COD REMOVAL BY RICE HUSK ACTIVATED CARBON

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A report submitted in fulfillment of the requirements for the degree of
Bachelor of Applied Science (Sustainable Science) with Honours

FACULTY OF EARTH SCIENCE
UNIVERSITI MALAYSIA KELANTAN

Year 2018

DECLARATION

I declare that this thesis entitled "COD Removal by Rice Husk Activated Carbon" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ACKNOWLEDGEMENT

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ABSTRACT

Wastewater from industrial, agricultural, and urban activities is channeled directly into the streams. High Chemical Oxygen Demand (COD) level in water indicated a vast amount oxidizable matter that consume a lot of dissolved oxygen in water. This results in adverse impacts on both aquatic ecosystems and human health. Wastewater from the fish cracker industry typically has high organic content and high COD value. In this study, rice husk was chose as adsorbent for it is abundance and economical. This study emphasized on the optimum adsorption parameters such as flow rate, time and initial COD concentration that affecting adsorption by rice husk activated carbon. Response Surface Methodology was used to optimize the variables affecting COD removal percentage. Activation of rice husk by phosphoric acid was done after it was carbonized at 450 °C for 2 h. The treatment was done in a continuous fixed bed column. The wastewater's WQI value was calculated to be 11.82 and thus considered as polluted. From the Box-Behnken design, it was determined that a high 68.09 % removal percentage resulted from a best combination of 4.5 hours' time, 1 ml/min of flowrate, and 5 % initial COD concentration. SEM micrograph shows the adsorbent consists of large amounts of pores. Based on the study, rice husk activated carbon is proved to be a good COD absorbent.

Penyingkiran COD oleh Karbon Teraktif Sekam Padi

ABSTRAK

Air sisa dari industri, pertanian, dan kegiatan urbanisasi telah disalurkan terus ke dalam sungai. Permintaan Oksigen Kimia (COD) yang tinggi menyatakan banyak bahan boleh dioksida yang mampu mengurangkan banyak oksigen terlarut dalam air. Hal ini menyebabkan implikasi buruk kepada ekosistem and kesihatan manusia. Air sisa dari industri keropok lekor biasanya mengandungi COD yang teramat tinggi. Dalam kajian ini, sekam padi dipilih sebagai penjerap atas sebab ia wujud dalam jumlah banyak dan juga murah. Kajian ini juga menitikberatkan parameter penjerapan optima (masa, kadar aliran, dan kepekatan COD awal) yang mempengaruhi penjerapan karbon aktif sekam padi. RSM digunakan untuk mengoptimumkan faktor-faktor mempengaruhi penjerapan COD. Pengaktifan sekam padi oleh asid fosforik dilakukan selepas ia telah dibakar selama 2 jam pada suhu 450 °C. Perawatan tersebut dijalankan melalui satu kaedah penjerapan kolum. Nilai WQI yang didapati melalui pengiraan ialah 11.82 dan air sisa tersebut dianggap tercemar. Merujuk kepada reka bentuk Box-Behnken, sebanyak 68.09 peratus penyingkiran telah dicatat melalui kombinasi faktor-faktor seperti 4.5 jam masa, 1 ml/min kadar pengaliran, dan 5 % kepekatan COD awal. Graf mikro SEM menunjukkan wujudnya banyak liang atas permukaan penjerap. Berdasarkan kajian ini, karbon aktif sekam padi terbukti sebagai penjerap COD yang baik.

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LIST OF ABBREVIATIONS

$(NH_4)_2S_2O_8$	Ammonium Persulfate
ANOVA	Analysis of Variance
AOPs	Advanced Oxidation Process
BET	Brunauer – Emmett – Teller
BOD	Biochemical Oxygen Demand
cm	Centimeter
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
DOE	Department Of Environment
dS/m	DeciSiemen per Meter
EC	Electrical Conductivity
EQA	Environment Quality Act
$FeCl_3$	Ferric Chloride
$FeSO_4$	Ferric Sulfate
H_2O	Water
H_2O_2	Hydrogen Peroxide
H_2SO_4	Sulfuric Acid
H_3PO_4	Phosphoric Acid
HCl	Hydrochloric Acid
HNO_3	Nitric Acid
hr	Hour
K_2CO_3	Potassium Carbonate

K_2S	Potassium Sulphide
$KMnO_4$	Potassium Permanganate
KOH	Potassium Hydroxide
L	Liter
LCAs	Low-cost Adsorbents
m^2/g	Meter Square per Gram
mg/L	Milligram per Liter
mL	Milliliter
mL/min	Milliliter Per Minute
N_2	Nitrogen Gas
NaOH	Sodium Hydroxide
O_3	Ozone
Ppm	Parts per million
RHAC	Rice Husk Activated Carbon
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopic
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
UV	Ultraviolet
WQI	Water Quality Index
$ZnCl_2$	Zinc Chloride

LIST OF SYMBOLS

%	Percentage
° C	Temperature (degree Celsius)
±	Plus or Minus
+	Plus
-	Minus
x	Multiply

CHAPTER 1

INTRODUCTION

1.1   Background of Study

About 71% of Earth's surface is covered with water but sadly, only a small mere 0.3% is usable by human (USGS, 2016). The leftover 99.7% is either underground water, oceans, icecaps, or water vapours where extensive energy is needed to harvest the usable water (Gleick, 1996). Imagine using just 0.3% of that by most people on Earth through various activities such as agricultures, industries, and domestic purposes. Even though surface water can be accessed easily, but it is not necessarily safe for drinking as it may be polluted or contaminated. This explains why there's still 1.1 billion of people lack access to safe drinking water (WHO & UNICEF, 2000).

Quality of rivers have deteriorated over the years and evolved into global pollution (Meybeck & Helmer, 1989). Industrial, agricultural, and urban activities are channelling their waste irresponsibly into the streams. High level of COD in water indicated a vast amount oxidizable matter that can consume a lot of dissolved oxygen in water (Hajali, 2016). Dissolved oxygen levels is often the important indicator of freshwater quality, severity of water pollution, and rivers' health. This can cause detrimental effect on aquatic lives' physiology, reproduction, growth, and biochemistry (Kirbria, 2004).

In Malaysia, Klang River is currently listed as one of the most polluted rivers in Malaysia. Since the river is located in high development area, various parties are taking this opportunity to dumb their wastes straight into the streams as it's convenient for them (Sharif et al., 2015). Sources of organic pollutants are originated from agricultural activities, industrial wastewater, urban run-off, and domestic sewage. According to Assmann et al., (2017), amount of organic matters in water is measured in indices such as Biochemical Oxygen Demand (BOD), Total Organic Carbon (TOC), and Chemical Oxygen Demand (COD).

Amanatidou et al., (2012) mentioned that COD is unmistakably a critical parameter used in determining the amount of waste in wastewater. COD measure the oxygen equivalent of organic materials in wastewater, while also being a widely used indicator of wastewater quality. If high level of COD is released into the natural waters, microorganisms present there will consume the organic matter and thus depleting dissolved oxygen in the process. This will ultimately lead to eutrophication if not controlled.

Gautam, Sharma, Mahiya, and Chattopadhyaya (2014) stated that there are various methods used to treat organic pollutants such as ion exchange, coagulation, filtration with coagulation, membrane filtration, reverse osmosis etc. But still, the operational cost and capital involved are considerably high. Of all the methods, adsorption process has been proven to be most advantageous due to the lower investment and operational cost while also simple to design. Activated carbon sourced from agricultural waste is also useful in reducing the waste which will be otherwise end up at the landfill. Activated carbon consists of 87-97% of carbon, numerous microporous structures, nonpolar nature, and

high degree of surface reactivity give the activated carbon its great adsorption properties. Adsorption can be explained when the particles or adsorbate, interact with adsorbent surface through weak Van Der Waals forces resulting from intermolecular attraction (Bouchelta, 2003).

Even though the usefulness of activated carbon has been well proven in treating wastewater, it still remained one of the costlier methods (Rahman, 2011). To counter this, wide range of agricultural wastes are being investigated to use as source of absorbent (Kadirvelu et al., 2003). For this study, rice husk is a very interesting absorbent because it is abundant, non-toxic, renewable, and biodegradable (Samson, Louis, Banu, & Sudha 2015). After being transformed into activated carbon, it will be focused solely on removal of COD in water sample. There are already some researches done by several authors for removal of heavy metals and COD in polluted water (Farida, Ibrahim, & Adel, 2014; Oliveira, Montanher, Andrade, Nóbrega, & Rollemberg, 2005).

1.2   Problem Statement

Fish cracker is one of the most favourable snacks in Malaysia and it is produced by states near the coastal areas such as Kelantan, Kedah, Terengganu, Johor, Pahang, Sabah and Sarawak. Nguyen & Dao (2012) stated that wastewater from the fish cracker industry typically has high organic content, and subsequently a high chemical oxygen demand (COD). When not properly treated, it can severely threaten the ecosystem. Currently the fish cracker industry releases the wastewater into the stream without any treatment. The treatment by using activated carbon as absorbent can be done. Adsorbent is sourced from low cost yet abundant agricultural waste such as rice husk.

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1.3   Objectives

The objectives of this study are:

i.   To identify the optimum adsorption parameters (flowrate, initial COD concentration, & time) that affecting adsorption by rice husk activated carbon by using Response Surface Methodology.

ii.   To identify characteristic of adsorbent using instrumental analysis.

1.4   Scope of Study

i.   To collect and preserve the wastewater sample from the fish cracker industry in Kelantan.

ii.   To characterize the wastewater based on ex-situ and in-situ analysis.

iii.   To prepare the rice husk activated carbon by using chemical activation method.

iv.   To characterize the rice husk activated carbon by using SEM.

v.   To treat the COD using column adsorption study and calculate the percentage of COD removal using spectrophotometer method.

vi.   To optimize the parameters affecting adsorption such as effect of initial concentration of COD waste water, time, and flow rate using Response Surface Methodology.

1.5   Significant of Study

The use of activated carbon derived from agricultural waste materials can help reducing the waste produced, which will otherwise end up in the landfill. It also helps develop suitable carbonaceous substances that can be used in treating wastewater and water. Besides, this can help reduce the cost in processing of activated carbon especially in large scale production, complying with the principle of waste minimization and cleaner production.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction to Wastewater

Water released from businesses, homes, commercial activities, institutions, industries and then channelled to treatment plants through engineered network of carefully designed pipes, is called wastewater (Asano, Burton, Leverenz, Tsuchihashi, & Tchobanoglous, 2007).   Wastewater can be put into more categories and definition conformably to its origin sources. Domestic wastewater is generated by various sources including activities as cleaning, laundry, and food preparation.   Industrial/commercial wastewater is flow generated and discharged from Commercial and manufacturing activities generated of used water is known as industrial wastewater. Their activities include food and beverage processing and production, printing, and many more. Large institutions such as educational and hospitals facilities, generated wastewater in term of institutional wastewater. USGS (2016) concludes that for every person connected to water system, he generates about 80 to 100 gallons of wastewater each day.

The fish-processing industries, fish cracker to be exact, contribute notably to the overall pollution of the aquatic ecological system. The effluent from this industry contain excessive organic matter in colloidal, particulate, and soluble forms (Tay, Show, & Hung, 2006). The process of handling the fish will determine the level of contamination released. Colic, Morse, Hicks, Lechter, & Miller (2008) stated that this process could be of heavy

(fish blood from facilities storage tanks, "stick water" from fishmeal processing), mild (fish filleting), or small (washing only). Regardless, all of these will cause chemical oxygen demand (COD) to skyrocket while being detrimental to the aquatic ecosystem. Unpleasant odour are yet another problem resulting from this.

2.2   Water Quality

Water quality is described as the condition of the water, including its biological, physical, and chemical characteristics, usually with respect to its designated purposes. A healthy environment where the quality water able to maintain a rich and varied community of living organisms and preserve public health. There are several standard parameters used to define water quality. In Malaysia, National Water Quality Standards provides the standards of river water parameters grouped into different classes of different quality levels.

Environment Quality (Industrial Effluents) Regulations 2009 stated the acceptable conditions for discharge of industrial effluent for mixed effluent of Standards A and B. Standard A represent the discharge upstream of any raw water intake, while for Standard B is the discharge downstream of any raw water intake. By implementing such discharges, the receiving waters and aquatic ecosystems living in there can be preserved. Not just that, human health can be protected from the deleterious effects from untreated sewage too. The common parameter for effluent discharge are Temperature, pH Value, BOD5, COD, Suspended Solids, Oil and Grease, Ammonical Nitrogen.

Chemical oxygen demand (COD) is a measure of the capacity of water to consume oxygen during the oxidation of organic material and inorganic chemicals (ammonia and nitrite), into carbon dioxide and water (Yang, Liu, & Yang, 2009). To simply put, it indirectly measures the amount of organic matter in sample. Higher COD levels translate into greater amount of oxidizable organic material in the sample, which will reduce dissolved oxygen levels (Hajali, 2016). As gauge of organic matter in water, COD is more advantageous than biochemical oxygen demand (BOD) because BOD relies on microorganism to break down the organic matter in sample which will take course over the period of typically 5 days. Whereas, it is only a matter of hours for COD test to complete, therefore speeding up the time for water treatment.

2.3   Wastewater Treatment Methods

2.3.1   Coagulation/Flocculation

Coagulation and flocculation are vital processes in treating of wastewater (Sahu & Chaudhari, 2013). Besides being used in production of drinking water and sludge conditioning, this process also widely used in wastewater treatment. This includes wastewater from industrial, municipal, and hazardous kind of wastewater (Meric et al., 2002). The popularity of coagulation and flocculation in water treatment are due to its high efficiency and ease of operation (Fendri, Khannous, Timoumi, Gharsallah, & Gdoura, 2013).

Coagulation and flocculation usually occur in successive steps to overcome the stabilizing forces of suspended particles, to activate and increase their collision rate, and

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thus allowing the growth of flocs or agglomerates (Sahu & Chaudhari, 2013). Coagulation is the process of adding positively charged metal salt ions or catalytic polyelectrolyte, such as aluminium sulphate (alum), and ferrous of ferric (iron) salts into wastewater (El-Karamany, 2010). Due to the negative charge of suspended particles' surface, they repelling each other and form a stable dispersed suspension. Addition of positively charged metal ions will thus neutralize the negative charge, caused destabilization of particles. Whereas for flocculation, it refers to the binding of the destabilized particles and results in flocs that is heavier than water, which will then sink to the bottom and settles out in a clarifier (El-Karamany, 2010).

One of the main disadvantages of this process is high operating cost, due to the use of chemical substances in coagulation process (Aygun & Yilmaz, 2010). Besides, it has recently been stated out that Alzheimer's disease may link to the residual aluminium-based coagulants that persist in drinking water (Mohammad, Tan, & Zainura, 2009).

2.3.2   Advanced Oxidation Process (AOP)

Advanced oxidation process (AOP) is a chemical wastewater treatment technology, which applied frequently for the oxidation of organic and toxic materials in industrial effluent (Yazdanbakhsh, Mohammadi, Sardar, Goudini, & Almasian, 2014). AOP involves the generation of highly unstable hydroxyl radicals (-OH) from ozone (O_3), hydrogen peroxide (H_2O_2), photo-catalysis or oxidants in combination with ultraviolet (UV) radiation (Krishnan, Rawindran, Sinnathambi, & Lim, 2017). Unstable hydroxyl radicals are powerful and non-selective oxidant for mineralization or degradation of

organic pollutants. It will quickly extract a hydrogen atom or an electron from nearest pollutant particles to attain stable state, which will then convert itself into hydroxyl ion or water (Feitz, 2005). The organic compounds will be fully broken down, and thus decreasing the concentration of pollutants in wastewater (Krishnan et al., 2017).

It is a highly suggested application due to the fast reaction rate and non-selective oxidation, where the treatment of multiple different contaminants happen simultaneously (Krishnan et al., 2017). Instead of transferring pollutants into another phase, AOP degrades the pollutants, mineralize the pollutants into CO_2, H_2O and salts or at least change the pollutants' molecular structure to remove the toxicity (Krzemińska, Neczaj, & Borowski, 2015). However, the application of AOP until complete mineralization of pollutants is very expensive, thus limiting the large-scale AOP application in wastewater treatment (Krzemińska et al., 2015).

2.3.3   Aerobic and Anaerobic Process

Aerobic process and anaerobic process are categorized under biological wastewater treatment. They rely on microbes to break down organic components in wastewater (Fluence News Team, 2017). Biological treatment is always being used as secondary treatment process where remaining material needed to be removed after primary treatment (Fluence News Team, 2017) .

Aerobic degradation is a relatively simple, low-cost and environmental friendly way to degrade wastes in the presence of oxygen (Mohammed & Youssouf, 2014). It involves the utilization of microorganisms (aerobes), which use molecular or free oxygen

to assimilate or convert the organic pollutants into safer carbon dioxide, water, and biomass (Mittal, 2011). Usually, aerobic treatment is used to treat wastewater with low to medium organic pollutants, by which the COD level is lower than 1000 ppm; or hard-to-biodegrade wastewater such as refinery and municipal wastewater (Mittal, 2011). There are several factors that can affect the aerobic degradation rate, including temperature, pH, nutrients amount, dissolved oxygen and toxic materials.

In contrast with aerobic treatment, anaerobic wastewater treatment is degradation of organic pollutants in the absence of oxygen (Mittal, 2011). The microbes in anaerobic medium can work in oxygen-free environment to make end products of sludge, carbon dioxide gas, and methane gas which can be use as fuel (Mittal, 2011). Usually, anaerobic treatment is used to treat wastewater with high biodegradable organic matter content, in which the BOD is greater than 500 mg L^{-1}; or used in further degradation of sludge.

By comparing both of the treatment process, anaerobic process has more advantages than aerobic process. High rate anaerobic system has lower cost due to low construction, operation and maintenance costs (Gašpariková et al., 2005). Besides, it is more sustainable than aerobic process as the yield of sludge is lower, and the valuable biogas produced can be used to further decrease the processing cost.

2.3.4 Adsorption Process

Among all the wastewater treatment methods, adsorption process has occupied an important position due to its efficiency in removing dissolved organic pollutants (Namasivayam & Kavitha, 2002; Nemr, Abdelwahad, El-Sikaily, & Khaled, 2009).

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Adsorption can be defined as a substance, or adsorbate, either in gas or liquid phase, accumulate on a solid surface, or adsorbent, due to the existing of an attractive force between the adsorbate and adsorbent surface (Mohammed, 2011).

Generally, adsorption are divided into physical and chemical. Physical adsorption is weaker because there is only Van der Waals forces, dipole interactions or hydrogen bonding exist between adsorbent and adsorbate, instead of exchanging electrons (Mohamed, 2011). By altering the temperature, pH, and concentration of the liquid, the adsorbent can be detached from the surface. This reverse process is known as desorption (Worch, 2012). Whereas for chemical adsorption which results from chemical link between adsorbent and adsorbate, the chemical and electronic properties of adsorbent has changed and give rise to its irreversible reaction (Mohamed, 2011).

Adsorption is an effective way to remove organic matter in wastewater in terms of capital, simple design, ease of operation and insensitivity to toxic substances (Lata, Garg, & Gupta, 2007); (Wang, Boyjoo, Choueib, & Zhu, 2005). Besides, it is a clean and sludge free operation (Kanawade & Gaikwad, 2011). The effectiveness of an adsorbent in adsorbing pollutant molecules greatly depends on its structure, degree of polarity, specific area and porosity. Some of the principle types of adsorbent include activated carbon, silica-based compounds, and organic polymers (Mohammed, 2011).

2.4   Adsorbents

In most cases, there are two main types of adsorbents used to treat pollution. Adsorbent sourced from natural environment is the first type. Natural adsorbents typically include zeolites, oxides, biopolymer or clay minerals. The second type of adsorbent is

mostly made up of altered or engineered natural products to further enhance its adsorption capabilities. These type of adsorbents are classified into oxidic, polymeric, and carbonaceous adsorbents. Worch (2012) mentioned that engineered adsorbents are adsorbent that exhibited the highest adsorption capacities. Their lines of production are often operated with near-constant properties of products while also being strictly-monitored process. As of today, more and more studies are done to use by-products and wastes as an alternative low-cost adsorbents (LCAs).

2.4.1   Factors Affecting Adsorption

The adsorption's efficacy was varied according to variables such as the effect of time, flow rate, surrounding pH, initial concentration adsorbate inlet, and adsorbent's dosage.

a)   Effect of Initial COD Concentration

The initial adsorbate concentration at the inlet flow can had several effects in the main process variables and also could become limiting factors. This factor was very crucial since a certain adsorbent mass could only treat adsorbate of fixed amount. For that reason, as the concentration of effluent increase, the smaller the volume of effluent that a fixed mass of adsorbent could be purified (Markovska, Meshko, & Noveski, 2001).

b)   Effect of Time

The decrease in adsorbate concentration is greatly depends on time. As the bed height increased, there were more time of time between adsorbent and adsorbate, causing more adsorption of contaminant by absorbent. Higher bed column resulted in a lower effluent concentration, but the process reached a certain point where the effluent's concentration remained almost constant. This may be due to the attainment of equilibrium between the adsorbent and adsorbate (Goswami, 2013).

c)   Effect of Different Flow Rate

One of the main factors in continuous mode study that can have much effect on the adsorption performance is flow rate. It can significantly altered the outcomes in column adsorption experiment and assessing the efficiency of adsorbent in a continuous treatment process of effluents on the industrial or pilot scale (Afroze, Sen, & Ang, 2016).

2.4.2   Preparation of Activated Carbon

Two main processes used today in activated carbon preparation are physical and chemical activation that depends on the required sizes and shapes of activated carbon. Precursors in physical activation are first undergo carbonization, and then followed by carbon dioxide or steam activation. While in contrary, chemical activation involves impregnation with an activating reagent and then heated with flow of an inert gas (Hayashi, Horikawa, Takeda, Muroyama, & Nasir Ani, 2002). The function of activating reagents are to decompose the constituents made up of cellulose of the precursor while also

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promoting cross-links formation (Örkün, Karatepe, & Yavuz, 2012). Chemical activation was used in this study because it is more advantageous than physical activation. This is due to the former operates with lower temperatures, higher surface area, produce higher yield, established well developed pores, only a single procedure is needed, and reduction of mineral matter content as compared to the physical activation (Cruz et al., 2012). However, the drawbacks as such the washing is necessary to dislodge the impurities formed by the activation process, and the agent exhibits corrosive characteristic (Lillo-Ródenas, Cazorla-Amorós, & Linares-Solano, 2003).

a)   Physical & Thermal Activation

Physical thermal activation made up of two main similar processes of activation and carbonization. Physical activation is referring to the dry oxidation steps where the reaction between the steam or mixture of gaseous, steam or gaseous and sample, at temperature reaching above 700 °C (Al-Qodah & Shawabkah, 2009). The use of CO_2 had been more preferred in common for its ease of handling, clean, and the activation process could be surely altered at temperature as CO_2 has slow reaction rate. Pores with better consistency also could be produced by activating using CO_2 as opposed to steam (Khezami, Ould-Dris, & Capart, 2007).

Carbonization is aim to lessen the starting material's volatile material and converting the resulting char into having fixed carbon of higher content. During the process of carbonization, carbon atoms were rearranged into graphitic-like structures,

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causing the char to have initial porosity. Further gasification then can follow to bring out high porosity in activated carbon (Daud, Ali, & Sulaiman, 2000).

The steps of physical activation by steam oxidation concerned with pre-oxidation, pyrolysis, and steam activation. In pre-oxidation, dilution of air was done in half using nitrogen. It is done towards reducing the oxygen concentration in preventing the excessive heat from high temperature reaction between coal and oxygen. The sense of activation was practically to better enhance the pore volume and quantities and create some ordering of the structure which resulted in activated carbon with high porosity (Baseri, Palanisamy, & Sivakumar, 2012).

b)   Chemical Activation

Chemical activation is also known as wet oxidation, involving a catalyst to be infuse into the precursor. With relatively low temperature from just 300 °C up to about 800 °C, this activation is more popular to produce activated carbon. Practically, the temperatures varied depending on the action of inorganic additives to degrade and draw out water from the materials containing cellulose in the precursor. In average, the more widely used temperature for chemical activation were at 450–600 °C (Molina-Sabio & Rodrıguez-Reinoso, 2004).

Activating agents are also associate with oxidants and dehydrating agents which could cause implication to the pyrolytic decomposition (Mahapatra, Ramteke, & Paliwal, 2012). It also could prevent the development of the ash or tar hence forming higher carbon yield (Malik, Ramteke, & Wate, 2006). The chemical catalysts act as oxidizing agents and existed in forms such as H_3PO_4 (Donald, Ohtsuka, & Xu, 2011), $ZnCl_2$, HNO_3, H_2SO_4,

KMnO$_4$, K$_2$S (Demiral, Demiral, Tumsek, & Karabacakoglu, 2008), H$_2$O$_2$, KOH, NaOH, (NH$_4$)$_2$S$_2$O$_8$, and K$_2$CO$_3$ (Adinata, Daud, & Aroua, 2007). The surface oxygen functional groups are brought into the precursor's carbon when reacting with activating agents (Jassim, Amlah, Ali, & Aljabar, 2012).

Washing of activated carbon was the last but not least steps because it is also one of the more important ones. The activated carbon is washed with acidic or alkali solution depending on the preparation's chemical reagent used. Distilled water is then used to wash it. The washing step removed the soluble constituents from the material. Previously, the soluble constituents blocking the pores on the activated carbon, thus washing the chemicals off helped to develop activated carbon with greater porosity (Lozano-Castello, Lillo-Rodenas, Cazorla-Amorós, & Linares-Solano, 2001).

2.4.3 Rice Husk Activated Carbon (RHAC)

Activated carbon is charcoal that has been enhanced to increase its microscopic pore network, which aid to its increased surface area (Alabadi et al., 2016). This characteristic provides a greater absorption power towards contaminants in water such as natural organic compounds, taste and odor compounds, and synthetic organic chemicals (Karanfil, 2006). However, commercially available activated carbon can be costly for its factors of intensive labor, energy, exchange rate and etc (Thomas & George, 2015). As cost is an important factor to consider when comparing the absorbents, substituting the source of activated carbon with low processing, natural, yet abundant wastes can be more economical while also help minimizing waste in the process. For this study, rice husk

activated carbon is chosen to remove COD as it meets the criteria of low-processing, natural, renewable and abundance.

Rice husk is largely produced from the rice industry. It is an agricultural waste material generated in rice producing countries, including Malaysia. Annually, production of rice in the world is not far from 500 million metric tons, of which 10–20% is rice husk. Dry rice husk contains 70–85% of organic matter (lignin, cellulose, sugars, etc.) and silica is one of the components too (Vempati, Musthyala, Mollah, & Cocke, 1995). Many industrial factories have successfully turned rice husk as fuel. Due to its low moisture content and ease of processing, rice husk is also used as bio-fuel to generate clean electricity. With rice husk as the source of activated carbon, it can minimize waste from agriculture by converting them into cheap source of adsorbent. Rice husk activated carbon portrays good characteristics as adsorbent and it has good resistance towards chemical, high mechanical strength, and its structure in granules that made it a good adsorbent to remove the contaminants such as heavy metals, dye and other organic or inorganic compound. The great abundance of rice husk have potential to produce a huge amount of the low-cost adsorbent that may overcome the concerning water pollution at a successful rate.

2.4.4 Production of RHAC

RHAC can be fabricated through pyrolysis and either chemical or physical activation. Chemical impregnation with KOH and NaOH of pyrolysed rice husk followed by activation at 650–800 °C gave rise to activated carbons with incredibly high surface areas of 1413–3014 m^2/g (Ahmedna, Marshall, Husseiny, Rao, & Goktepe, 2004). In other

study, rice husk that has been through pyrolysis, activation by H_3PO_4 with higher temperature of 700–900 °C can yield a surface area of 450 m^2/g in rice husk activated carbon (Kennedy, Vijaya, & Sekaran, 2004). Nakagawa, Molina-Sabio, & Rodriguez (2007) proved that activated carbon produced by chemical activation with KOH or H_3PO_4 achieved higher yield and removal efficiencies comparable to those of commercial products. Another useable chemical agents studied included $ZnCl_2$, $FeCl_3 \cdot 6H_2O$, KCl, $CaCl_2 \cdot 7H_2O$ & $FeSO_4 \cdot 7H_2O$. At 600°C activation temperature, these agents can produce surface areas ranging from 168 to 480 m^2/g on activated carbon (Yalçın & Sevinc, 2000).

2.5   Response Surface Methodology

In order to produce the best possible response from the parameters, optimization process by response surface methodology (RSM) is used. RSM one of the most pertinent multivariate methods and is consists of mathematical and statistical techniques based on the fit of a polynomial equation to the experimental data (Bezerra, et al., 2008). By carefully designed experiments, the aim is to optimize a response (output variable) which is affected by several independent variables (input variables). An experiment is a series of tests, called runs, in which input factors is varied so that the causes for variables in the output response can be found. A preliminary study is conducted to find out the minimum and maximum value of each parameters. After getting the result, minimum and maximum value for each factor is then coded as -1, 0, and +1 respectively.

The experimental design of Box-Behnken used here was to produce a total of 17 reaction tests with set parameters, from only three variables. Through this design, the

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optimum combination of variables are determined and its response pattern are studied too. From the graph produced by the software, the highest response can be obtained through the optimal combination of variables. Adopting Box-Behnken design can noticeably reduce the number of experimental sets without sacrificing the optimization's accuracy, compare with traditional factorial design methods.

On numerous occasions, experiments are run at different factor values, or named levels. Each of an experiment's run demands a combination of levels of the factors that are being investigated. The Box-Behnken design is a design that involves only three levels to run an experiment. It is a special three-level design because there is no points at the vertices of the experiment region. The corners of the cube contain points that represent impossible or prohibitively expensive test of level combinations due to constraints of physical process. The following Figure 2.1 and Table 1 shows an example of a Box-Behnken design with three factors:
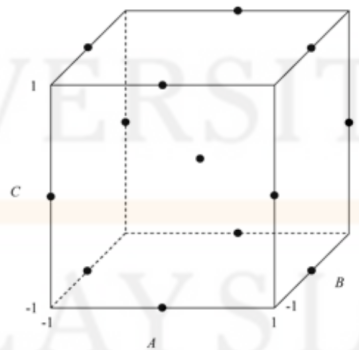
Figure 2.1: Geometric representation of Box-Behnken design for three factors.

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Runs	Factors		
	A	B	C
1	-1	-1	0
2	-1	1	0
3	1	-1	0
4	1	1	0
5	-1	0	-1
6	-1	0	1
7	1	0	-1
8	1	0	1
9	0	-1	-1
10	0	-1	1
11	0	1	-1
12	0	1	1
13	0	0	0

Figure 2.2: Table of Box-Behnken design for three factors.

Commonly, there are four main steps in applying Box-Behnken in RSM. Firstly, based on the chosen conditions an experimental plan is provided. Then experiments designed by statistic methods are performed. Afterwards, an estimation is made on the coefficients in the mathematical model and the model accuracy is checked too. The last step involved performing Response analysis to forecast optimal conditions, and these forecasts are experimentally confirmed.

CHAPTER 3

MATERIALS AND METHODS

3.1   Materials and Wastewater Sampling

Rice Husk was collected from rice mill in Jitra, Kedah. In this study, wastewater from fish cracker industry was selected to be an adsorbate due to a redundantly high content of COD. The wastewater was taken from Kedai Pak Su Do, a fish cracker processing shop in Tumpat, Kelantan. The shop and its processing material of were pictured in Appendix A.

3.2   Preparation of Rice Husk Activated Carbon (RHAC)

In order to remove dust and other impurities, rice husk were washed thoroughly with distilled water for several times. It was then put into oven to dry at 100 ± 5 °C for 24 hours and blended to smaller size (approximate to 2 mm) to ensure even impregnation by the activating agent. Activation treatment using 3 M phosphoric acid was done at 80 °C for 3 hours. The pre-treated product are washed thoroughly and oven-dried at 100 ± 5 °C for 24 hours. Last step of carbonizing required the pre-treated rice husk to be carbonized at 450 °C for 2 hours. Rice Husk Activated Carbon (RHAC) obtained were then put into sterile containers and placed in desiccator for subsequent application. This process was repeated until substantial amount of carbon are obtained. Figure 3.1 revealed rice husk before and after activated.

Figure 3.1: Raw rice husk and its activated carbon form

3.3   Wastewater Characterization

a)   Preservation

The wastewater was collected into clean plastic bottles. 2 ml per liter of 50 % sulphuric acid was added to the bottle to reduce the pH so that to create an acidic environment where microbe activities are lowest. It was later placed in refrigerator at 4 °C to preserve the parameters for a maximum of 30 days.

b)   COD Analysis

The sample was first blended until no more solids visible and then poured into beaker. Hach COD reactor was preheated to 150 °C. The wastewater were diluted into 10, 20, 30, 40 and 50 % concentration to be tested. High range of 20-1500 mg/L Hach COD Digestion Kit was used as wastewater here contained visible particles and high cloudiness.

By using a micropipette, 2 ml of sample with different concentration were put into different vials as shown in Appendix A. The vial must be closed tightly after done because the hypothermic reaction occurred inside was generating pressure as well. Then, the vial is hold by the cap and gently inverted several times to mix over a sink. The vials got very heated during mixing.

After several vials are filled with wastewater, they were put in the preheated reactor and left in there for 2 hours. After 2 hours, they were let cooled in the reactor until the temperature dropped from 150 °C to 120 °C, then the vials just can be taken out to further cooling to a manageable temperature. For the next step, the concentration of COD was determined using HACH UV-RIS Spectrophotometer DR 6000.

c)   **BOD Analysis**

A buffer solution is prepared beforehand. 1 sachet of BOD Nutrient Buffer Pillow was dissolved into the 3 L of distilled water in Schott's bottle. The Schott's bottle was swirled gently to homogenize the sample dilution water.

BOD bottles with 300 ml size are prepared for 2 bottles. One for sample dilution water and another for dilution water blank. Each of the BOD bottles was filled with 290 ml of buffer. At different points, the water samples are collected and 10 ml of each were added into the BOD bottles labelled Point 1 and Point 2 respectively. 10 ml from blank solution was added to the BOD bottle and labelled 'blank'. The solutions were mixed by inverting the bottles several times to ensure even mixing. The bottles were incubated at about 20 °C for five days. After 5 days incubation, the sample is taken out and a Portable Dissolved Oxygen Meter with Probe is used to measure the dissolved oxygen content in

samples. The value of BOD5 were recorded and calculated by using formula in equation 3.3.

$$BOD5 = \frac{D1-D2}{P} \qquad (3.3)$$

where,

D1 = initial DO of the sample

D2 = final DO of the sample after 5 days, and

P = decimal volumetric fraction of sample used.

d)   Ammonia Nitrogen Analysis

Analysis is done using salicylate method to determine the ammonia nitrogen in sample. Three sample cells were prepared. The first blank sample cell was filled with 10 ml of distilled water, while for the other two, 10 ml from point 1 and 10 ml from point 2 is put into each sample labelled 'sample 1' and 'sample 2' respectively. Ammonia salicylate powder pillow was added to each sample cell. The sample cells were shaken gently to ensure complete that reagent has completely dissolved. Then, the sample cells were then left undisturbed for 3 minutes. After 3 minutes has passed, Ammonia cyanurate powder pillow was added to each sample cell. Both the sample cells were shaken gently then left undisturbed for another 15 minutes. A bright green colour was revealed confirming the present of ammonia nitrogen in sample. After 15 minutes, the sample vial was measured by using calorimeter.

e)   **Suspended Solid Analysis**

A blender is used to blend 100 ml of water sample collected from point 1 and point 2 at high speed for 2 minutes and then poured into a stirring beaker. Immediately, a sample cell is filled with 10 ml of water sample. 10 ml of distilled water is put into the sample cell and labelled as blank. All the sample cells were cleaned and measured by using calorimeter. The sample cell with water sample was swirled to remove formation of air bubbles.

3.4   Column Adsorption Study

Around 18 g of rice husk activated carbon was needed to fill the plastic column of 3 cm diameter and 25 cm height, to a bed height of 10 cm in the column. Gauze were placed at both the bottom and upper part inside the column to avoid absorbent loss with the liquid flow. Fish cracker's wastewater was constantly stirred at medium speed on a magnetic stir plate to give a more consistent feeding to the column. Its flow rate was controlled with a peristaltic pump and set up as shown in Figure 3.2. Distilled water was fed into the column to further compact and wet the media in order to further improve the adsorption capabilities. The removal efficiency of the COD and the adsorption capacity was calculated using equation 3.1 and 3.2.

Figure 3.2: Set up of column study experiment

$$\text{Removal Efficiency, P} = \frac{Ci - Ce}{Ci} \times 100\% \qquad \text{(Eq 3.1)}$$

$$\text{Absorption Capacity, } q_e = (Co - Ce)\frac{V}{M} \qquad \text{(Eq 3.2)}$$

where,

M mass of adsorbent.

Ci and Co are the initial and final concentration (mg/L) respectively.

V volume of solution.

3.5 Optimization Using Box-Behnken Design

A preliminary study was carried out on the three parameters of time, flow rate and initial COD concentration to find out the minimum and maximum values of each parameter to be used in RSM software. The time for example, the preliminary study was carried out by fixing the other two parameters while varying the time from 1 to 24 hour.

The removal percentage increased with time but then dropped after 8 hours of time. From here, the minimum time was 1 hour and the maximum was 8 hours.

For the parameter of flow rate, it was first carried out with 5, 7, and 10 ml/min with fixed initial COD concentration and time. However, the flow rate of 10 ml/min was deemed too fast when the removal percentage from result was only around 5 % after 4 hour. At the same time, experiment conducted for 5 ml/min and 7 ml/min shown a higher removal percentage at lower flow rate. On that account, lower values of flow rate, 1 ml/min and 2.5 ml/min were put into tests. The acquired results stated that the suitable range of flow rate was between 1 to 7 ml/min (Refer Appendix B).

In the beginning, 20 % of initial COD concentration were diluted from raw wastewater and tested in the system for 4 hours. With fixed flow rate of 5 ml/min, the column system proved that as much as 58.92 % of removal percentage is achieved. For that reason, both the ranges that was lower and higher than 20 % concentration had to be tested for its removal percentages. The results from 5 %, 10 %, 30%, and 40 % are established with all the value except for 40 % COD concentration, exhibited almost the same removal percentages. Since 40 % of concentration only produced very low removal percentage, it was safe to conclude that the initial COD concentration's ranges is 5 %, 10 %, 20 %, and 30 %.

The three parameters of time, flow rate, and initial COD concentration, which are used to produce 17 experimental runs in order to obtain optimum combination of parameters. Table 3.1 shown the 17 runs produced. In order to apply this design, each independent factor, was set at one of three values which are spaced equally, usually coded as -1, 0, and +1. For example, for three factors it was involving three blocks, in each of which two factors are varied through the four possible combinations of high and low. The

ranges of the variables in this study were as shown in Table 3.2. The parameters and the level selected for this experiments were COD concentrations, flow rate, and the time. When compared with Central Composite Inscribe and Central Composite Face-centered, Box-Behnken design required fewest runs in three-factor case. The experiments set were conducted randomly by software Design Expert Version 7.1.6.

Table 3.1: Experimental design of the response surface design

Run no.	A: Time (h)	B: Flow Rate (ml/min)	C: Initial Concentration (%)
1	4.5	7	5
2	1	4	5
3	8	4	5
4	1	4	30
5	4.5	4	17.5
6	8	1	17.5
7	1	7	17.5
8	4.5	1	5
9	4.5	7	30
10	8	4	30
11	4.5	1	30
12	1	1	17.5
13	4.5	4	17.5
14	4.5	4	17.5
15	4.5	4	17.5
16	8	7	17.5
17	4.5	4	17.5

Table 3.2: Independent factors and their coded levels investigated using Box-Behnken Design.

Factors	Low	Medium	High
	-1	0	+1
X_1: Time (hr)	1	4.5	8
X_2: Flow rate (mL/min)	1	4.0	7
X_3: Initial COD concentration (%)	5	17.5	30

3.6   Characterization of RHAC

The surface morphology of Rice husk activated carbon was observed. It was studied by employing Scanning Electron Microscopy (SEM), as presented in Appendix A, to obtain images of surface topography and sample composition. A highly-conductive metal coating was needed to makes the non-conductive samples conductive, to avoid over-heating the sample which may cause thermal damage (Stokroos, Kalicharan, Jongebloed, & Van Der Want, 2002). For this experiment, the samples were coated with thin layer of gold by using a gold sputtering device. The gold coating aided in higher sample stability and enabled for production of clearer image. SEM works by utilizing a focused beam of electrons instead of light to scan the specimen's surface and can observe the surface composition directly at magnifications up to 2,000,000x (Achaw, 2012). The operation took place in a vacuum environment or otherwise the air molecules collided with electrons rather than reaching the sample.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Wastewater Characterization

Table 4.1 shows the results for each parameter through in-situ and ex-situ analysis of wastewater. All the readings of COD, BOD_5, and SS of fish cracker's wastewater exhibited the largest difference from the set EQA standard, with 9612 mg/L of COD which had far exceeded the effluent standard B. Also, the values of AN and SS of wastewater were recorded at well above their respective standard B. Not to mention the BOD value was greatly over the range of standard B as well while only pH value of wastewater was in the acceptable range.

Table 4.1: Water Quality Results of Fish Cracker's Wastewater

Physio-chemical Parameter	Average Reading	EQA Standard B	Sub-Index for WQI
DO (%)	0.25	-	0
pH	6.71	5.5-9.0	11.82
SS (mg/L)	1018	100	0
AN (mg/L)	65.6	25	0
COD (mg/L)	9612	200	0
BOD_5	2411	50	0
Total WQI			11.82

From the values of the parameter obtained, Water Quality Index value was calculated and the product is 11.82 (refer Appendix A). This value was a serious indication that the wastewater discharged was certainly polluted as it was between the ranges of 0 to 59 of polluted status as stated in the DOE Water Quality Classification based on WQI (refer Appendix A). Therefore, the fish cracker's wastewater can certainly pollute the water and critically harming the ecosystem if it was being channelled directly into the irrigation system without treatment.

4.2   Characteristics of Adsorbent

The Scanning Electron Microscope Quanta FEG 450 was used to obtain the surface topography of raw rice husk, RHAC before adsorption, and saturated RHAC after adsorption. The SEM used was shown in Appendix A. The micrographs are displayed in Figure 4.1, 4.2, and 4.3 respectively, with various magnification and accelerating voltage. It could be seen at the Figure 4.1 that when the rice husk was raw, its outer shell consisted of substantial amount of tiny dimples with no visible pore of any kind.

(a)   (b)
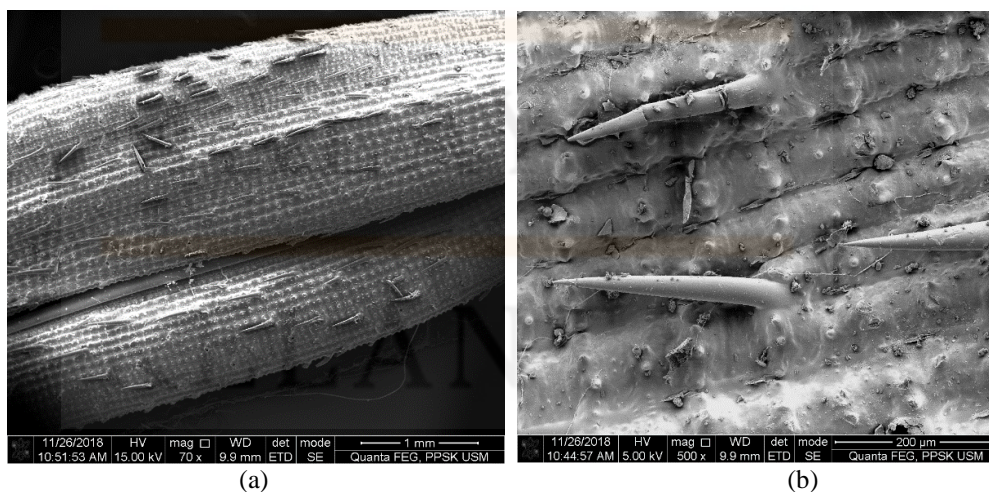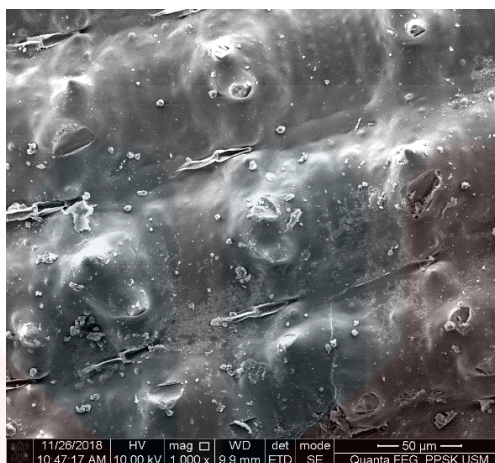
(c)

Figure 4.1: Surface view of raw rice husk with magnification (a) 70x with 15 kV, (b) 500x with 5 kV, and 1000x with 10 kV.

It was during pyrolysis of rice husk, the volatile fragments of cellulose and hemicellulose were removed, causing some of the carbon fraction to lose (Viswanathan, Neel, & Varadarajan, 2009). However, as the carbon fractions were lost, the remaining left consisted of many micropore (Correa Rodriguez, Otto, & Kruse, 2017). After rice husk was transformed into activated carbon in Figure 4.2, its cross-section revealed that pore cavities are present with irregular cracks and crevice on heterogeneous surface that might facilitate the solution flow and enhance the adsorption kinetics.

This rose in surface area could be due to the phosphoric acid permeation and washing process that could had removed the residual tars and unorganized carbon materials at low temperature, and thereby enlarging the pores (Rosas, Bedia, R. M., & Cordero, 2009; Somasundaram, Sekar, Gupta, & Ganesan, 2013) . Another contributing factor could had been when the phosphoric acid reacted with silica, forming water-soluble phosphates that can be washed off easily (Liou & Wu, 2009; Li, et al., 2011; Srinivasakannan, 2003).
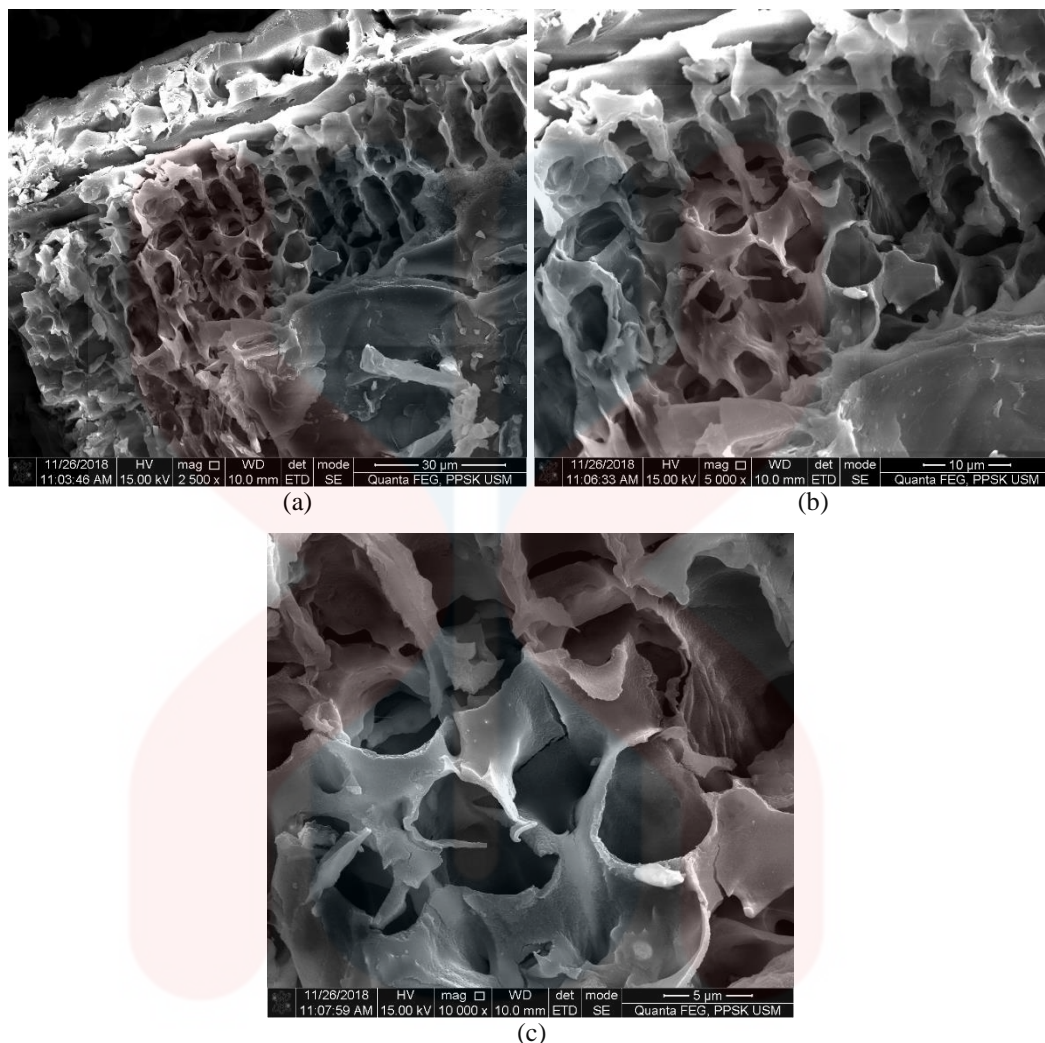
Figure 4.2: Pores on the RHAC before adsorption with magnification (a) 2500x with 15 kV, 5000x with 15 kV (b), and 10 000x with 15 kV (c)

It was indicated that lignin is the principal element which responsible for most of the production of char. Zanzi, Sjostrom, & Bjornbom (2002) studied that higher lignin content of substance produced higher yield of char. Basically, these properties of rice husks were reported to vary according to factors including: geographical location, rice variety, climate, soil chemistry, fertilizer used in paddy growth (Benassi, et al., 2015; Deiana, et al., 2008; Mansary & Ghaly, 1997).

Whereas, the pore cavities became less visible in Figure 4.3 under SEM. This was due to the fact that contaminants, for this case COD, had filled up the pores after the adsorption process. The atoms at the surface of activated carbon have imbalanced forces as compared to atoms inside the activated carbon. Hence, adsorbate molecules attempted to stabilize the imbalance, get attracted to the surface through molecular attraction (Satish, 2003). Not to mention that the samples might not be completely dried as there are noises in images from Figure 4.3. Outgassing caused by present of water in sample led to its atoms to interact with electron beam, partially deflecting the electrons, thus adding to the noise in SEM images (Raspolini, 2017).

(a)   (b)
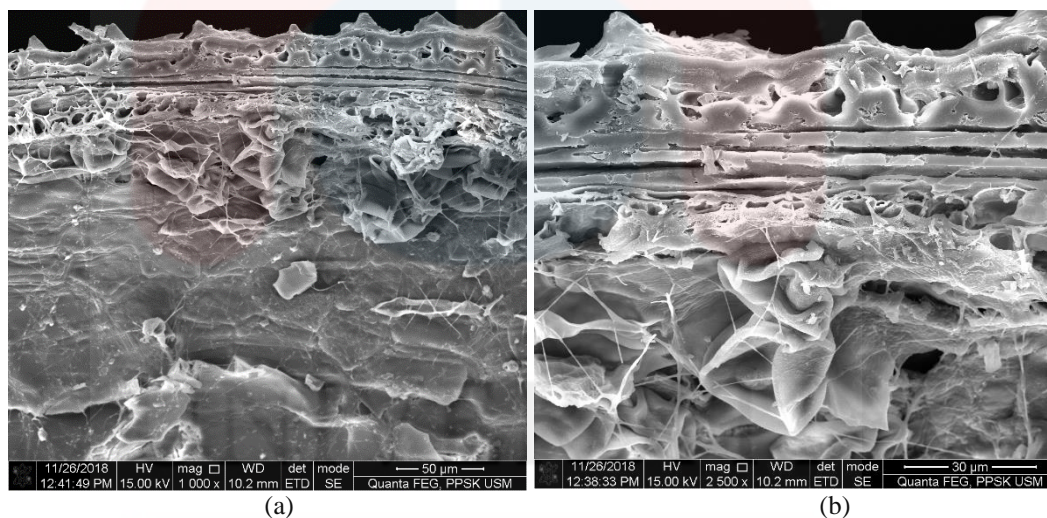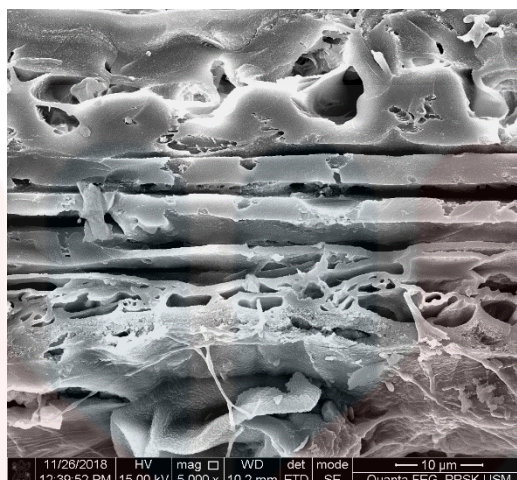
(c)

Figure 4.3: Pores of RHAC after adsorption with magnification (a) 1000x, (b) 2500x, (c) 5000x, with all of the magnifications using the same 15 kV

4.3   Response Surface Methodology

4.3.1   Optimization Using a Box-Behnken Design

The percentage removal of COD in wastewater by using rice husk activated carbon was modelled using the method of RSM, utilizing three reaction parameters: time (h), initial COD concentration (%), and the flow rate (ml/min). The effect of three experimental factors and their interaction were established. Table 4.6 shown the result of 17 experimental designs needed to be tested.

Table 4.2: Experimental design for COD removal percentage.

Run no.	A: Time (h)	B: Flow Rate (ml/min)	C: Initial Concentration (%)	Percentage Removal (%)
1	4.5	7	5.0	16.76
2	1.0	4	5.0	8.97
3	8.0	4	5.0	25.28
4	1.0	4	30.0	8.04
5	4.5	4	17.5	36.92
6	8.0	1	17.5	47.63
7	1.0	7	17.5	72.80
8	4.5	1	5.0	62.90
9	4.5	7	30.0	25.63
10	8.0	4	30.0	17.35
11	4.5	1	30.0	45.19
12	1.0	1	17.5	47.65
13	4.5	4	17.5	33.29
14	4.5	4	17.5	31.76
15	4.5	4	17.5	38.49
16	8	7	17.5	13.50
17	4.5	4	17.5	29.62

Based on the experiment data and Design Expert Version 7.1.6, a regression analysis produced a model with best fit in Equation 4.1. The data that fit variety of models and their subsequent ANOVA demonstrated that a quadratic polynomial model was

characterising the percentage removal of COD appropriately. The significant terms and the equation, in terms of coded factors are showed as follows:

$$Y\ (\%) = 34.62 - 0.74A - 14.93B - 1.34C - 6.94A^2 + 14.02B^2 \\ - 11.02C^2 - 11.12AB - 1.00AC + 6.65BC$$
(Equation 4.1)

Where,

Y = percentage removal of COD (%),

A = initial COD concentration (%),

B = time (hour), and

C = flow rate (ml/min).

A quadratic model was suggested, admitting that its R^2 and adjusted-R^2 (Adj-R^2) value is lower than that of a cubic model. This is by reason of the cubic model is aliased, which signified that each variable's effect that contribute to different signals become imperceptible. For a linear relationship, the R^2 are 0.9590 and Adj-R^2 are 0.9062. It can be seen clearly that the linear relationship is not adequate for the experimental data. Therefore, a quadratic model is suggested.

The mean squares ratio's significance of statistics due to regression and mean square regression residual error are tested using ANOVA. ANOVA is a method of statistics which put the total variation in a set of data into subdivisions. The component parts then linked with particular sources of variation with intention to test hypotheses on the parameter of the model (Rusly & Ibrahim, 2010). The ANOVA result for percentage removal of COD (%) is shown in Table 4.5.

The Model F-value of 18.18 implied the model was significant. There was only a 0.05% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob >

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F" less than 0.0500 indicated model terms were significant. In this case B, AB, BC, A^2, B^2, and C^2 were significant model terms. Values greater than 0.1000 indicated the model terms are not significant.

The "Lack of Fit F-value" of 1.55 implied the Lack of Fit was not significant relative to the pure error. There was a 33.21% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good and it was the model we want to fit. The "Pred R-Squared" of 0.6174 was not as close to the "Adj R-Squared" of 0.9062 as one might normally expect. This might indicate a large block effect or a possible problem with this model and/or data. Things to consider are model reduction, response tranformation, outliers, etc.

Table 4.5: Analysis of variance (ANOVA) for Response Surface Quadratic Model

Source	Sum of Square	Degree of Freedom	Mean Square	F-Value	Prob > F	
Model	3946.22	9	438.47	18.18	0.0005	Significant
A	4.35	1	4.35	0.18	0.6837	
B	1784.43	1	1784.43	74.00	< 0.0001	
C	14.31	1	14.31	0.59	0.4663	
AB	494.62	1	494.62	20.51	0.0027	
AC	4.00	1	4.00	0.17	0.6960	
BC	176.62	1	176.62	7.32	0.0304	
A^2	202.82	1	202.82	8.41	0.0230	
B^2	827.56	1	827.56	34.32	0.0006	
C^2	510.91	1	510.91	21.19	0.0025	
Residual	168.80	7	24.11			
Lack of Fit	90.78	3	30.26	1.55	0.3321	Not significant
Pure Error	78.02	4	19.50			
Cor Total	4115.02	16				
R^2	0.9590					
Adj-R^2	0.9062					

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4.3.2   Effect of Time and Flow Rate

Figure 4.4 indicated that the effect of time and flow rate with constant initial COD concentration of 23.92 mg/L. The run numbers of 2 and 4 both were conducted with the same 1 hour time and 4 ml/min of flow rate but the former's initial concentration was only 5 % while it's 30 % for the latter. Run 2 produced 8.97 % removal percentage and Run 4 only had removal percentage of 8.04 %. It was found that the column performed better at lower flow rate. This could be explained by the longer exhaustion and breakthrough time. As the flow rate raised, it lowered the adsorption capacity for inadequate dwelling time of the adsorbate in the column, causing the diffusion of adsorbate into the pores of adsorbent to lessen, thus the adsorbate left the solution earlier before equilibrium occurred (Patel & Vashi, 2014).
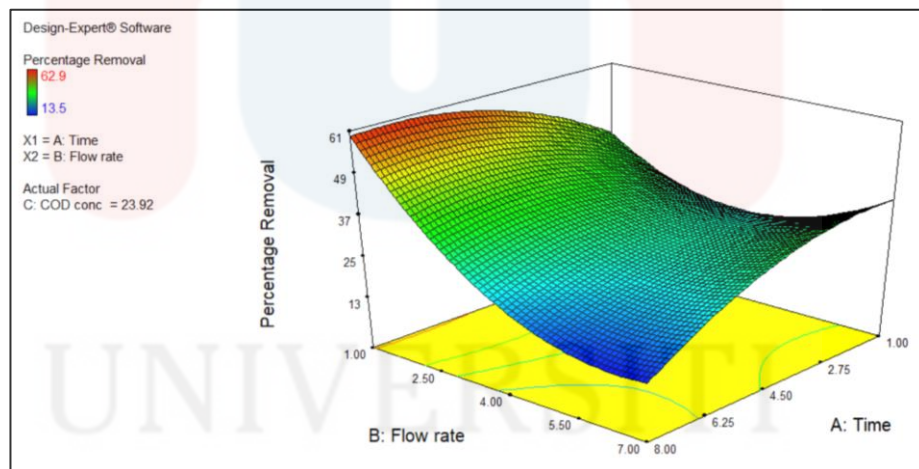
Figure 4.4: Response surface 3D curve showing the effect of time (A) and flow rate (B)

4.3.3   Effect of Time and Initial COD Concentration

Figure 4.5 presented the effect of time and initial COD concentration, with a constant flow rate of 4 ml/min. As there is an escalation in the initial substrate concentration, the COD removal efficiency drops (Vishali & Mullai, 2007). The low removal efficiency was low when the solution is in high concentration might be on

account of the insufficiency of available active sites on the surface, compared to the relatively massive required number of sites. Kannan and Jeya Ganesh (2001) also observed the same pattern in the study done. Also can be noted that removal percentage increased gradually with an increment of the variables of COD concentration and time, to reach a maximum value at around where the initial COD concentration and time were 17.50 % and 4.5 hour respectively. Beyond these two values, removal percentage declined (Pan, et al., 2011).
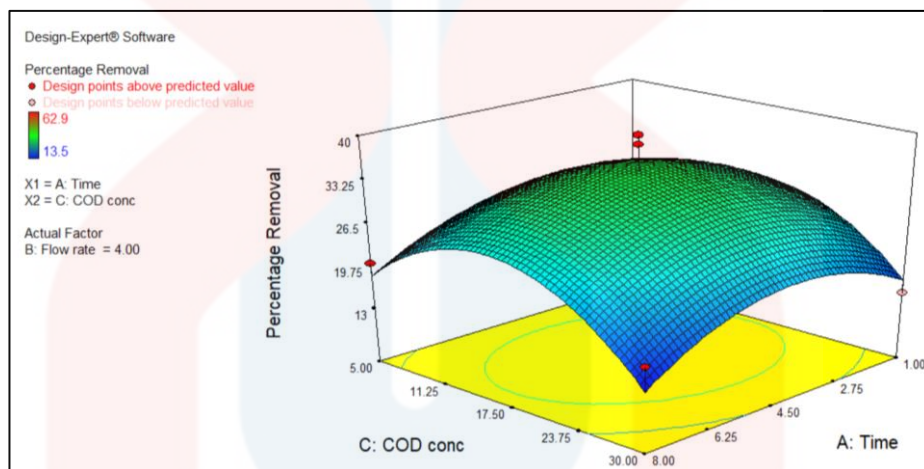
Figure 4.5: Response surface 3D curve showing the effect of time (A) and Initial COD concentration (C)

4.3.4   Effect of Flow Rate and Initial COD Concentration.

At 30 % of initial COD concentration, the removal percentage gave the lowermost result (17.35 %) at flow rate of 4 ml/min while at 1 ml/min with the 17.5 % of initial COD concentration resulted in a considerably high removal percentage of 47.65 %. Both lower flow rate and initial COD concentration could be advantageous in high removal percentage in column study. This confirmed that there were strong physical and chemical interactions between COD and the activated carbons (Pan, et al., 2011).
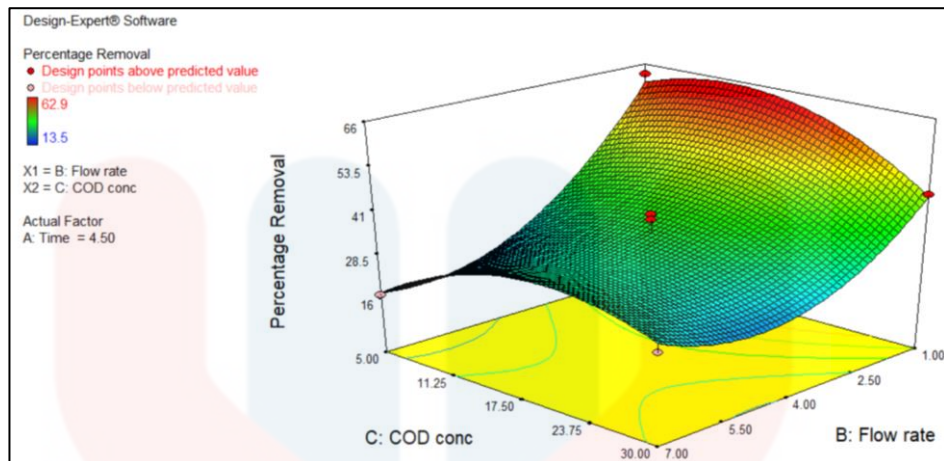
Figure 4.6: Response surface 3D curve showing the effect of flow rate (B) and Initial COD concentration (C)

4.3.5   Suggestion for Optimum Condition

The highest removal percentage of 68.09 % is obtained from run of 1 ml/min flowrate at time of 4.5 hour to treat 5 % of wastewater. Optimizing adsorption process is necessary to obtain highest percentage removal. Therefore, a statistically assisted optimized process was a proper procedure to counter this problem. In this particular, attaining a high degree of conversion was possible using Design Expert Version 7.1.6 and purely seeking the optimum point on the response surface. The determination of optimum point indicates the necessary optimal condition of variables to achieve the highest percentage removal.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1   Conclusion

Response surface methodology with Box-Behnken design were executed to optimize COD removal by rice husk activated carbon. Adsorption reactions were carried out and the time, initial COD concentration, and flow rate were taken as its factors. Under SEM, it was found out that there were many pores developed after carbonisation and activation. The capability of adsorption by RHAC was well explained with aid of RSM. After optimization, it was found that the highest percentage removal was 68.09 % with time of 4.50 hour, flow rate of 1.00 ml/min, and COD concentration of 5.00 %. Based on the data, rice husk activated carbon proved to be a good absorbent on COD.

5.2   Recommendation

There were also few recommendations were suggested in order to improve the adsorption efficiency. Firstly, the size of the rice husk activated carbon should be smaller to increase surface area. Because when it is seen under SEM, there pores are much hidden due to the large size of the raw rice husk before carbonization process. Not to mention that the Surface Area Analyzer could be used to find the surface area and pore volume of sample. Following, the activation temperature should be higher than 600 °C. After passing this range of temperature, the pores of the activated carbon produced could become more widen and deepen to aid more adsorption on COD.

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APPENDIX A

Fish Cracker Processing Shop

Figure A-1: Shop where the fish is process into cracker

Figure A-2: Bucket of fish head that is not used in the processing of cracker.

COD Analysis of Wastewater

Figure A-3: Higher COD concentration gave the solution a greenish colour, while lower concentration caused the solution to be yellow; concentration in between produced orange colour.

Absorbent Characterized by Using SEM

Figure A-4: Quanta FEG 450 with Tungsten Filament

Figure A-5: Gold-coated sample before being scanned in SEM

Wastewater Characterization

A. Water Quality Parameter

Water Quality Parameter	1st Reading	2nd Reading	Average
Temperature (℃)	27.71	27.71	27.71
Conductivity (mS/cm)	2.846	2.842	2.844
TDS (g/L)	1.759	1.757	1.758
Salinity	1.39	1.39	1.39
DO (%)	3.1	3.3	3.2
DO (mg/L)	0.24	0.26	0.25
pH	6.71	6.71	6.71
Turbidity (NTU)	1092	109	1092
SS (mg/L)	1023	1013	1018
AN (mg/L)	61.0	70.2	65.6
COD (mg/L)	9264	9960	9612
BOD$_5$	2498	2324	2411

Calculation

1. BOD value

Equation used to determine BOD$_5$ value is:

$$BOD_5 \ (mg/L) = \frac{(D1 - D2)}{P}, \text{ where}$$

D1 = Initial DO of the sample

D2 = Final DO of the sample after 5 days

P = Decimal volumetric fraction of sample used

Since 10 mL of sample are diluted to 300 mL, then P = 10ml/300ml=0.033

B. Water Quality Index (WQI) Analysis

The equation used to calculate WQI is as below

WQI = (0.22 × SIDO) + (0.19 × SIBOD) + (0.16 × SICOD) + (0.15 × SIAN) +

(0.16 × SISS) + (0.12 × SIpH)

Where the

- SIDO = SubIndex DO (% saturation)
- SIBOD = SubIndex BOD
- SICOD = SubIndex COD
- SIAN = SubIndex NH_3-N
- SISS = SubIndex SS
- SipH = SubIndex pH
- 0 < WQI < 100

Parameter	Data Collection		
	1st Reading	2nd Reading	Average
pH	6.71	6.71	6.71
Total Suspended Solid, TSS (mg/L)	994	1042	1018
Oxygen Demand, DO (%)	3.1	3.3	3.2
Biochemical Oxygen Demand, BOD (mg/L)	2498	2324	2411
Chemical Oxygen Demand, COD (mg/L)	9264	9960	9612
Ammonia Nitrogen, AN (mg/L)	61.0	70.2	65.6

1. SubIndex for COD

SICOD = -1.33x + 99.1	for x ≤ 20
SICOD = $103 \times \exp^{(-0.0157x)}$ - 0.04x	for x > l20

Since the COD value for wastewater was 9612 mg/L which is sat above 120, therefore the equation used is

$$SICOD = 103 \times \exp^{(-0.0157x)} - 0.04x$$
$$= 103 \times \exp^{(-0.0157(9612))} - 0.04(9612)$$
$$= -384.48$$
$$= 0$$

2. SubIndex for DO (In % saturation)

SIDO = 0	for x ≤ 8
SIDO = 100	for x ≤ 92
SIDO = $-0.395 + 0.030x^2 - 0.00020x^3$	for 8 < x < 92

The DO (%) value for wastewater was 3.3 %, which was less than 8, therefore the equation used is

$$SIDO = 0$$

3. SubIndex for BOD

SIBOD = 100.4 - 4.23x	for x ≤ 5
SIBOD = $108 \times \exp^{(-0.055x)}$ - 0.1x	for x > 5

The BOD value of 2411 mg/L is way more 5, so we need to use the equation of

$$SIBOD = 108 \times \exp^{(-0.055x)} - 0.1x$$
$$= 108 \times \exp^{(-0.055(2411))} - 0.1(2411)$$
$$= -241.1$$
$$= 0$$

4. SubIndex for SS

SISS = 97.5 × exp$^{(-0.00676x)}$ + 0.05x	for x ≤ 100
SISS = 71 × exp$^{(-0.0061x)}$ + 0.015x	for 100 < x < 1000
SISS = 0	for x ≥ 1000

Since the SS value was 1018 mg/L, it has just a little bit over 1000, therefore the equation used for calculation is

SISS   = 0

5. SubIndex for pH

SIpH = 17.02 - 17.2x + 5.02x^2	for x < 5.5
SIpH = -242 + 95.5x - 6.67x^2	for 5.5 ≤ x < 7
SIpH = -181 + 82.4x - 6.05x^2	for 7 ≤ x < 8.75
SIpH = 536 - 77.0x + 2.76x^2	for x ≥ 8.75

Since the pH value for wastewater was 6.71, which was in the range of 5.5 ≤ x< 7, so we must use the equation

SIpH   = -242 + 95.5x - 6.67x^2

= -242 + 95.5(6.71) - 6.67(6.71)^2

= 98.49

6. SubIndex for AN

SIAN = 100.5 - 105x	for x ≤ 0.3
SIAN = 94 × exp$^{(-0.573x)}$ – 5 × [x – 2]	for 0.3 < x < 4
SIAN = 0	for x ≥ 4

The value of wastewater AN was 65.6 mg/L which was higher than 4, therefore we use the equation

SIAN = 0

Calculation used to calculate WQI is:

WQI = (0.22 × SIDO) + (0.19 × SIBOD) + (0.16 × SICOD) + (0.15 × SIAN)
       + (0.16 × SISS) + (0.12 × SIpH)

SI Parameter	Value
SIpH	98.49
SISS	0
SIDO	0
SIBOD	0
SICOD	0
SIAN	0

= (0.22 × 0) + (0.19 × 0) + (0.16 × 0) + (0.15 × 0) + (0.16 × 0) + (0.12 × 98.49)

= 0 + 0 + 0 + 0 + 0 + 11.82

= 11.82

Water Quality Status Based On Water Quality Index

Sub Index & Water Quality Index	Index Range		
	Clean	Slightly Polluted	Polluted
Biochemical Oxygen Demand(BOD)	91 - 100	80 - 90	0 - 79
Ammoniacal Nitrogen(NH3-N)	92 - 100	71 - 91	0 - 70
Suspended Solids(SS)	76 - 100	70 - 75	0 - 69
Water Quality Index(WQI)	81 - 100	60 - 80	0 - 59

Acceptable Standard for Discharge of Industrial Effluent

Parameter	Unit	Standard	
		A	B
Temperature	˚C	40	40
pH	-	6.0-9.0	5.5-9.0
BOD_5	mg/L	20	40
Suspended Solids	mg/L	50	100
Ammoniacal Nitrogen	mg/L	10	20
COD	mg/L	80	200

APPENDIX B

1. Preliminary Study

To determine the ranges of time, the flow rate and initial concentration are kept at constant values.

Table 4.2: Preliminary study on time

Time (Hr)	Initial COD concentration (mg/L)	Final COD concentration (mg/L)		Average	Percentage Removal (%)
		1st	2nd		
1	1408	747	655	701.0	50.21
2	1408	683	674	678.5	51.81
4	1642	673	676	674.5	58.92
8	1423	696	700	698.0	50.95
16	1108	643	648	645.5	41.74
24	733	712	694	703.0	4.09

Table 4.3: Preliminary study on initial COD concentration

Initial COD concentration (%)	Initial COD concentration (mg/L)	Final COD concentration (mg/L)		Average	Percentage Removal (%)
		1st	2nd		
5	207	167	161	164.0	20.77
10	471	369	375	372.0	21.02
20	1672	673	676	674.5	58.92
30	1372	1080	1088	1084	21.02

Table 4.4: Preliminary study on flow rate

Flow rate (ml/min)	Initial COD concentration (mg/L)	Final COD concentration (mg/L)		Average	Percentage Removal (%)
		1st	2nd		
1.0	1012	723	724	723.5	28.52
2.5	1168	883	900	891.5	23.67
5.0	1009	722	702	712.0	29.44
7.0	897	796	781	775.0	13.60