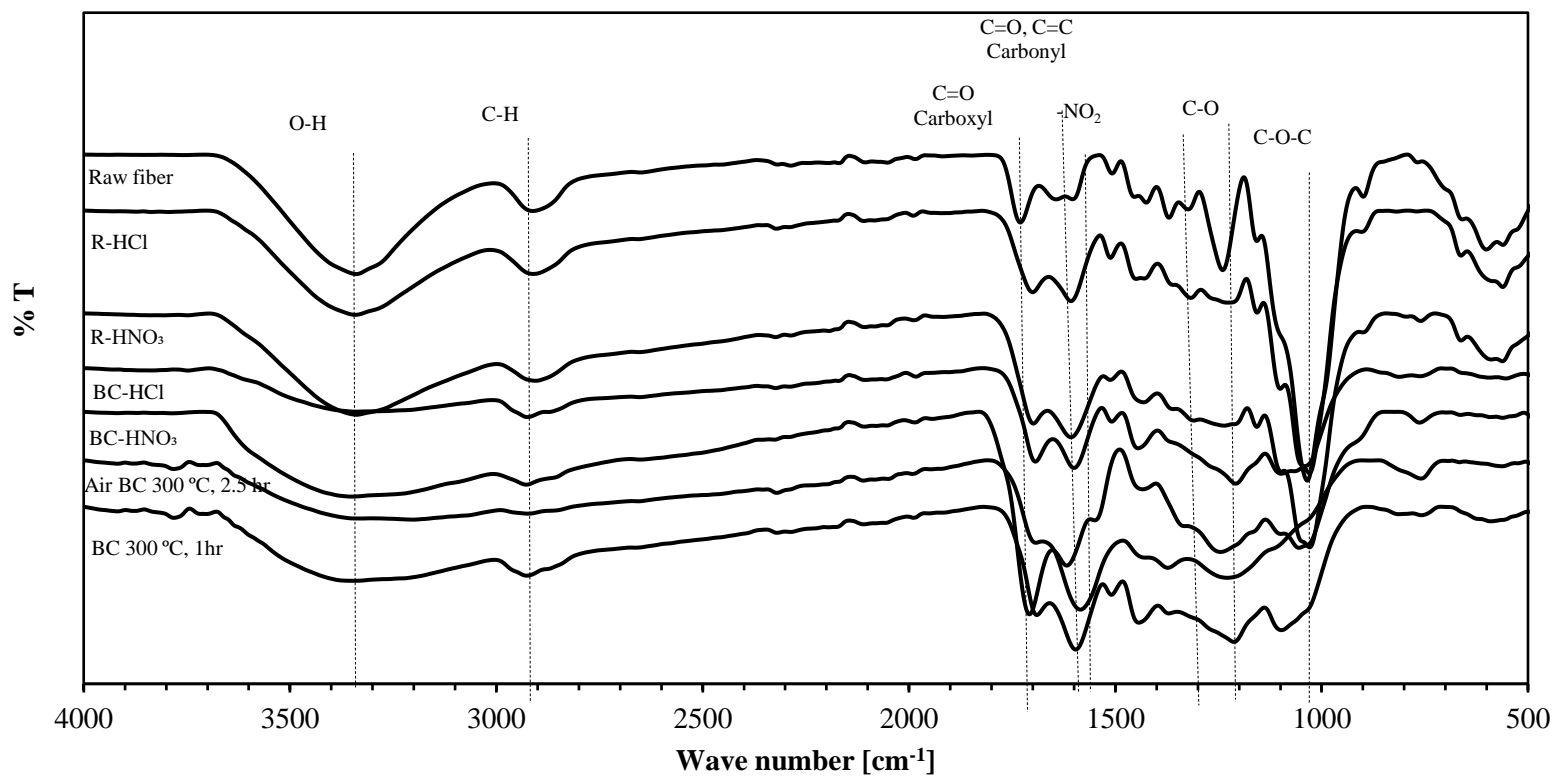
Figure 4.6: ATR-IR results of adsorbent samples

Table 4.1: EDX elemental analysis of the adsorbent samples

Elements	OPF biochar	BC-HNO$_3$ (% weight)	BC-HCl (% weight)
C	75.30	73.25	76.56
O	23.57	26.19	22.88
Mg	0.04	-	-
Al	0.05	0.04	0.03
K	0.24	-	-
Ca	0.06	-	-
Cu	0.51	0.25	0.25
Zn	0.36	0.18	0.20
Si	0.05	0.09	0.07

In this study we did not impregnate the adsorbent with metals, to reduce the cost of making the biochar and not to contaminate the biochar with metals as the spent biochar is expected to be used as soil conditioner or fertilizer in future. Thus, the next step in this research study is to optimize air injection procedure to produce OPF biochar via DOE software (version 13.0).

4.2. Design of experiments for OPF biochar

Response surface methodology (RSM) based on central composite design (CCD) has been applied in DOE software (version 13.0) for optimization. RSM is used for developing, improving, and optimization of the process using a combination of mathematical and statistical methods. It explains the effect of variables, alone or in combination, on the process. In

addition to this, a standard RSM design using CCD developed a set of consecutive experiments for various independent variables. During analysis, this experimental methodology develops an empirical model (quadratic model) which described the corresponding quantity of the process (Amiri, Shahhosseini and Ghaemi, 2017). However, to develop the 2nd order quadratic model, three level factorial design is needed. The factorial design gives more experiments compared to CCD. Therefore, CCD could be used for the optimization of suitable parameters with the minimal number of experiments and for the analysis of the interaction between parameters (Iberahim *et al.*, 2019).

4.2.1. The design

The preparation of air injection biochar was optimized using Design Expert® software 13.0. Three variables were chosen: air injection (50 – 250 ml/min), holding time (0.5 – 4.5 hr) and pyrolysis temperature (200 – 400 °C). The alpha value was fixed as 0.5. The adsorption efficiency was taken as the response. **Table 4.2** summarizes the experimental design. The design has 20 set of experiments, in which 6 were repeated to confirm the error.

Table 4.2: Design of experiments generated from Design-Expert® software

Run	x_1 : carbonization temperature (°C)	x_2 : holding time (min)	x_3 : air injection (ml/min)	y_1 : NH₃-N adsorption efficiency (%)
1	300	150	150	62.5
2	200	30	250	4.69
3	300	150	150	59.24
4	300	150	150	60.33
5	300	150	100	71.56
6	300	150	150	67.39
7	300	150	200	59.6
8	400	270	250	5.56
9	400	270	50	26.77
10	200	270	50	4.55
11	300	150	150	65.76
12	250	150	150	52.6
13	400	30	50	40.4
14	300	90	150	58.15
15	400	30	250	29.82
16	200	30	50	4.69
17	300	210	150	63.64
18	350	150	150	51.63
19	200	270	250	5.21
20	300	150	150	64.67

The results were configured in accordance with the empirical model developed by applying a polynomial equation (second-degree) (Iberahim *et al.*, 2019) as shown in Eq.4.1.

$$y = b_0 + \sum_{i-1}^{n} b_i x_i + \sum_{i-1}^{n} b_{ii} x_{ii}^2 + \sum_{i=1}^{n-1} .. \sum_{j=i+1}^{n} b_{jj} x_i x_j \qquad (4.1)$$

Where y is the predicted response, b₀ is the constant coefficient, bi is the linear coefficient, bjj is the interaction coefficient, bii is the quadratic

coefficient, and x_i to x_j are the coded values of the variables. The total number of experiments calculated was 20 (calculated from $= 2^3 + 2k + 6$ where k is the number of factors).

The results indicates that the adsorption efficiency at carbonization temperature at 300° C is higher compared to 200 °C and 400 °C. Further, increasing the holding time (up to 150 min) increases the adsorption efficiency of NH_3-N and further decreases. At higher injection rate of air, the biochar burns and have low effects on the removal of NH_3-N. The highest adsorption efficiency of 71.6 % was achieved for NH_3-N. After adsorption tests, a regression analysis was performed using a statistical correlation. Analysis of Variance (ANOVA) was used for the determination of significant parameters in the experiments. By relating the response with a significant parameter, the relationship between experimental and predicted results are correlated by ANOVA. The values of F and p indicate the significance of the coefficient. The model becomes significant if the p-value is less than 0.05, and insignificant if it increase 0.1 (Iberahim *et al.*, 2019).

4.2.2. ANOVA analysis

For the preliminary testing to optimize the best OPF biochar, the adsorption parameters were fixed. The response for the study was the adsorption efficiency of NH_3-N. **Table 4.3** contains the variance analysis (ANOVA) results. Based on the results, the quadratic model was developed for the response was termed as "significant". Only taking the significant

terms, the final empirical model in coded factors is stated as an equation (4.2).

NH₃N model:

$$y_1 = +63.40 + 9.76x_1 - 4.09x_2 - 4.37x_3 - 4.78x_1x_2 - 4.06x_1x_3$$
$$- 48.14x_1^2 \qquad\qquad (4.2)$$

In the above equation (4.2), x_1, x_2, and x_3 are used for the input variables of carbonization temperature, holding time, and air injection flow rate, respectively. The term with a positive and negative sign represents its synergistic and antagonistic effect respectively. The probability value (p-value) and Fisher's variance ratio (F-value) has been used for the significance of the derive model. These values indicate how effectively the model explains data variance around its mean value. The terms are "significant" if the F-value is larger, and p-value is <0.05. The model for the response is statistically significant as mentioned in **Table 4.3**. The variable x_1 (carbonization temperature) was the most significant variable compared to others. Moreover, the validity of the empirical model can be verified by the coefficient of determination (R^2 value), adequate precision, coefficient of variation (C.V.%), and standard deviation. The coefficient of determination (R^2) of NH₃-N is 0.9800. This indicates that about 98 % of the regression model is attributed to the studied experimental variables.

Table 4.3: ANOVA results for response surface quadratic model for NH_3-N

	Sum of Squares	df	Mean Square	F-value	p-value
Model	11884.85	6	1980.81	106.10	< 0.0001
x_1	809.01	1	809.01	43.33	< 0.0001
x_2	142.19	1	142.19	7.62	0.0162
x_3	162.02	1	162.02	8.68	0.0114
$x_1 x_2$	183.07	1	183.07	9.81	0.0080
$x_1 x_3$	131.63	1	131.63	7.05	0.0198
x_1^2	10456.93	1	10456.93	560.09	< 0.0001
Residual	242.71	13	18.67		
Lack of Fit	192.11	8	24.01	2.37	0.1781
Pure Error	50.60	5	10.12		
R^2	0.9800				
Adeq. precision	23.89				
Std. dev	4.32				
Mean	42.94				
C.V.%	10.06				

The model will give a more accurate predicted value that will be closer to the actual if the R^2 value is closer to 1.0 (unity). **Table 4.3** shows that the R^2 value for NH_3-N is very high, indicating that the experimental and predicted results are very close to each other. The model could be applied to navigate the design space, as the adequate precision ratio is more than 4 (Iberahim *et al.*, 2019). **Figure 4.7** represent the predicted versus actual results for NH_3-N adsorption. The findings shows that the model agreed well for the NH_3-N adsorption efficiency as the predicted results are close to the actual values.
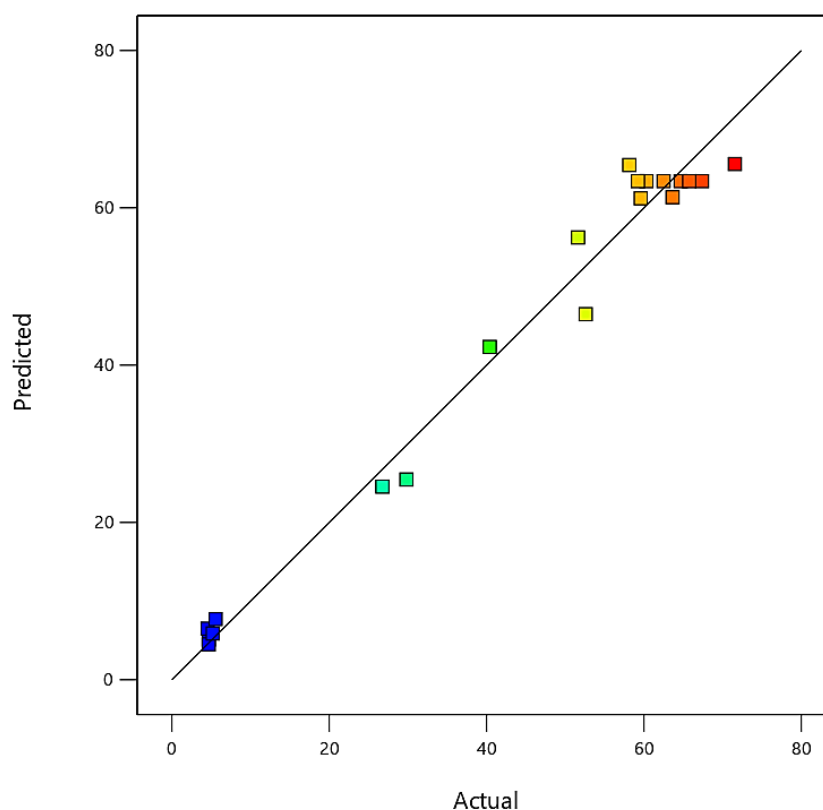
Figure 4.7: Predicted versus actual adsorption efficiency of NH_3-N

4.2.3. Effect of variables on NH_3-N adsorption

Figure 4.8 shows the 3-D response surface graph for the input variables of NH_3-N adsorption. It was noticed when the pyrolysis temperature increases to 300 °C the adsorption efficiency of NH_3-N increases while decreases at higher temperature such as 350 and 400 °C. The decrease in the efficiency is occur because at higher temperature the biochar loses the oxygen functional group. It has been reported that oxygen functional group has positive correlation with the adsorption of NH_3-N (Wang *et al.*, 2015). Also, it was found that at 300 °C the holding time of 2.5

hr was the best for the adsorption of NH_3-N and adsorption decreases with increasing the holding time.
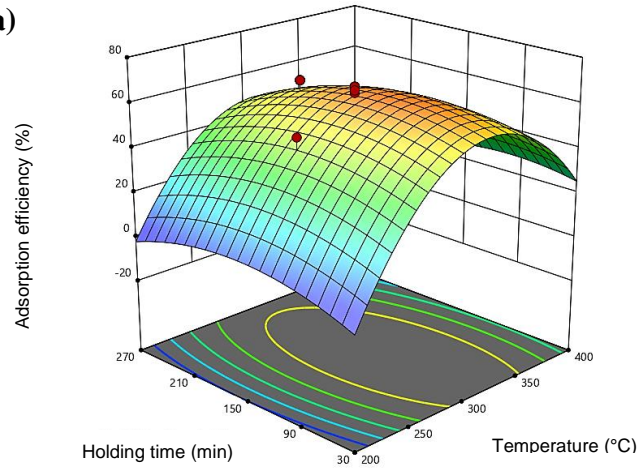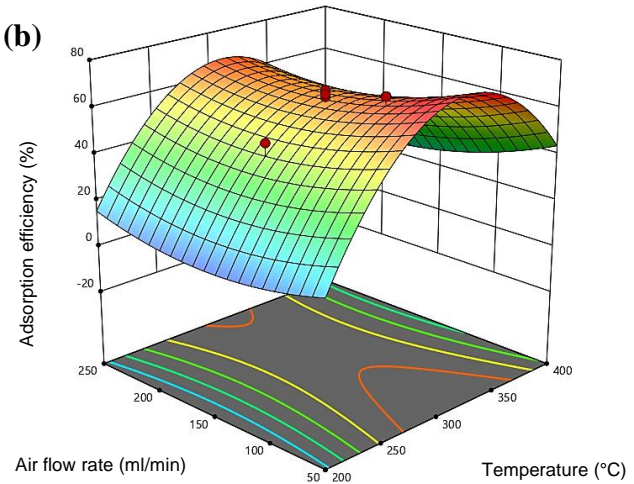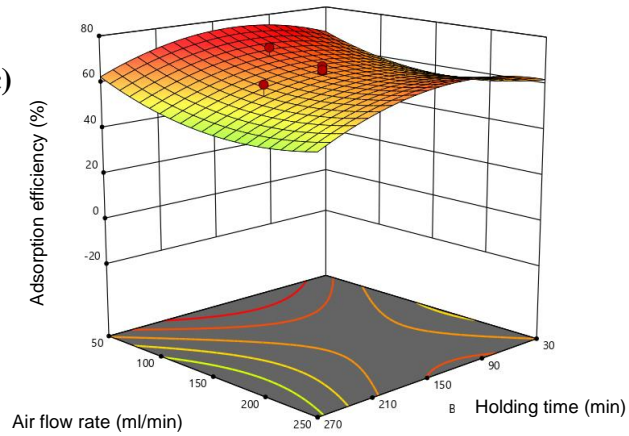
Figure 4.8: Response surface plot of **(a)** pyrolysis temperature versus holding time **(b)** pyrolysis temperature versus air flow rate, and

(c) holding time versus air flow rate for NH_3-N adsorption

Increasing the holding time may cause an increase in quantity of volatile compound resulting in the decrease of negative surface charge at same carbonization temperature (Shaaban *et al.*, 2014). Increasing the air injection flow rate to 100 ml/min increases the adsorption efficiency of the NH_3-N while decreases at higher injection flow rate at carbonization temperature 300 °C. Increasing the air injection more than 100 ml/min causes increased burn off of the OPF biochar and increased the ash content. Similar result has been found by (Xiao *et al.*, 2018) when increasing the holding time at the same carbonization temperature or keeping holding time constant and increase the temperature. Additionally, the injection flow rate shows the least effect on the adsorption of NH_3-N. It was also noticed during experimental work that higher holding time and injection of air flow rate burn the biochar sample and convert it into ash. The highest adsorption efficiency and capacity of 71.6 % and 1.6 mg/g for NH_3-N was observed respectively, at 300 °C, 2.5 hr, and 100 ml air/min and selected as OPF biochar for further studies.

4.2.4. Validation of the model and optimization

Using the software-developed model, the parameters were optimized to achieve the highest NH_3-N adsorption efficiency. The solutions were automated by RSM according to set criteria. RSM recommended several solutions. Three (3) best solutions were chosen with the desirability close to unity as shown in **Table 4.4**.

Table 4.4: Model Validation of the predicted and experimental results

Temperature (°C)	Holding time (min)	Air flow rate (ml/min)	Desirability	Removal efficiency (%)		Error
				Predicted	Actual	
327.1	171.1	98.8	1	66.5	66.7	0.1
338.4	169.4	70.3	1	69.2	68.9	0.2
330.5	181.7	111.7	1	63.4	67.1	2.6

The biochar samples were prepared, and the experimental results were compared to the model predicted values as illustrated in **Table 4.4**. The actual experimental and predicted adsorption efficiency of NH_3-N were nearly the same, having less than 3 % error. Hence, the model was significant in predicting the removal efficiency of NH_3-N.

4.3. Effect of initial concentration of NH_3-N

The initial concentration of NH_3-N was investigated on the OPF biochar at a range of 5 – 20 ppm while the dosage (1 g), temperature (25 °C), and contact time (90 min), was kept constant. The removing efficiency of the NH_3-N decreases from 79.8 % to 61.5 % when the initial concentration of the solution was increased from 5 to 20 ppm as mentioned in **Figure 4.9**.
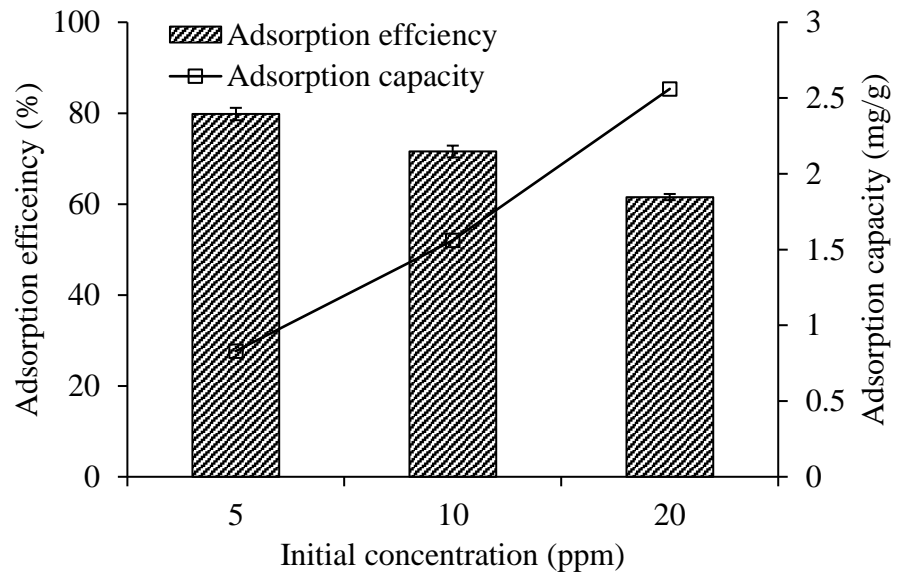
Figure 4.9: Effect of initial concentration of solution on adsorption efficiency of OPF biochar for NH_3-N recovery

At low concentration, the adsorption of NH_3-N occurs faster because of higher availability of the adsorbent site on the adsorbent surface and improve the adsorption efficiency. While at high concentration, the exterior surface of the adsorbent rapidly saturated by adsorbate molecules and hence, reduce the adsorption efficiency. Furthermore, due to the contact and collision between the adsorbent and adsorbate the adsorption capacity increases at higher initial concentration (Godini et al., 2017).

4.4. Characterization of OPF biochar

The characterization of the raw fiber, OPF biochar and spent OPF biochar discussed here. FESEM analysis was conducted to observe the morphologies of the raw fiber and the OPF biochar. **Figure 4.10** represents the raw fiber structure at different magnifications. The FESEM results show that the raw fiber structure is smooth, and non-porous structure. However, some pore can be seen in **Figure 4.10** it might be occur because of cutting the OPF as the pore looks open on both side and is difficult to contribute to the adsorption process.
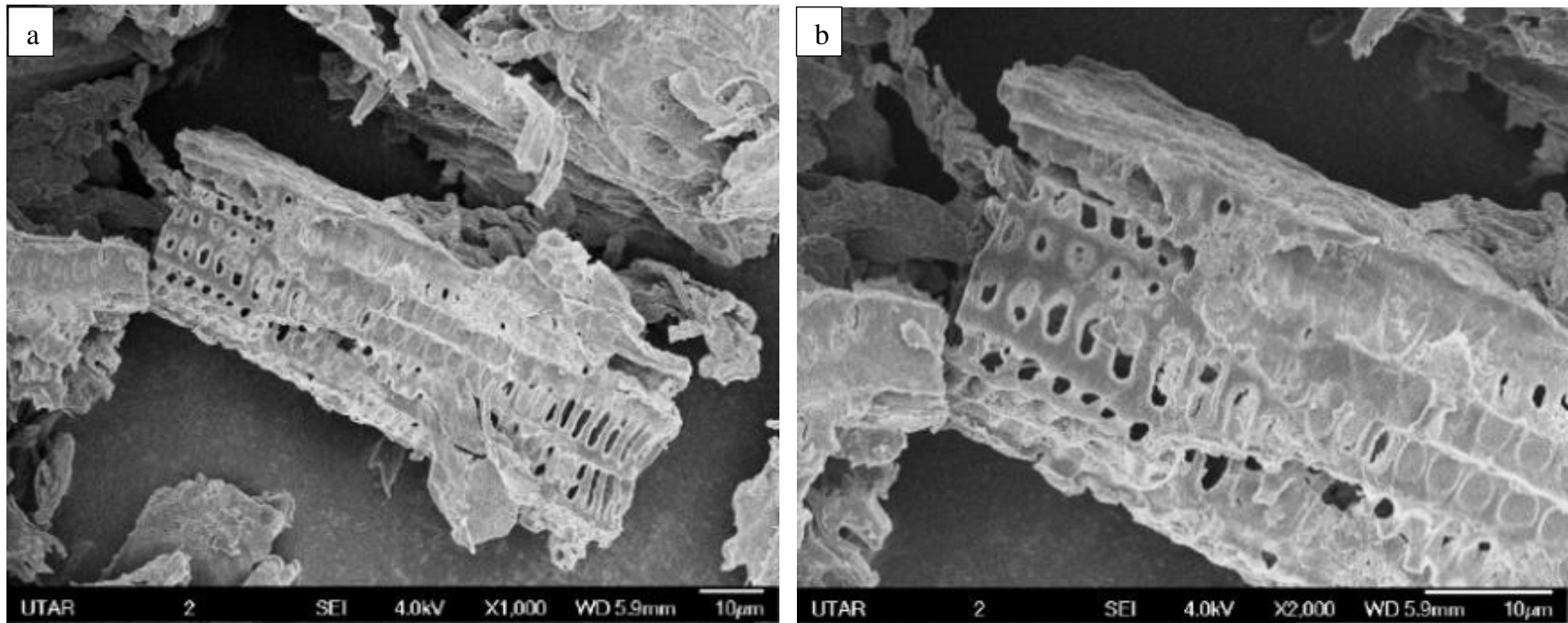
Figure 4.10: FESEM image of raw fiber at different magnification (a) 1000X,

and (b) 2000X

The OPF biochar structure is well developed honeycomb like porous structure as given in **Figure 4.11**. The outer surface of the biochar is smooth and have no pore while the inner surface is porous and evenly distributed. The pores are formed as a result of the volatilization, destruction, and deformation of the lignocellulose structure of biomass when carbonized at high temperature. These pores structures are useful for liquid-solid adsorption and could enhance the recovery of adsorbate molecule (Shaaban *et al.*, 2014). The adsorbate molecule is expected to diffuse onto the adsorbent's upper surface, then into the pores, and finally attach (Min, Ahmad and Lee, 2017).

After adsorption of NH_3-N, the spent OPF biochar has a similar structure and no changes have been observed in the morphology, as shown in **Figure 4.12** compared to OPF biochar.
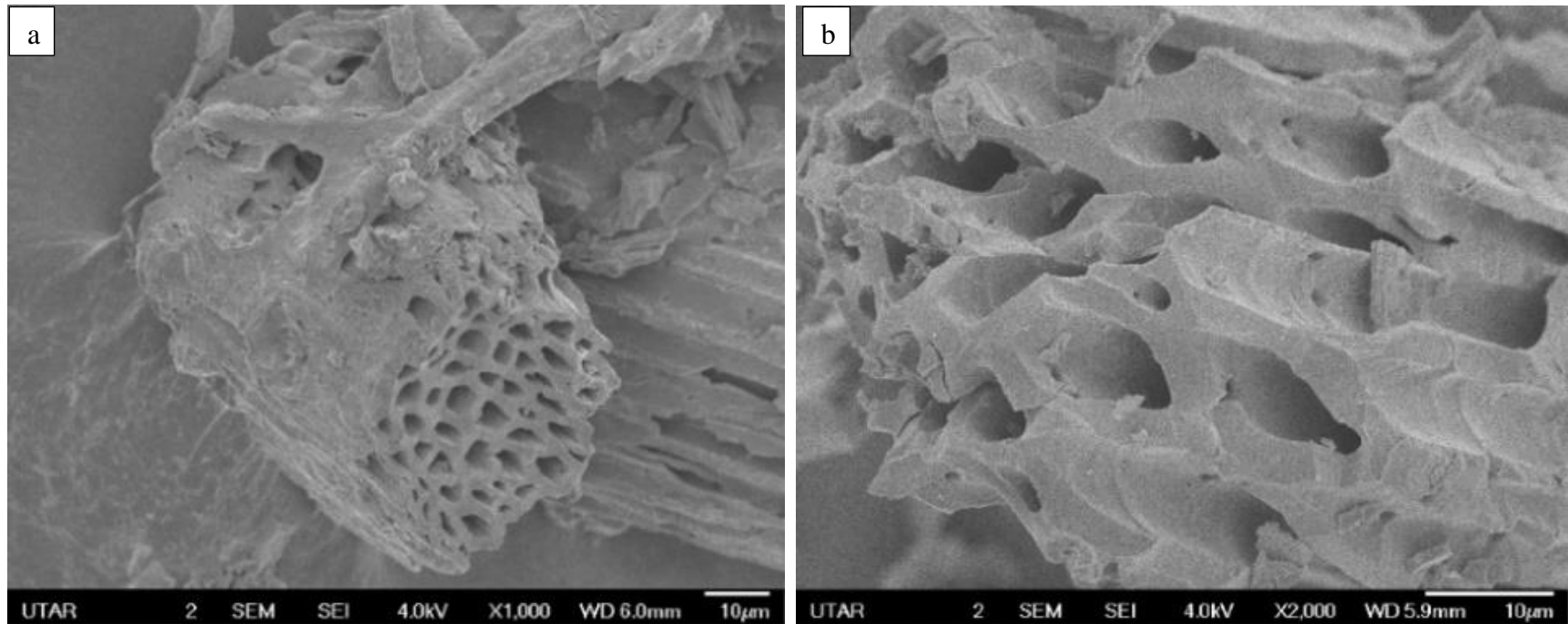
Figure 4.11: FESEM image of OPF biochar at different magnification
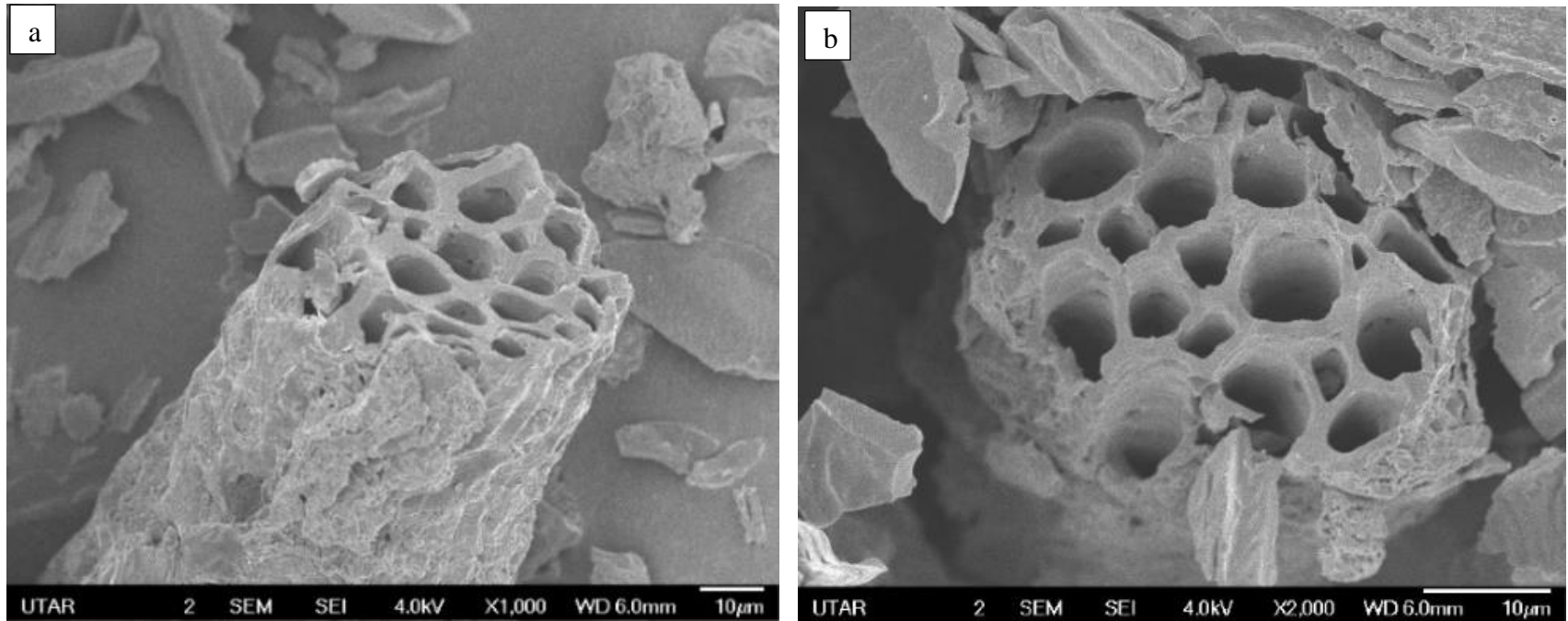
(a) 1000X, and (b) 2000X

Figure 4.12: FESEM image of spent OPF biochar at different

magnification (a) 1000X, and (b) 2000X

In addition to this, the proximate analysis in **Table 4.5** of the OPF biochar samples reveals that after the pyrolysis the percentage content of volatile matter decreases. During carbonization process the lignocellulosic compound destruction occur and vaporized from the material at higher temperature (Shaaban *et al.*, 2014). The decomposition of hemicellulose occurs in the temperature range of 224 – 333 °C while the cracking of cellulose happens at 327 – 370 °C. Unlike hemicellulose and cellulose, the degradation of lignin was observed in a wide range of temperature from 297 – 460 °C (Chen *et al.*, 2022). The fixed carbon content increases to 44.98 % because of the formation of more polyaromatic graphite like carbon structure in OPF biochar, and ash increases to 10.26 % as most of the volatile compounds are removed from the raw material. However, the moisture content is nearly similar in the sorbent samples. The ultimate analysis of the OPF biochar and spent OPF biochar, given in **Table 4.5**, represents that, the percentage weight of the elements such as carbon, hydrogen, and nitrogen are increased in the spent OPF biochar after treatment of AQW.

Table 4.5: Physical characteristics of raw fiber and OPF and spent OPF biochar

Samples	Raw OPF	OPF biochar	Spent OPF biochar
BET Surface area (m^2/g)	0.60	0.63	
Proximate analysis (% weight)			
Moisture content	4.0	6.0	
Volatile matter	76.2	47.8	
Fixed carbon	11.8	37.4	
Ash	8.0	8.9	
Ultimate analysis (% weight)			
C		61.5	63.1
H		3.9	4.2
N		1.4	2.3
EDX elemental (% weight)			
C	60.56	75.30	80.02
O	38.81	23.57	19.02
Mg	0.0	0.04	0.06
K	0.0	0.24	0.06
Ca	0.04	0.06	0.04
Al	0.03	0.05	0.05
Cu	0.30	0.51	0.45
Zn	0.19	0.36	0.28
Si	0.07	0.05	0.02

The increase in nitrogen and hydrogen is because of the adsorption of NH_3-N. The carbon increase might be due to adsorption of some organic compound from the wastewater. The BET surface area of the OPF biochar sample did not improve as well, when the raw OPF is carbonized at 300 °C. this could be due to insufficient removal of volatile compound at lower temperature as noticed in the proximate analysis in **Table 4.5.** The OPF biochar still contains a high percent volatile matter. Similar result has been reported by others that biochar produced at lower temperature has a smaller

BET surface area compared to the ones prepared at high temperature (Shaaban *et al.*, 2014). When the volatile matter releases from the raw OPF the pores are formed during the formation of polyaromatic graphite like carbon structure polymerization structure which increase the BET surface area.

The SEM-EDX analysis is shown in **Table 4.5.** The results confirmed that after adsorption, the elemental composition of OPF biochar is significantly affected. The weight percent of some elements such as K^+, Ca^{2+}, Cu^{2+}, and Zn substantially reduces in spent OPF biochar after adsorption, demonstrating the NH_3-N recovery using ion exchange process. It has been reported that the positive ion on the surface of biochar can remove NH_4^+ from the environment by ion exchange process (Dai *et al.*, 2020). Decreasing the metal content in the ash of biochar decrease the adsorption capacity of NH_4^+. When the pig manure biochar was treated with acid the value added metals such as K^+, Ca^{2+} etc. were decreased in the pig manure biochar which causes a reduction in the adsorption capacity of NH_4^+ from 13.66 mg/g to 4.72 mg/g (Yu *et al.*, 2016). However, the amount of carbon was increases because the OPF biochar was tested in real AQW and could adsorbed the organic carbon in wastewater treatment.

CEC is a crucial surface chemical characteristic that affects the adsorption of positively charged ions such as NH_4^+ and reduces as the pyrolysis temperature increases (Gai *et al.*, 2014). OPF biochar produced at 300 °C has a higher CEC value than that of 400 °C as shown in **Figure 4.13**.

100

Lower CEC value at 400 °C is because of the loss of volatile matter with negative charge functional groups during the pyrolysis process (Mukherjee, Zimmerman and Harris, 2011; Rahman, Nachabe and Ergas, 2020).
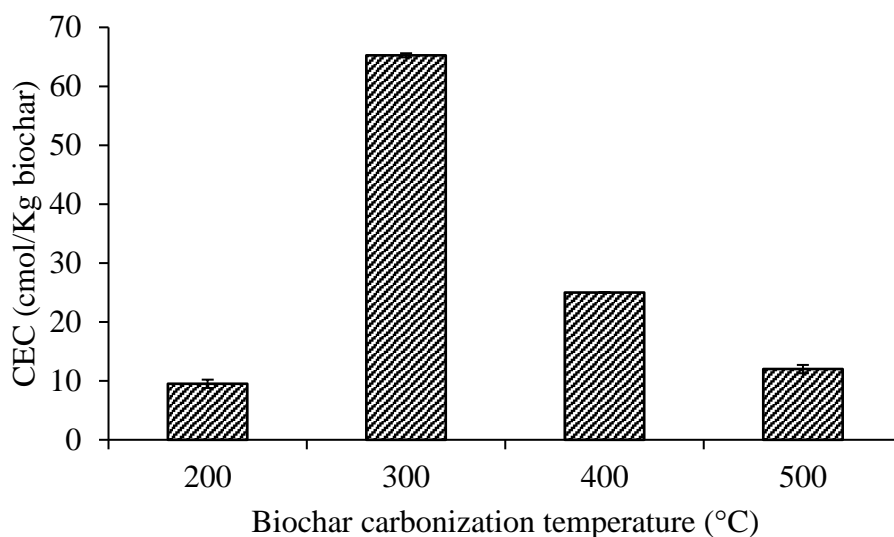
Figure 4.13: CEC of OPF biochar prepared at different carbonization temperature

Some researchers reported that negative charges on the carbonaceous material can be neutralized by positively charged ions such as NH_4^+, K^+, Ca^+ etc. (Mukherjee, Zimmerman and Harris, 2011; Hale *et al.*, 2013).

In addition to this, the CEC of OPF biochar shows direct correlation to the recovery of NH_3-N adsorption as illustrate in **Figure 4.14**. The higher the CEC value of the adsorbent sample, the higher the adsorption efficiency of NH_3-N. The OPF biochar in **Figure 4.14** prepared at various conditions such as 200 °C, 0.5 hr (□), 300 °C, 1 hr (×), 300 °C, 2.5 hr (Δ), 400 °C, 0.5 hr (○), 500 °C, 1 hr (◊). Also, after the adsorption of NH_3-N the OPF biochar does not change the color and still brownish after the treatment.
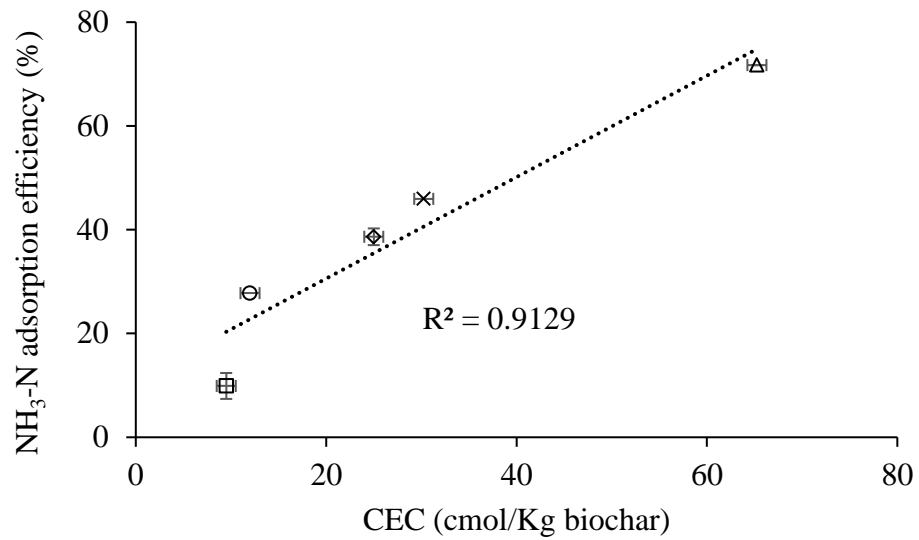
Figure 4.14: Effect of CEC of OPF biochar versus NH_3-N adsorption efficiency

The ATR-IR results of the OPF biochar and spent OPF biochar is given in the **Figure 4.15**. The distinct peak at ~1600 cm^{-1} was corresponded to carbonyl C=O and aromatic C=C stretching vibration. The peak at ~1700 cm^{-1} reveals the carboxyl group C=O stretching. The peak at ~1246 corresponds to aromatic alkoxy stretching, most probably from phenolic C-O bonds (Ibrahim *et al.*, 2021). The absorption band range from 3000 – 3600 cm^{-1} corresponds to O-H. The smaller peak at 2925 cm^{-1} represent C-H stretching. (Ahmad *et al.*, 2021). From the ATR-IR spectra, it is apparent that the intensity of C-O at ~ 1245, carbonyl at ~1600 and carboxyl at ~1700 peak increases and became more stable after NH_3-N adsorption. It implies that during adsorption, those surface functional groups interact with NH_3-N molecule. The increasing in the peaks demonstrating the formation of chemical bonds. It has also been reported that oxygen functional groups

adsorbed NH_4^+ onto biochar via hydrogen bonding as well as electrostatic interaction (Cai *et al.*, 2016). The hydrogen bond or electrostatic force of attraction is formed between the positive charge NH^{4+} molecule with the negative charge oxygen atom in the surface functional groups (C=O or C-O) of the biochar that cause the adsorption of NH_3-N.
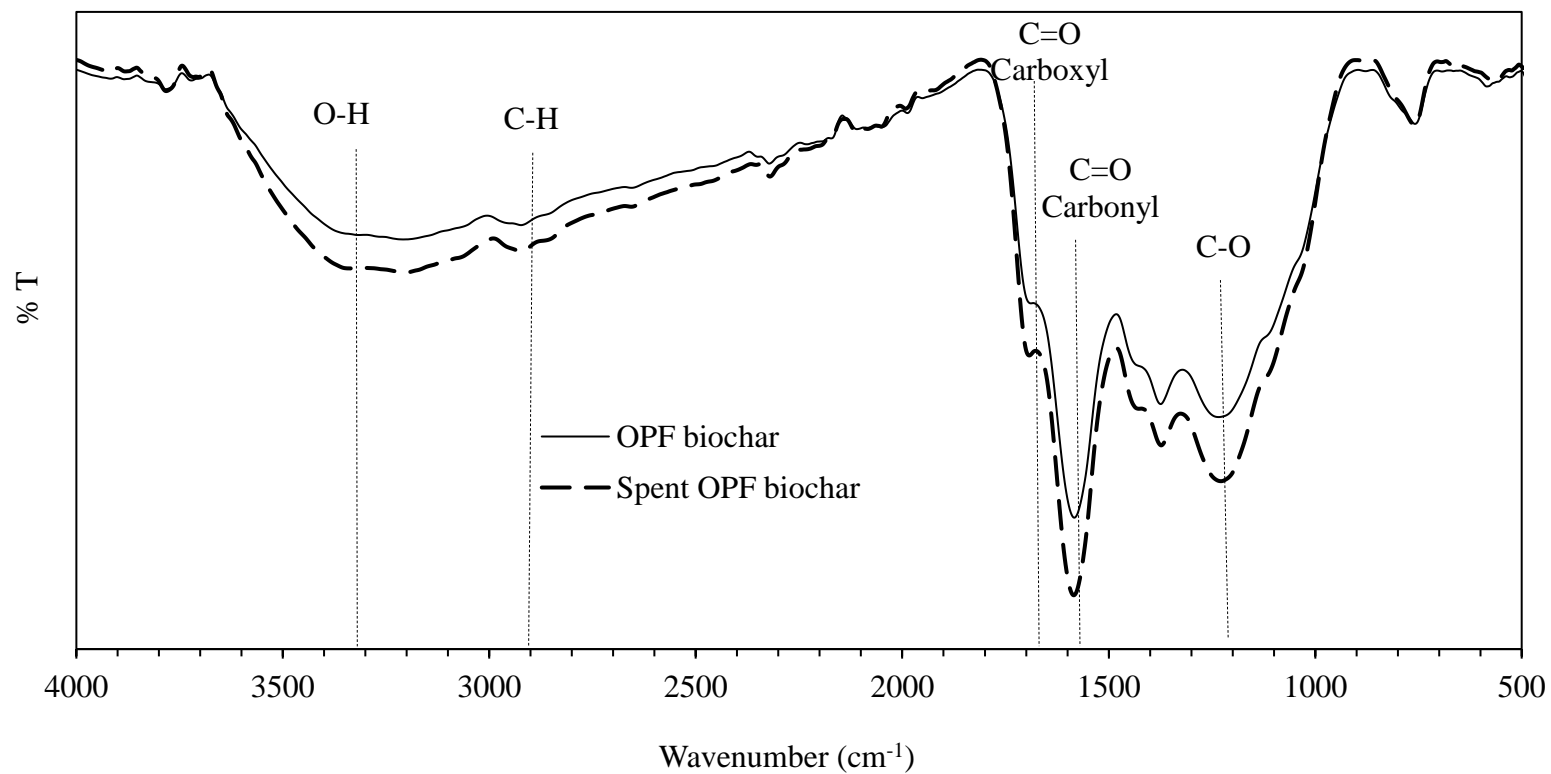
Figure 4.15: ATR-IR results of the OPF biochar at optimum adsorption condition (dosage (2 g), shaking speed (150 rpm), contact time (3 hr), pH (8.16), temperature (25 °C), and initial concentration of NH_3-N (5.3 ppm))

Similar results have been observed for NH_4^+ adsorption onto zeolite. After adsorption of the NH_4^+, the oxygen functional group increases and becomes more stable showing the formation of chemical bonds (Liu *et al.*, 2022). It can be concluded that oxygen functional groups take part in the recovery of NH_3-N.

Zeta potential analysis is performed for the predicting of the nutrients recovery (Yuan, Xu and Zhang, 2011). The pH at which the zeta potential becomes zero is the isoelectric point. As a function of pH, the pHzc and zeta potential values of the OPF biochar samples were determined and presented in **Figure 4.16**. The OPF biochar samples represent negative zeta potential. The negative charge on the OPF biochar decreases with the increase in the pyrolysis temperature. In the studied pH range, the zeta potential of the OPF biochar indicates that the surface of biochar is negatively charged, and the magnitude of the charge increases as pH increases. Similar results have been observed for the sorghum distiller grain biochar at acidic pH (3.0). The value of zeta potential was low at pH 3.0 (~ -5 mV) and became higher when the pH was increased to 10.0 (~ -48 mV). At pH 3.0 the adsorption capacity of NH_4^+ was 3 mg/g and it increased to 12 mg/g when pH was increased to 9.0. This is because NH_4^+ has positive charge and a higher negative value of the zeta potential facilitate adsorption through electrostatic attraction (Hsu *et al.*, 2019). A lower pH, the adsorption capacity of NH_4^+ was low as well due to decrease in negative charges.
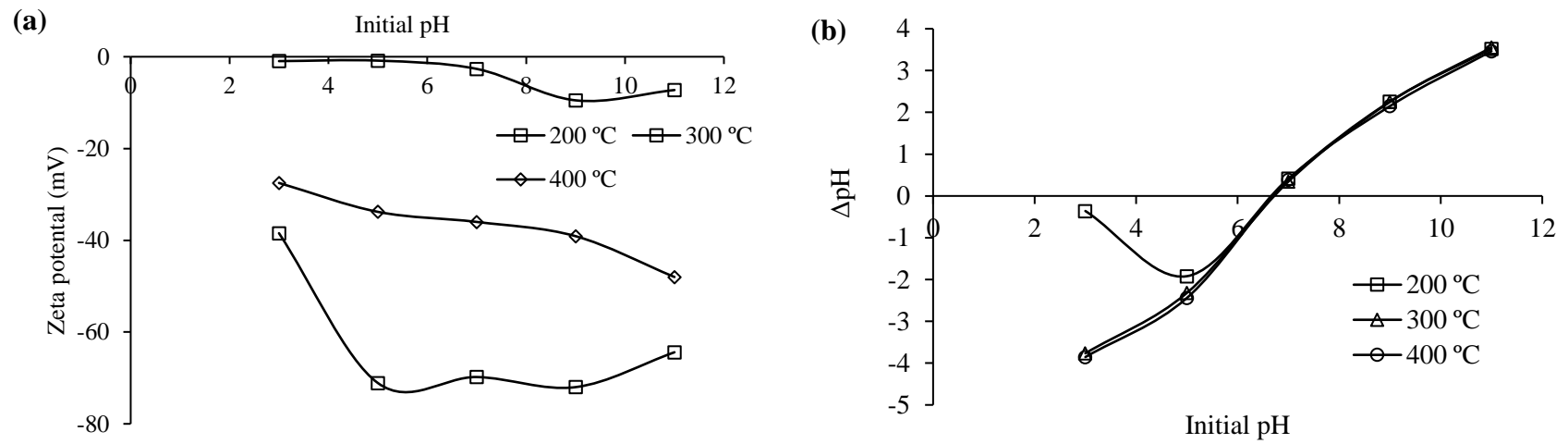
Figure 4.16: (a) Zeta potential and **(b)** pHzc of the OPF biochar samples

4.5. Adsorption process study on actual AQW

The different process parameters have been evaluated for the optimization of NH_3-N adsorption onto OPF biochar using actual AQW to reflect the actual adsorption scenario. Further, the process parameter data were used to find out the ruling adsorption mechanism of NH_3-N onto OPF biochar using adsorption isotherms, and kinetics models.

4.5.1. Contact time

The contact time effect on NH_3-N removal was studied by changing the contact time from 15 to 240 min dosage (1 g), shaking speed (150 rpm), and temperature (25 °C) without any changes in pH. **Figure 4.17** shows that the adsorption efficiency of OPF biochar improved with increasing the contact time. At a contact time of 180 min, the highest adsorption of NH_3-N of 61.54 % was observed. Further increase of time up to equilibrium (24 hr) shows very minimum increase only (63.5 %).
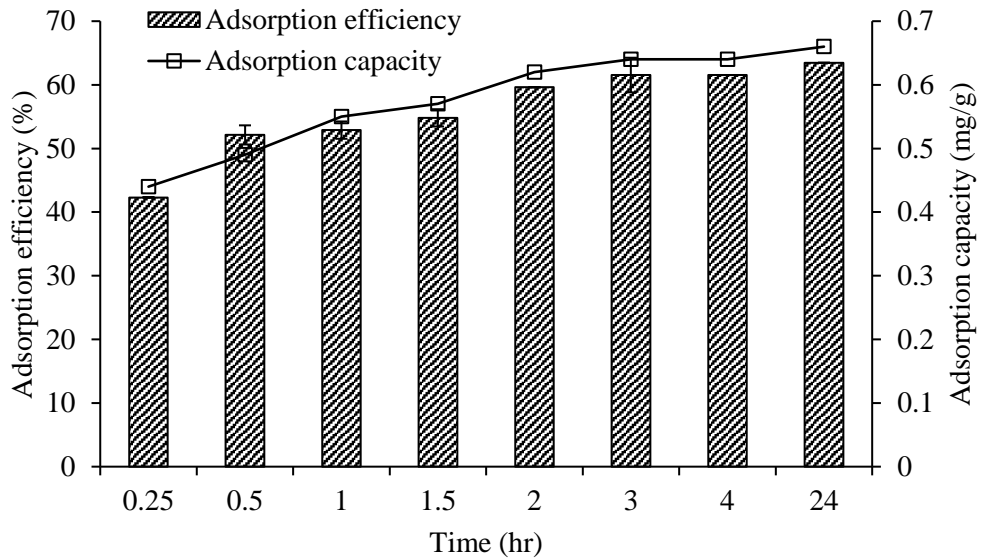
Figure 4.17: Effect of contact time of adsorption efficiency/capacity onto OPF biochar

Compared to the synthetic wastewater results shown in Section 4.3 (79.8 %), the NH_3-N removal efficiency was comparatively lower. The adsorption efficiency was lower in actual due to the presence of many other pollutants which hindered the adsorption of NH_3-N.

In the beginning of the adsorption process, the uptake was promoted by greater solute concentration gradient as well as a larger number of available adsorbent sites (Yang *et al.*, 2018). Furthermore, fast adsorption is also facilitated by the NH_4^+ ion initial interaction with negatively charged surface anion groups including carboxylate (COO-) and hydroxyl (OH-). Following the first hour, the adsorption rate slow down, indicating the ionic equilibrium between the adsorbent and the aqueous solution (Kizito *et al.*, 2015). Similar findings were reported, whereby fast adsorption of NH_4^+ occurred for 1 to 2 hours and it slowed and stabilized after 10 to 24 hours or

even after 4 hours due to the saturation and equilibrium of the adsorption sites (Gao *et al.*, 2015). The adsorption efficiency (61.5 %) was slightly greater than that of 120 min, hence the optimum contact time of 180 min was chosen for the next parameter.

4.5.2. Effect of shaking

The impact of shaking speed was investigated by varying the orbital shaker's agitation speed from 50 to 250 rpm. While other operating parameters were remained unchanged. The removal efficiency of the NH_3-N versus shaking speed is illustrated in **Figure 4.18**. The uptake of NH_3-N increased initially when the speed was increased from 50 to 150 rpm, followed by a steady condition at 200 rpm. Increase in efficiency was occurred due to contact between the adsorbate and adsorbent, which promotes adsorbate diffusion toward the biochar surface indirectly.
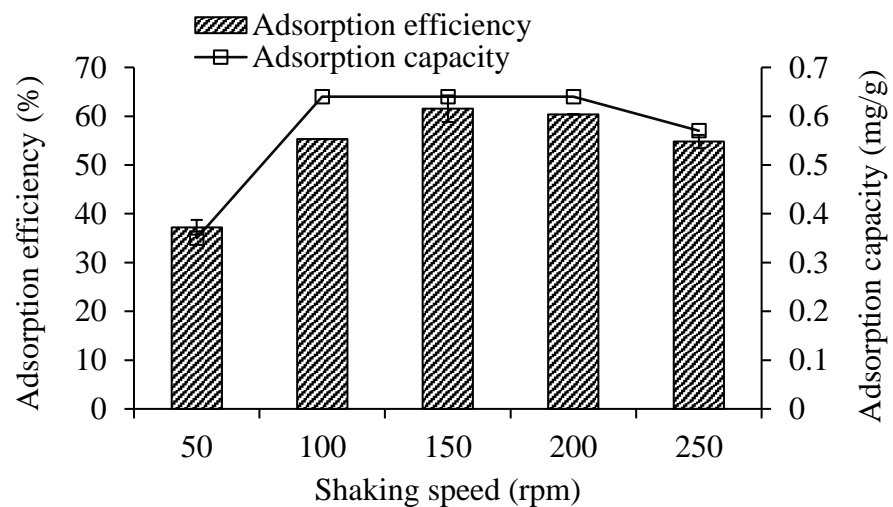
Figure 4.18: Effect of various shaking speed on the adsorption efficiency/capacity of NH_3-N onto OPF biochar

The increase of the adsorption efficiency with shaking speed is reported that the increase of turbulence and decrease of the thickness of the boundary layer, the rate diffusion surrounding sorbent from the bulk liquid to the liquid boundary layer surrounding sorbent enhances (Murithi, Onindo and Muthakia, 2012). It has been also suggested for good diffusion rate, increasing the shaking speed increases he external film mass transfer coefficient and hence enhanced the uptake (Murithi, Onindo and Muthakia, 2012). When the shaking speed exceeds 250 rpm, the removal efficiency reduces. The reduction in adsorption efficiency at 250 rpm is due to increase in kinetic energy of adsorbate and adsorbent which initiates collision between them. This enhances weakly bonded molecules of adsorbate detach from the adsorbent particles (Jamil *et al.*, 2014).

4.5.3. Effect of OPF biochar dosage

The impact of OPF biochar dosage on the effectiveness of NH_3-N adsorption was studied in a range of 0.5 – 4 g by shaking speed (150 rpm), temperature (25 °C), contact time (180 min), and pH constant. The dose of OPF biochar influences the availability of adsorption sites. **Figure 4.19** shows that by increasing the biochar dose, the removal efficiency of NH_3-N increased linearly.
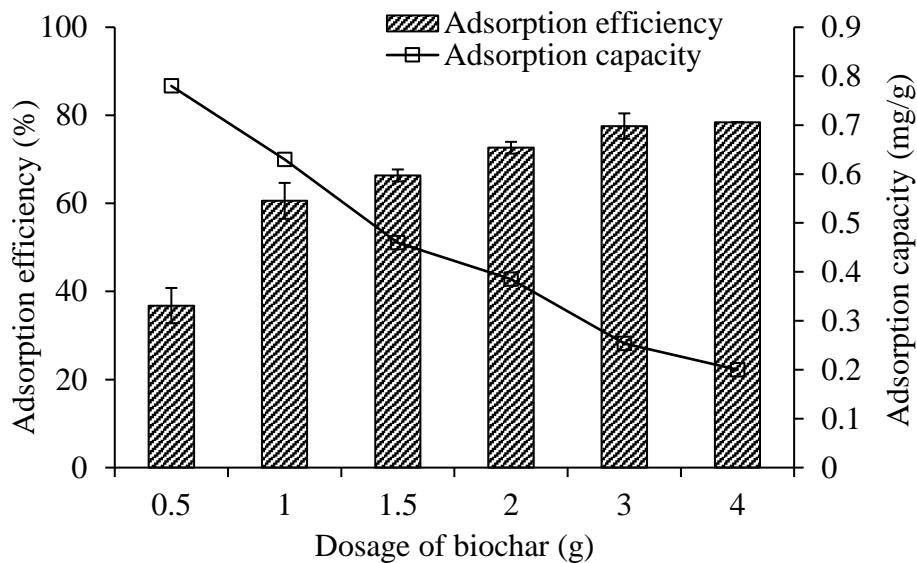
Figure 4.19: Effect of the OPF biochar dosage on the adsorption efficiency/capacity of NH_3-N

More sorption sites are available with a higher dose, which helps NH_3-N to bind more onto the biochar surface. The removal efficiency does not improve much after 2 g of dose and did not achieve higher efficiency than 90 %. It is due to the overlapping of adsorbent layers phenomenon, the increase in adsorbent mass covers accessible active sites. Also, similar results for NH_4^+ adsorption onto biochar has been observed (Kizito *et al.*, 2015). The decrease in adsorption capacity (mg/g) with increasing mass of the adsorbent is due to the split in concentration gradient between the solute concentration in the solution and the solute concentration on the surface of the adsorbent. At higher dosage the particle aggregation takes place, and as a result the capacity of NH_3-N decreases (Villabona-Ortíz, Figueroa-Lopez and Ortega-Toro, 2022). It has been reported that increasing the dosage of adsorbent led to the insufficiency of the adsorbate molecule in the solution with respect to the binding adsorbate molecule (Murithi, Onindo and

Muthakia, 2012). Thus, with an increase in the adsorbent amount, the amount of adsorbate molecule sorbed on the unit weight of the sorbent gets reduced, causing a decrease in adsorption capacity with increasing adsorbent dosage. Hence, 2 g was taken as the optimized dosage for the next parameter.

4.5.4. Effect of pH

The influence of pH adjustment of the AQW was examined in the range of 3 – 11, keeping the dosage (2 g), temperature (25 °C), shaking speed (150 rpm), and contact time (180 min) constant. The pH was adjusted by adding 0.1M NaOH or HCl. The original pH of AQW was slightly alkaline 8.16). The removal efficiency and capacity without any pH adjustment were 72.6 %, and 0.4 mg/g respectively. When the pH of the solution was adjusted to an acidic pH (3.0), the removal efficiency of NH_3-N immediately dropped to 58.5 %. However, when the pH adjusted to alkaline condition *i.e.*, 11 and increase in removal efficiency was noticed. Biochar represent high negative zeta potential at higher pH and facilitate the adsorption through electrostatic interaction (Hsu *et al.*, 2019), as mentioned in **Figure 4.20**. The findings for NH_3-N at acidic pH were unfavorable because of protonation of the surface binding site of OPF biochar also the adsorbent contains extra positive charges from hydrogen ions, that might produce large repulsion (Kizito *et al.*, 2015). The OPF biochar performs best at alkaline and neutral pH values.
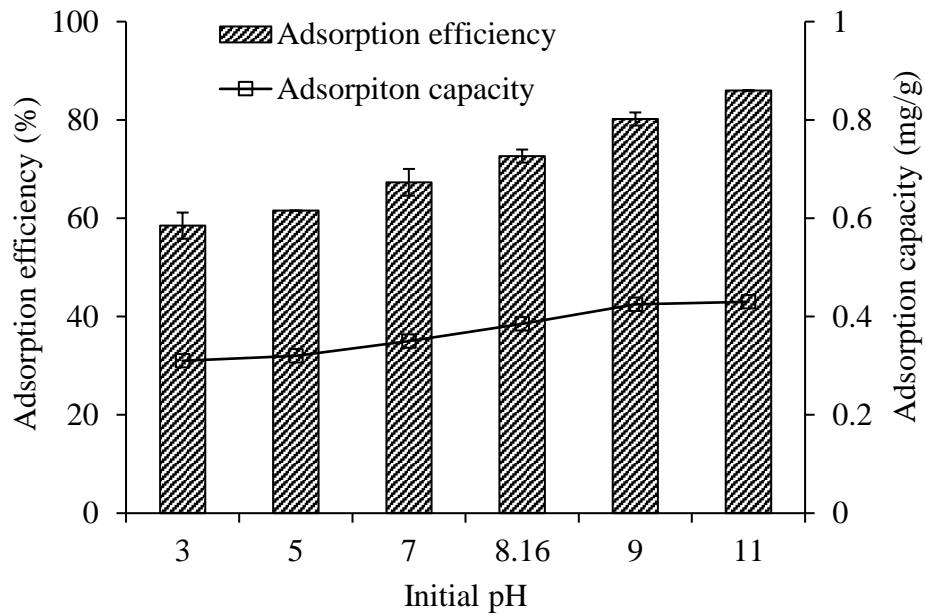
Figure 4.20: Effect of initial pH on the adsorption efficiency/capacity of

NH$_3$-N onto OPF biochar

4.5.5. Effect of temperature

The effect of temperature on NH$_3$-N was investigated from room temperature (25 °C) to 40 °C keeping dosage (2 g), shaking speed (150 rpm), and contact time (3 hr), constant. **Figure 4.21** shows that slightly increase in the adsorption efficiency of NH$_3$-N was occurred when temperature was increased from 25 to 40 °C. The increase in adsorption efficiency expresses that the adsorption onto OPF biochar was endothermic. For achieving the maximum adsorption, temperature higher than ambient temperature will be needed. This type of trend has been described that the diffusivity of the adsorbate from the external laminar layer in the micropore of biochar increases at higher temperature because of higher reaction rate between the surface functional groups of biochar and NH$_4^+$ (Long *et al.*, 2008). Also, the

adsorption tests higher than 40 °C were not conducted because of the equipment limitation as well as economic reason as the change in the adsorption efficiency was not very high. Moreover, it is not feasible to change the temperature of the AQW in real application. Similar results has been reported that increasing the temperature enhanced the adsorption of NH_4^+ (Kizito *et al.*, 2015).
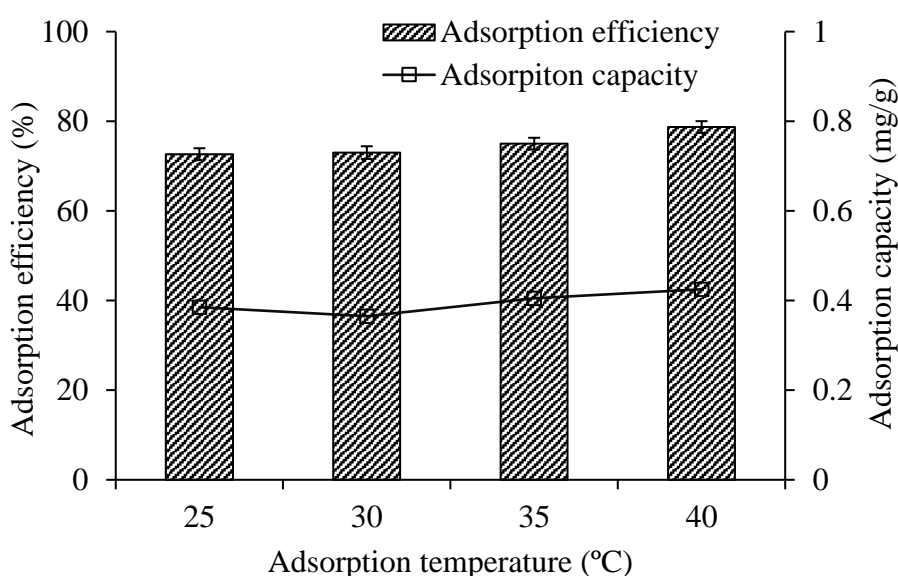
Figure 4.21: Effect of temperature on the adsorption efficiency/capacity of NH$_3$-N onto OPF biochar

4.6. Thermodynamics analysis

The value of ΔH°, and ΔS° was calculated using the slope and intercept from the Linear plot of lnK_C and $1/T$ as shown in **Figure 4.22**. **Table 4.6** contains the measured value of ΔH°, ΔS°, and ΔG°. The degree of entropy between the atom is represent by ΔS°.
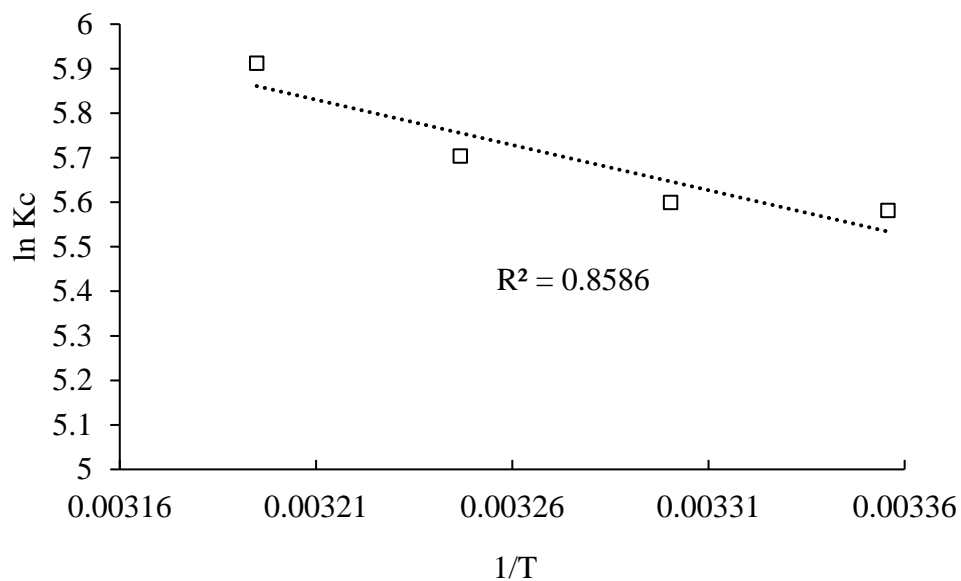
Figure 4.22. Linear plot of lnKc vs 1/T

Table 4.6. Thermodynamic parameters for adsorption of NH_3-N onto OPF biochar

Temperature (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/mol.K)	Ea (kJ/mol)
298	-13.83			
303	-14.11	16.90	102.72	35.12
308	-14.61			
313	-15.39			

The positive $\Delta S°$ of NH_3-N indicated an increase in randomness at OPF biochar interface during the adsorption process (Pholosi, Naidoo and Ofomaja, 2020). $\Delta G°$ is used to determine the spontaneous and nonspontaneous adsorption. The adsorption of NH_3-N onto OPF biochar is spontaneous as $\Delta G°$ value is negative which shows the process is thermodynamically favorable. The value of $\Delta H°$ was noticed in the range of

-20 to 40 kJ/mol for physical adsorption (Raghav and Kumar, 2018). In the present work, that adsorption type is physisorption and endothermic in nature because the value of is $\Delta H°$ positive. It is important to note that both PFO and PSO both showed good correlation and near to 1 so, the adsorption mechanism may be both physical and chemical adsorption as the thermodynamic parameters calculation also proven the occurrence of the physical adsorption. It has also reported that increasing the temperature, the value of the intercept, indicating the boundary diffusion, in the intraparticle diffusion increases, resulting in enhanced the surface adsorption (Pholosi, Naidoo and Ofomaja, 2020). Based on these results, the conclusion can be made that both physisorption and chemisorption. Similar findings are reported for the adsorption of NH_4^+ onto biochar (Kizito *et al.*, 2015).

An Arrhenius plot of lnK vs 1/T, with slope equal to $-(Ea/R)$ gives the activation energy (Ea). The activation energy calculated for NH_3-N is presented in **Table 4.6**. The minimum energy required for starting a chemical reaction is called the activation energy. The positive value of Ea in the adsorption process implies that the process is endothermic (Ebelegi, Ayawei and Wankasi, 2020).

4.7. Adsorption equilibrium and kinetics

To further analyze the ruling factor for the adsorption capacity of the OPF biochar, the experimental data obtained from **Figure 4.19** were fitted

with Linear and non-Linear Langmuir and Freundlich models. The isotherm

plots are illustrated in **Figure 4.23** and the results are presented in **Table 4.7**.
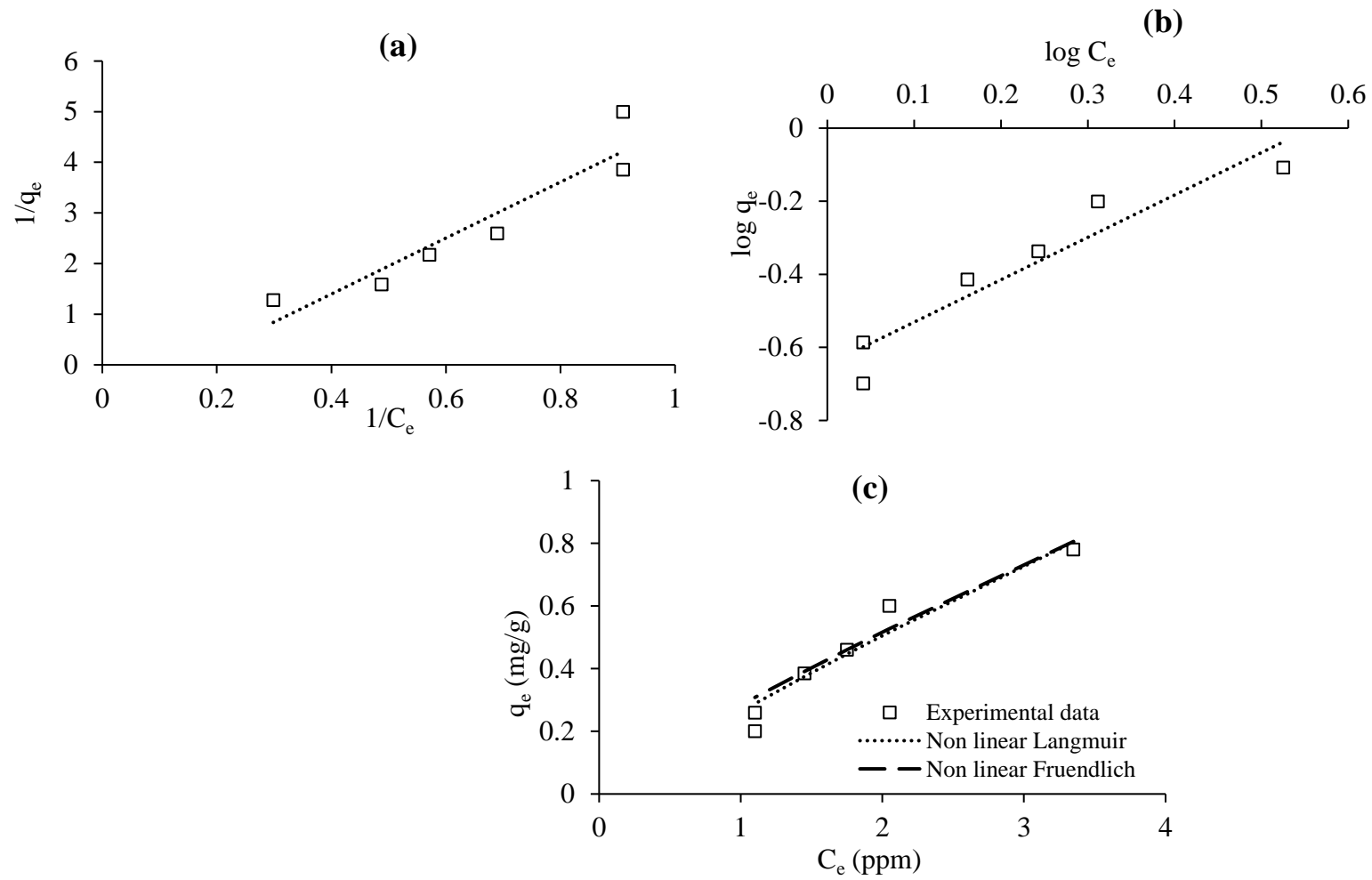
Figure 4.23: Adsorption isotherm (a) Linear Langmuir (b) Linear Freundlich (c) Linear and non-Linear

Table 4.7. Isotherm parameters for NH_3-N adsorption onto OPF biochar

Isotherms	Parameters	Linear model	Non-Linear model
Freundlich	K_F (mg/g)/(ppm)^n	0.22	0.28
	n	1.16	0.86
	R^2	0.9009	0.9518
	χ^2	0.05	0.05
Langmuir	Q^o_{max} (mg/g)	1.22	6.42
	K_L (L/mg)	0.15	0.04
	R_L	0.57	0.82
	R^2	0.8794	0.9303
	χ^2	1.07	0.04

According to **Table 4.7**, NH_3-N adsorption by OPF biochar was heterogeneous because the correlation factor ($R^2 = 0.9009$) of NH_3-N of the Freundlich models agreed well compared to Langmuir models. The heterogeneous characteristics of biochar surface is strongly associated to the adsorption of NH_3-N (Kizito *et al.*, 2015). Moreover, higher coefficient of determination ($R^2 = 0.9518$) was observed in the case of non-Linear Freundlich model, when applied to experimental data and shows better fit compared to Linear model.

On the basis of R^2 and χ^2 values, the comparison effectiveness of the non-Linear and Linear isotherm models can be evaluated. The error analysis of the non-Linear and Linear models in the form of isotherm models is shown in **Table 4.7**. A smaller value of χ^2 indicates a higher fit to the model. The non-Linear and Linear Freundlich models have the same error function value

of χ^2 implies that both models agreed well with the experimental findings. However, comparing the R^2 values, the non-Linear Freundlich model agreed the most to experimental data.

The influence of contact time was used to measure the adsorption kinetics. The PFO and PSO non-Linear and Linear models were evaluated. The details are given in **Table 4.8. Figure 4.24** illustrates the model plots. The correlation coefficient (R^2) value for the adsorption of NH_3-N is 0.9950 for non-Linear models, and 0.9988 for Linear models, demonstrating that PSO fits more to the experimental findings than PFO. The q_e value calculated by PFO is smaller than experimental results (0.60 mg/g) however, the q_e (mg/g) determined by PSO is identical to the experimental result. Based on the better fit by the PSO model, it can be deduced that rate controlling step is the chemical adsorption and there is no validation for chemisorption if the experimental data follow the PSO (Tran *et al.*, 2017). Further, the characterization of ATR-IR and EDX reveals that adsorption of NH_3-N is occur chemically because the interaction between oxygen functional groups as well as the value-added metals are involved in the adsorption process.

Table 4.8. Kinetic parameters for adsorption of NH_3-N onto OPF biochar

Model	Parameters	Linear model	Non-Linear model
Pseudo first order	q_e (mg/g)	0.24	0.57
	K_1 (1/min)	0.0168	0.086
	R^2	0.9861	0.9843
	χ^2	7.07	0.008
Pseudo second order	q_e (mg/g)	0.63	0.63
	K_2 (g/mg.min)	0.196	0.222
	R^2	0.9988	0.9950
	χ^2	0.004	0.002
Intra-particle diffusion model	k_p (mg/g $\times min^{0.5}$)	0.022	-
	C	0.70	-
	R_i	0.47	
	R^2	0.9767	-
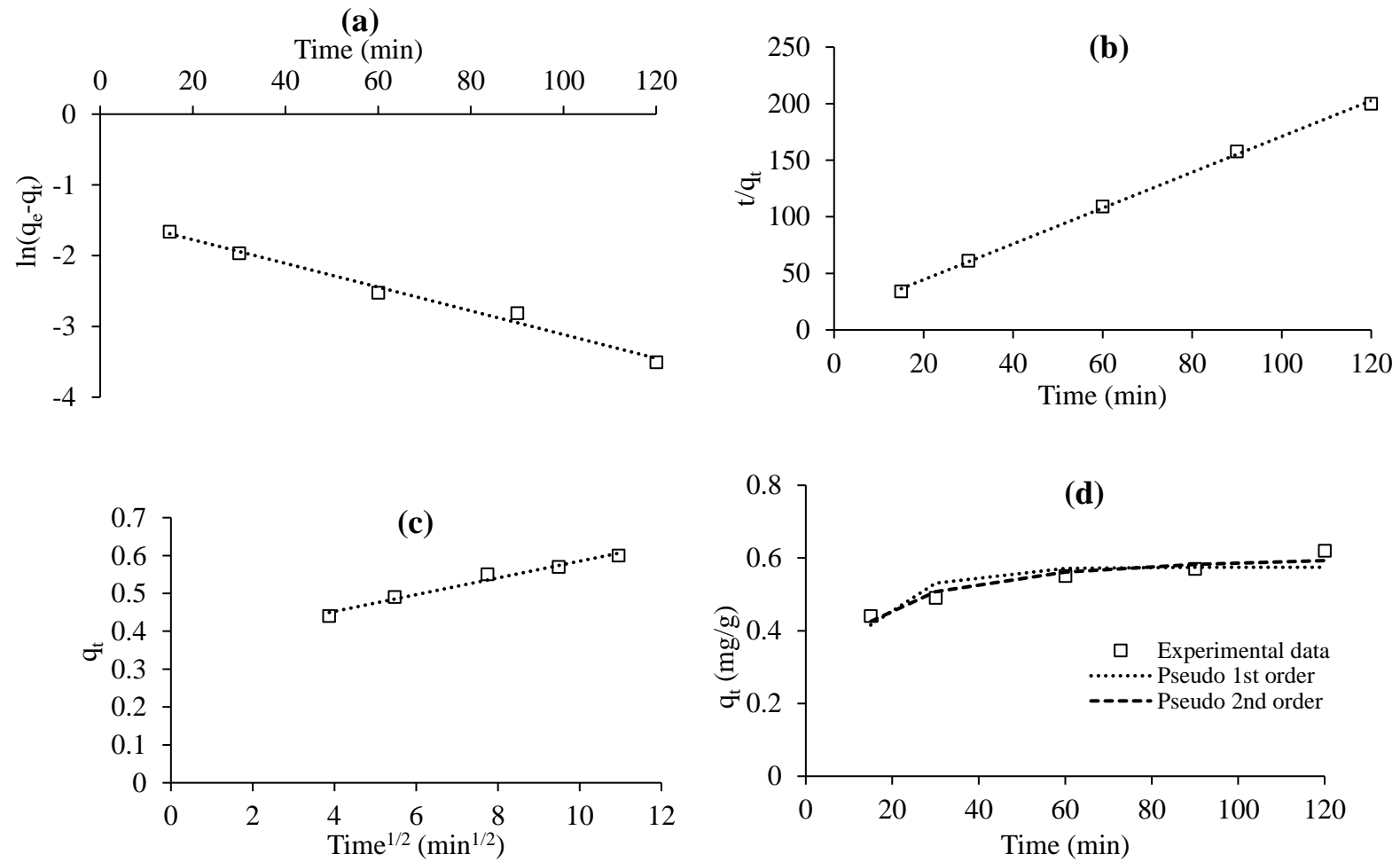
Figure 4.24: Plot for **(a)** Linear model of pseudo first order model **(b)** Linear model of pseudo second order **(c)** Linear model of intra-particle diffusion model **(d)** Non-linear kinetics models

The effectiveness of the models (non-Linear and Linear) could be examined by observing χ^2 and comparing the estimated q_e values with to the experimental q_e values. The q_e value ($q_e = 0.63$ mg/g) of non-Linear PSO is nearly identical to the experimental result. In addition to this, the non-Linear PFO also has a similar q_e value to the experimental value but the R^2 value is slightly lower than the non-Linear PSO. In Table 4.8 the non-Linear and Linear kinetic models the error analysis is demonstrated. Error analysis of the kinetic models (non-Linear and Linear) are shown in the **Table 4.8**. The non-Linear PSO model represent smaller χ^2, which means the model agrees well to the experimental results.

Figure 4.24 (c) represent the intra-particle diffusion model's plot. The analysis of experimental results using the intra-particle diffusion model, it was found that the plot did not pass through the origin but with a significant intercept, indicating that intraparticle diffusion was not the rate-limiting step. **Table 4.8** contains the parameters determined using intra-particle diffusion model. Where the value of the initial characteristic curve (R_i) shows strong initial adsorption because $R_i = 0.47$ is between $0.5 > R_i > 0.1$. The R_i value has been divided into four zones: $1 > R_i > 0.9$ is called weakly adsorption (zone 1); $0.9 > R_i > 0.5$, intermediate initial adsorption (zone 2); $0.5 > R_i > 0.1$, strong initial adsorption (zone 3); and $R_i < 0.1$, approaching completely initial adsorption (zone 4). For example, $R_i = 0.1$ means that the initial adsorption has already reached 90 %, and later on the adsorption proceeds following the intraparticle diffusion. Also, when $R_i = 0.5$ i.e., the other 50 %

of the adsorption governed by intraparticle diffusion (Wu, Tseng and Juang, 2009).

In addition to this, it has been reported that the various functional groups ((carbonylic, carboxylic, hydroxylic, and phenolic hydroxyl group) on the surface of biochar (Li *et al.*, 2013, 2018) are account for the ion exchange (between the NH_4^+ and the functional groups) in adsorption of nitrogen compounds (Liu *et al.*, 2010; Yin *et al.*, 2017; Dai *et al.*, 2020). The mechanism of hydroxylic, carboxylic and sulfonic acid groups and NH_4^+ on the biochar surface is expected as follows:

$$-\text{OH} + \text{NH}_4^+ = -\text{O} - \text{NH}_4 \tag{4.1}$$

$$-\text{SO}_3 - \text{H} + \text{NH}_4^+ = -\text{SO}_3 - \text{NH}_4 \tag{4.2}$$

$$-\text{COOH} + \text{NH}_4^+ = -\text{COO} - \text{NH}_4 \tag{4.3}$$
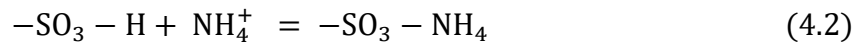
4.8. Nutrient recovery from actual AQW

To investigate the adsorbent performance for other pollutants in the actual AQW, the optimized process parameters were used for OPF biochar. The optimized parameters are temperature 25 °C, contact time 3 hr, shaking speed (150 rpm), and dosage 2 g. **Table 4.9** details the quality of the AQW before and after being treated with OPF biochar.

Table 4.9: Composition of aquaculture wastewater before and after treatment

Parameters	Characteristics of AQW (average)		Removal efficiency (%)	Malaysian Standard
	Initial	Treated		
pH	8.5 ± 0.12	8.6 ± 0.02	-	6-9
NH_3-N	5.3 ± 0.26 ppm	1.45 ± 0.07 ppm	72.64 ± 1.33	10
NO_2^--N	0.03 ± 0.001 ppm	0.03 ± 0.001 ppm	-	-
NO_3^--N	0.8 ± 0.10 ppm	0.8 ± 0.07 ppm	-	-
PO_4^{3-}-P	1.06 ± 0.04 ppm	1.09 ± 0.01 ppm	-3.15 ± 1.33	-
TP	1.23 ± 0.18 ppm	1.29 ± 0.02 ppm	-5.71 ± 1.73	-
COD	45.2 ± 3.89 ppm	48 ± 3.54 ppm	-6.13 ± 0.65	80
Turbidity	3.2 ± 0.10 NTU	1.5 ± 0.042 NTU	54.06 ± 1.32	-
Salinity	0.09 ± 0.00 $^0\!/\!_{00}$	0.09 ± 0.00 $^0\!/\!_{00}$	-	-

The pH of AQW is similar before and after treatment, because the OPF biochar has not been modified and is alkaline in nature. The were no obvious change in the pH. Thus, addition of OPF biochar do not change the pH of water to be discharged and no pH adjustment is required. The NH_3-N recovery from actual AQW was 72.6 %. The recovery of NH_3-N is lower compared to the one reported for synthetic wastewater (79.8 %) in Section 4.3. This could be due to the existences of other pollutants in the actual AQW. The pollutants could have cause competitive adsorption. The concentration of NO_2^- -N and NO_3^--N is lower than 1 ppm, making it difficult to adsorb onto biochar because the interaction of the adsorbate molecule and adsorbent is very low. It has been reported that biochar contains acid surface functional groups and can repulse the negative charge NO_2^--N and NO_3^--N molecule (J. Yang *et al.*, 2017). The concentration of PO_4^{3-}-P is slightly increase after treatment with OPF biochar. The increase in PO_4^{3-}-P occurs because our OPF biochar leaches PO_4^{3-}-P even when tested in synthetic wastewater. A similar behavior of PO_4^{3-}-P leaching was reported when synthetic wastewater was treated with various biochar (Yao *et al.*, 2012). A small increase in chemical oxygen demand (COD) was noticed because biochar is an organic material and some organic compound leached into the water after treatment. It has been found that various light aromatic compounds leached from biochar using ultrapure water (Lievens *et al.*, 2015). But still the COD is lower than the effluent standard and can be disposed to the water body without further treatment. The OPF biochar reduced the turbidity by 54.1 %. The reduction in turbidity may be due to adsorption (electrostatic interaction and Brownian motion between the

surface of the pore and the particles), straining/size exclusion (due to size difference between the pore opening and the particle), and/or sedimentation/gravity settling (due to density difference between the carrying effluent and the particles) (Khiari *et al.*, 2020). In Brownian motion the random motion of suspended particle during this motion the smaller particle enter to porous structure of the biochar and adsorbed. In straining/size exclusion the particles are stuck inside the pores and depends on the size of the particle or molecule and the opening of the pores in the OPF biochar. The salinity of AQW did not change after treatment with OPF biochar. It could be the lower presence of the Na^+, K^+, Ca^{2+} in the wastewater (Yang *et al.*, 2019). Also, lower salinity of the treated wastewater is better for the growth of aquatic organism and can be released to the water bodies (Velasco *et al.*, 2019). Without major change in salinity, pH and other components, this makes the treated water safe for fish and can be even recycled back to the pond for reutilization. Moreover, it will be much healthier as the NH_3-N content has been reduced drastically. For selective recovery of NH_3-N in real AQW the OPF biochar will be a suitable adsorbent. The spent OPF biochar (nutrient rich) can be further tested for its feasibility to be used as fertilizer or soil conditioner. In addition, OPF biochar is an environmentally friendly and biodegradable sorbent (Shang *et al.*, 2018) . For the spent adsorbent, there is no requirement for a separate treatment process and can be simply disposed of. This directly decreases the overall recovery process of the cost. After the recovery of the nutrient, the addition of OPF biochar to the AQW did not alter any of the AQW's fundamental properties, such as pH and salinity.

A comparison was also made with the Malaysian standards as shown in **Table 4.9** (DOE Malaysia, 2009). The industrial effluent should meet the requirement before discharge. After treatment of the AQW with OPF biochar, pH, NH_3-N, and COD are within the standard limits. As a result, it is safe to release the treated AQW to water bodies or recycle the treated water back to the pond or fish tank.

4.9. Comparison of OPF biochar with different adsorbents

In **Table 4.10**, a comparison of the OPF biochar with the adsorbents used in actual AQW is given. The adsorption performance of the carbon-based adsorbent is lower than the OPF biochar. Among the carbon-based adsorbent, commercial activated carbon shows the highest adsorption efficiency of 58.82 % NH_3-N at a dosage of 75 g/L adsorbent and contact time of 3 days (Karia *et al.*, 2022). In our study, the OPF biochar removed 72.64 % of NH_3-N within 3 hr with very lower dosage of 10 g/L.

Other adsorbents such as Clay 1 and aged refused have slightly higher performance than OPF biochar because of higher adsorbent dosage. Further coal cinder zeolite ball were chemically modified with polyvinyl alcohol and succinic acid (Tian *et al.*, 2016) and mordenite impregnated with magnesium (Yao *et al.*, 2022) did not performed well for removal of NH_3-N. Among all the adsorbents, the bentonite-hydrochar (composite material) completely removed the NH_3 in a continuous study with in 7.5 min (Ismadji *et al.*, 2016).

Except the composite material, the adsorption efficiency of OPF-based biochar for NH_3-N at low concentration was found to be comparable with other adsorbents and activated carbon, indicating that this developed OPF-based adsorbent can be used on any scale of wastewater treatment processes.

Table 4.10: Comparison of different adsorbents with OPF biochar for NH_3-N in AQW

Adsorbent	Contact time (hr)	Dosage (g/L)	Removal efficiency (%)	Ref.
Clay 1	3	75	~ 75	Zadinelo *et al.*, 2015
Bentonite-hydrochar	0.125	-	100	Ismadji *et al.*, 2016
Coal cinder zeolite ball	-	-	15.7 – 49.9	Tian *et al.*, 2016
Zeolite	7 days	1×10^{-11}	61.27	Aly *et al.*, 2017
Q2	5	10	55.08	Bernardi *et al.*, 2018
Aged refuse	1	20	88	Anijiofor *et al.*, 2018
Sawdust	Overnight	10	44.4	El-sherbiny, El-chaghaby and El-Shafea, 2019
Mg-mordenite	0.17	9	0	Yao *et al.*, 2022
Activated carbon filter	0.9 – 1.8	-	17.78	Jegatheesan *et al.*, 2007
Activated carbon	3	0.33	38.77	Sichula *et al.*, 2011
Pyrolyzed chicken feather fiber	0.5	3.3	40.47	Moon *et al.*, 2017
Commercial activated carbon	3 days	75	58.82	Karia *et al.*, 2022
OPF biochar	3	10	72.64	Present study

4.10. OPF biochar production cost analysis

The results and discussion sections have shown that OPF-based biochar is effective in adsorbing NH_3-N from AQW. Waste-based carbons were found to be as good as or better than commercially available activated carbon in the adsorption of NH_3-N. As a result, if the product is expected to be commercialized, the following process scale-up to produce biochar can be considered. The potential will aid in determining the biochar's ultimate marketability. The process flow diagrams for OPF-based biochar production, as well as their economic evaluation, were discussed in this section.

4.10.1. Process flow design

The process flow for the industrial scale-up was designed based on the lab setup tested. Each process of the lab test was scaled up. Different types of equipment were chosen and designed to suit the lab setup. **Figure 4.25** indicates the overall process flow design. First the raw sample was pick up in the truck from oil palm mill and brought to the pilot plant site and put in the storage place. Then the raw OPF from storage is transferred to the shredder via conveyor belt to be converted into small pieces and further carried (using conveyor) to the rotary kiln for carbonization process. After carbonization process, the biochar is directly shift to the rotary cooler to cool down the samples. In lab scale the amount is small so no need of the cooler but in actual pilot plant design cooler is necessary because of the continuous process and high amount of the product. After, the rotary cooler the prepared

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biochar was further gone to packaging process and stored in the storage room. In this design, during the rotary kiln, the prepared biochar converted into powder form, so there is no need for a grinder after the cooling process. Some design ideas were adapted from Ng *et al.*, (2003), who has designed a similar system for the preparation of activated carbon. Based on market demand, a rotary kiln is slected to produce aound 1500 kg of biochar on a daily basis.
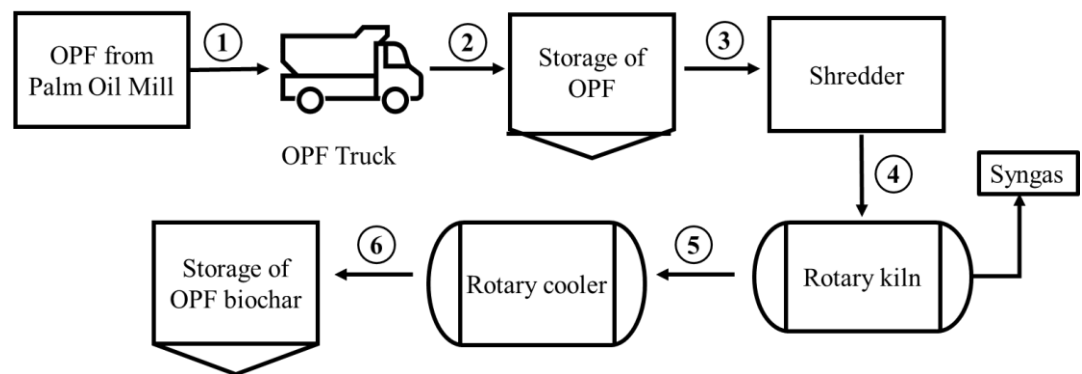
Figure 4.25: Process flow diagram to produce OPF biochar

The scale-up production cost study was performed using equipment design, sizing, and capital cost estimates(Ng *et al.*, 2003). A comparable production system for activated carbon from pecan shell was reported by Ng et al. (2003). The palm industry produces EFB and mesocarp fiber approximately 15.8 and 9.6 million tons annually (Marsin *et al.*, 2018). Converting the annual to daily production of EFB and mesocarp fiber to 43,267 and 26,301 kg/day. So, it easy to get 5,000 kg of OPF on daily basis from the palm industry. The projected cost of electricity usage for OPF

biochar preparation based on 5,000 kg/day of OPF feed is shown in **Table 4.11**. The estimated cost of each equipment in the pilot plant scale is calculated using Equation given in section 3.9. The electric tariff 1-200 kWh is RM 0.38 in Malaysia and RM 0.44 higher than 200 kWh. The operation time and power of each equipment are given in **Table 4.11**. The capacity of conveyor belt is 250 kg/min, and it took 0.33 hr to transport 5000 kg of the material. The shredding process takes 10 hr as the crusher has a capacity of 500 – 800 kg. The carbonization kiln has an effective volume of 4-8 m^3 that will take 5 hr to prepare around 1500 kg of biochar in two batches. The rotary cooler has capacity > 1.2 ton and took 2 hr to cool down the biochar to room temperature. Similar time has been reported for rotary cooler for decreasing temperature from 750 °C to less than 100 °C (Lai and Ngu, 2020). The equipment details are given in the Appendix. The total operation cost per day and per annual (320 days operation per year) for the OPF biochar at 300 °C is mentioned in **Table 4.11**.

Table 4.11. Electricity consumption for OPF biochar

Items	Purpose	Power (kW)	Time (hour)	Total (kWh)	Cost (RM) 1-200 kWh	Cost (RM) Total
Conveyor	Transport OPF from Storage to crusher	1.5	0.33	0.5	0.19	0.19
Shredder	Cut the OPF into smaller pieces	7.5	10	75	28.5	28.5
Conveyor	Transport OPF from crusher to Rotary kiln	1.5	0.33	0.5	0.19	0.19
Rotary kiln	Carbonization of OPF at 300 °C	22	5	110	41.8	41.8
Rotary cooler	Cool down the biochar 300 °C prior grinding process	7.5	2	15	5.7	5.7
Conveyor	Transport biochar 300 °C from rotary cooler to storage tank	1.5	0.33	0.5	0.19	0.19
Total cost per day						**76.564**
Total cost per annual (320 operation day)						**24,500.58**

*Electric Tarrif (TNB., 2014)

4.10.2. Manufacturing of OPF biochar at 300 °C

Palm oil mills with a daily supply capacity of 5,000 kg of OPF per day was chosen for this study. OPF biochar from OPF is a straightforward procedure that requires very little capital equipment. Sample preparation, crushing, and post treatment / sample collection are the unit processes. **Figure 4.25** shows the general design of the procedure and the conversion of OPF to biochar involves six processing steps. Initially, the OPF was delivered to the production side by OPF truck (step 1) and kept in the OPF storage tank (step 2) while waiting for the shredding process (step 3). 2500 kg of OPF per batch shall be added to the crusher machine through a conveyor, with a power of 1.5 kWh and a maximum capacity of 250 kg/min. The shredded OPF was then added to the rotary kiln (step 4) for pyrolysis. The OPF biochar was cooled down in a rotary cooler (step 5). Finally, it is stored in preparation for packaging (step 6). Long-term OPF storage was not included in this design since it was believed that the 5,000 kg/day of OPF would be processed on the same day.

The received dried OPF were fed into a 7.5 kW of commercial biomass crusher and shredded the OPF to 1 – 2 cm particle size. The larger particle size was recycled back to the crusher. Fine particle can be disposed or used other purposes. The process stream, with an 95% or 4,750 kg/day recovery, was directed to a rotary kiln.

Upon crushing, OPF was added to the rotary kiln and the temperature of the rotary kiln was increased to 300 °C to pyrolyze the OPF to become biochar under limited air injection for 2.5 hours. The yield of OPF biochar is approximately 30 % on dry basis. Based on the daily input of 4,750 kg of OPF, it is estimated 1,425 kg of OPF biochar will be produced respectively.

Once the pyrolysis process is completed, the OPF biochar shall be transported to a rotary cooler to cool down the biochar sample to room temperature The rotary cooler is driven by a 7.5 Kw motor with a maximum capacity of 1.2 ton/hour. After being cooled, the OPF biochar will be stored for future packaging.

4.10.3. Cost analysis

The scale-up production cost study was performed using Ng et al. (2003) equipment design, sizing, and capital cost estimates. A comparable production system for producing activated carbon from a pecan shell was reported by (Ng *et al.*, 2003). The estimated cost of electricity consumption for OPF biochar preparation based on 5,000 kg/day OPF feed is shown in **Table 4.11** and discussed in Section 4.9.1. The estimated capital cost to produce biochar was calculated, in **Table 4.12,** according to the design flow diagram and the method discussed in Section 3.9. For the pilot plant, the price of the equipment (asset cost) and capital cost such as land, installation, building construction, engineering supervision, electrical installation etc. are given in detail in the **Table 4.12,** which shows that the estimated capital cost

of the pilot plant is RM 0.46 million. For the operation cost of 1,425 kg/day of biochar, the assumptions are discussed in Section 3.9. Therefore, 456,000 kg/year will be produced from 320 working days. **Table 4.13** shows the total operating cost of the OPF biochar. The total annual operating cost is RM 0.53 million to produced 456,000 kg/year.

Table 4.12. Estimated equipment capital cost for OPF biochar

Equipment	Cost RM
Shredder	5,947.89
Conveyor (3 units)	6,869.70
Rotary kiln	89,044.56
Rotary cooler	41,218.20
Total equipment cost (a)	**143,080.35**
Equipment installation	35,770.09
instrumentation	8,584.82
Piping and material transport (augers)	114,464.28
Electrical installation	14,308.04
Building	18,543.21
Yard improvement	14,308.08
Service facilities	42,924.11
Land	11,446.43
Engineering and supervision	42,924.11
Construction expense	2,317.90
Contractor's fee	2,317.90
Contingency	7,154.02
Capital cost (b)	**315,062.93**
Total capital cost (c) = (a) + (b)	**458,153.28**

Table 4.13. Estimated annual operating cost for OPF biochar

Item	Annual operating cost (RM)
Raw materials	
OPF	0.00
Utilities	
Electricity	24,500.58
Labour	
Operating labour	276,480.00
Maintenance labour	41,472.00
Supervision	41,472.00
Fringe benefits	44,236.8
Supplies	
Operating supplies	429.24
Maintenance supplies	2,861.61
General works	
General and administrative	55,296.00
Property insurance and tax	30,905.36
Depreciation	14,864.33
Total annual operating cost	**532,517.91**

The cost of the pilot plant is summarized in **Table 4.14**. The estimated OPF biochar cost is RM 2.17/kg. This study demonstrates that OPF-based biochar is simple to make and does not need tedious operations.

Table 4.14. Summary of the cost

Items	Summary of costs (RM)
Total equipment cost **(a)**	143,080.35
Capital cost **(b)**	315,062.93
Total fixed capital investment **(c) = (a) + (b)**	458,153.28
Total annual operating cost **(d)**	532,517.91
Estimated total production cost = (c) + (d)	**990,671.19**
Estimated annual production of biochar (kg)	**456,000.00**
Estimated cost (RM/kg)	**2.17**

Table 4.15 shows the comparable price in US dollars ($=USD) for the biochar and activated carbon production and the details of the commercial online markets is given in Appendix. Compared to activated carbon, the biochar is cheaper. If the current study is compared to commercial prices of the activated carbon/biochar and to the literature activated carbon/biochar as well the cost of our biochar is comparable to that of the literature. While much lower than commercial prices. Among the biochar cost according to literature, the biochar prepared from rice husk is the lowest (0.52 $/kg) however, the lowest commercial price (0.77 $/Kg) for biochar was found on online commercial selling website Lazada Malaysia. The price of OPF biochar is 0.49$/kg (based on USD 4.4). In addition to this, the remaining cost/prices reported in literature or commercial selling website is higher.

Table 4.15. Comparative cost of biochar and activated carbon production

Raw material	Material	Region	Cost/kg USD	Ref.
Rice straw	Biochar	India	0.55	Sakhiya, Vijay and Kaushal, 2022
Rice husk	Biochar	India	0.52	Praveen *et al.*, 2021
Fruit peel	Biochar	China	4.96	Hu *et al.*, 2020
-	Commercial activated carbon	China	45.71	
Coal	Activated carbon	China	1.9	Alibaba (https://www.alibaba.com/)
Palm kernel shell	Activated carbon	China	1.19	
Orchard biomass	Biochar	USA	0.45-1.85	Nematian, Keske and Ng'ombe, 2021
Biomass from black spruce forest	Biochar	Canada	0.74	Keske *et al.*, 2020
-	Commercial Humichar	Singapore	25.62	Amazon (https://www.amazon.sg/)
-	Commercial activated carbon	Singapore	30.94	

Table 4.15. Continued.

Raw material	Material	Region	Cost/kg USD	Ref.
Oil palm wastes	Activated carbon (chemically activated)	Malaysia	2.93 -3.24	Lai and Ngu, 2020
	Activated carbon (physically activated)		2.73	
Coconut shell	Commercial activated carbon		6.6	
-	Commercial biochar	Malaysia	1.02	Shopee (https://shopee.com.my/)
-	Commercial activated carbon		1.78 – 2.22	
-	Activated carbon	Malaysia	1.33	Lazada (https://www.lazada.com.my/)
-	Biochar		0.77	
Oil palm fiber	Biochar	Malaysia	0.49	This study

Based on our calculation and flow diagram, the process is very simple, and few equipment's are required for biochar production compared to literature. The raw material (OPF) used in our study is abundantly available and free of cost in Malaysia which directly affects the operating cost. Also, in our study no chemicals have been used for the activation process which makes the OPF biochar cheaper and cost effective as well as environmentally friendly.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In this work, OPF biochar was tested as an adsorbent for NH_3-N recovery from AQW. Based on the experimental results, the following conclusion are made:

Physical and chemical activation of OPF biochar did not improve the adsorption efficiency of NH_3-N. Air injected OPF biochar shows better adsorption performance of NH_3-N compared to N_2 biochar, due to addition of oxygen functional groups.

Upon preliminary study, air was used to prepare OPF biochar (partial oxidation). The preparation was optimized using RSM and synthetic AQW. Parameters such as carbonization temperature, holding time, and air flow were varied for biochar preparation. Biochar prepared at carbonization temperature of 300 °C, holding time of 2.5 hr and air flow rate of 100 ml/min shows the best recovery of NH_3-N. The adsorption efficiency and capacity were deduced as 71.6 % and 1.6 mg/g respectively at 10 ppm of synthetic NH_3-N.

ANOVA analysis presented the model for air OPF biochar preparation in line with NH$_3$-N removal. Among the variables the carbonization temperature was the most significant. The coefficient of the determination (R^2) of NH$_3$-N is 0.98. The error between the experimental and predicted value was less than 3 % and further confirmed the validity of the model.

The adsorption process parameters have been evaluated on the OPF biochar in actual AQW. The initial concentration of the actual AQW studied was 5.3 ± 0.26 ppm. The optimum adsorption efficiency of 72.6 % and capacity of 0.4 mg/g for NH$_3$-N was achieved at conditions; contact time (3 hr), dosage (2 g), and temperature (25 °C). The removal efficiency of the OPF biochar is the same to synthetic wastewater but the capacity reduces because higher dosage was needed to recover more NH$_3$-N from the actual AQW, due to the presence of other pollutants which hinder the performance of the OPF biochar.

The non-Linear and Linear adsorption isotherms and kinetic models represent that the non-Linear model agrees well with the experimental data. The experimental data best fit to Freundlich model compared to Langmuir model. Therefore, the adsorption is multilayer and heterogeneous onto OPF biochar. The kinetic model reveals that PSO represent the experimental data well, which means that the adsorption process is chemisorption. The non-Linear PSO represents better performance compared to the Linear model. The intraparticle diffusion model indicates strong initial adsorption, and the

intraparticle diffusion is not the rate-limiting step because the plot did not pass through the origin but with a significant intercept. The thermodynamic parameters express that the adsorption process is endothermic and spontaneous. The entropy value suggests that the randomness increases on the interface of OPF biochar during the adsorption process. In addition to this, the surface functional groups such as hydroxyl, carboxyl, and sulfonic acid on the surface of biochar adsorbed NH_3-N in which the hydrogen atom of the surface functional groups is replaced by NH_4^+.

The characterization reveals different properties of the adsorbent. The FESEM represent that the OPF biochar has well developed honeycomb like structure. The EDX result shows that various value-added metals in spent biochar are significantly reduced, which confirms the adsorption process through the ion exchange process. The BET surface area of the OPF biochar did not increase and has no correlation with the adsorption efficiency of NH_3-N. The CEC and zeta potential of biochar samples decrease with increasing carbonization temperature and exhibits direct correlation with the adsorption of NH_3-N. Furthermore, the ultimate analysis shows significant increase in weight percent of the nitrogen content which can be as a fertilizer or soil conditioner.

The cost of the OPF biochar using pilot plant scale is RM 2.17 ($0.49). The cost analysis work suggests that production of OPF biochar is cost effective, and the price value is comparable to the biochar prepared in the literature. Further, the price of our biochar lower than the commercial

activated and can be commercialized for the treatment of the treatment of NH$_3$-N in low concentration as well as the OPF biochar can be used for other type of wastewater containing NH$_3$-N such as domestic wastewater, urban drainage wastewater, landfill leachate etc.

5.2. Future recommendation

The following recommendation can be made to further improve the performance of OPF based sorbent for removal of NH$_3$-N:

- The biochar preparation can be tested using hydrothermal carbonization. This method is expected to increase the oxygen functional groups on the surface of biochar and improve the NH$_3$-N adsorption.

- Biochar can be modified with different metals such as Fe, Ca, Na, Zn etc. to enhance the adsorption efficiency and simultaneously remove other pollutants.

- The column study is needed to be investigated for the removal of NH$_3$-N and further will extend to the treatment of the large volume of wastewater.

- More kinetics and isotherms models will be evaluated for the detail adsorption mechanism of the NH3-N onto OPF biochar.

- The effect of co-existing ion such as Na^+, Ca^{2+}, etc on the adsorption efficiency of NH_3-N will evaluated.

- Test the spent biochar on plant germination study to prove the spent biochar can be applied as a plant fertilizer. The spent biochar contains adsorbed NH_3-N, thus making the spent OPF biochar a nutrient rich biochar for soil fertility.

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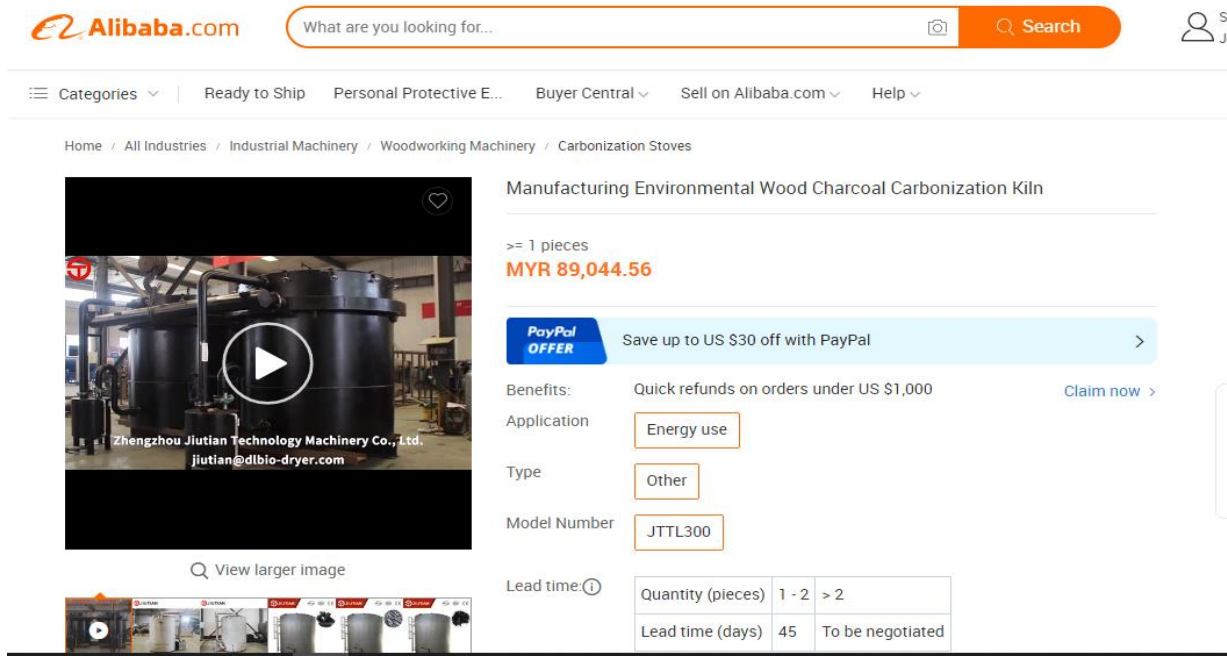
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List of Publications

1. Tanveer Ahmad, Sumathi Sethupathi, Mohammed J.K Bashir, Sin Ying Tan "Appraising the Performance of Oil Palm Fiber Biochar for Low Concentration Ammoniacal Nitrogen Recovery from Aquaculture Wastewater". *Environmental Technology*, A*ccepted 2022.* doi.org/10.1080/09593330.2022.2152735.

2. Tanveer Ahmad, Sumathi Sethupathi, Mohammed J.K Bashir, Sin Ying Tan "Evaluation of various preparation methods of oil palm fiber (OPF) biochar for ammonia-nitrogen (NH_3-N) removal" in *IOP Conference Series: Earth and Environmental Science*, p. 012020. doi: 10.1088/1755-1315/945/1/012020.

3. Tanveer Ahmad, Sumathi Sethupathi, Mohammed J.K Bashir, Sin Ying Tan "Optimization and economic analysis of oil palm fiber biochar for ammoniacal nitrogen recovery from Aquaculture wastewater" *Environmental Science and Pollution Research*, *Under Review.*

Appendix

Pricing data for cost analysis from commercial websites.

Item	Website Link	Screenshot
Rotary kiln	https://www.alibaba.com/	

Product Description   Working Principle   Application   Product Paramenters   Successful Case   Company Introduction

Essential details

Place of Origin:	Henan, China	Condition:	New
Video outgoing-inspection:	Provided	Machinery Test Report:	Provided
Marketing Type:	New Product 2020	Warranty of core components:	1 Year
Core Components:	Motor	Brand Name:	Jiutian
Effective Volume:	4-8 m3	Dimension(L*W*H):	Customized
Voltage:	220V-10KV	Power:	15-22kw
Warranty:	1 Year	Key Selling Points:	Energy saving
Applicable Industries:	Manufacturing Plant	Showroom Location:	None
Weight (KG):	8000	Product name:	Carbonization Kiln
Capacity:	300kg/4-6h	Diameter:	1.45-2.15m
Height:	1.85-2.2m	Heating source:	Biomass, natural gas, diesel, coal
Application material:	Wood chips, rice husks, peanut shells, plant stalks, bark	Material:	Carbon Steel, Refractory
		Feature:	Continuous Machine
Weight:	Customized	Certification:	ISO:9001

Product Paramenters

Model	CAPACITY	DIAMETER	HEIGHT	Material
JTTL-300	300kg/4-6h	1.45m	1.85m	Carbon steel, refractory
JTTL-500	500kg/4-8h	1.8m	1.9m	Carbon steel, refractory
JTTL-1000	1000kg/5-8h	2.15m	2.2m	Carbon steel, refractory

Biomass crusher	https://www.alibaba.com/	

Overview

Quick Details

Place of Origin:	Henan, China	Brand Name:	SUNRISE
Condition:	New	Video outgoing-inspection:	Provided
Machinery Test Report:	Provided	Marketing Type:	Ordinary Product
		Warranty of core components:	1 Year
Core Components:	Motor	Voltage:	220/380 V
Power:	7.5 kw	Dimension(L*W*H):	1.25*0.7*0.9 m
Warranty:	1 Year	Key Selling Points:	Long Service Life
Applicable Industries:	Manufacturing Plant, Energy & Mining	Showroom Location:	None
Weight (KG):	400	Item:	Wood crusher
Usage:	crushing waste wood	Raw material:	waste wood
Material:	Carbon Steel	Spare parts:	blade and sieve
After-sales Service Provided:	Online support	Weight:	400 kg
		Certification:	CE ISO

Rotary cooler	https://www.alibaba.com/	

Conveyor belt	https://www.alibaba.com/	

Prices of biochar and activated carbon from commercial websites

Items	Website link	Screen shot
Biochar	https://www.amazon.sg	

| Activated carbon | https://www.amazon.sg | |

Activated carbon	https://www.alibaba.com/	

Activated carbon	https://www.alibaba.com/	

| Activated carbon | https://www.lazada.com.my/ | |

| Biochar | https://www.lazada.com.my/ | |

Biochar	https://shopee.com.my/	

| Activated carbon | https://shopee.com.my/ | |

| Activated carbon | https://shopee.com.my/ | |