NUR ILYANI KHAIRUNNISA BINTI OMAR
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BLACK TEA WASTE AS NATURAL AND ECO-FRIENDLY ADSORBENT FOR METHYLENE BLUE DYE REMOVAL

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by

NUR ILYANI KHAIRUNNISA BINTI OMAR

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DECLARATION

I declare that this thesis entitled “Black Tea Waste as Natural and Eco-Friendly Adsorbent for Methylene Blue Dye Removal” 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.

Signature : ______________________________

Name : ______________________________

Date : ______________________________

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LIST OF SYMBOLS

Al	Aluminium
Fe	Iron
Zn	Zinc
Mn	Manganese
Ca	Calcium
Li	Lithium
CO_2	Carbon dioxide
SO_2	Sulphur dioxide
NO_2	Nitrogen dioxide
NaOH	Sodium hydroxide
HCl	Hydrochloric acid
H_3PO_4	Phosphoric acid
pH	Potential of hydrogen
g	Gram
M	Molar
° C	Degree Celcius
rpm	Revolution per minute

LIST OF ABBREVIATIONS

AC	Activated carbon
BAC	Bead activated carbon
BET	Brunaure, Emmett and Teller
BTW	Black tea waste
COD	Chemical oxygen demand
EAC	Extruded activated carbon
GAC	Granulated activated carbon
MB	Methylene blue
PAC	Powdered activated carbon
STL	Spent tea leaves
UV-Vis	Ultraviolet-Visible spectrophotometry

ABSTRACT

Dyes are used extensively in many industries making the research on colour production more important. Despite that, dyes are important class of pollutant in which it is disposed in water resources and causes major environmental problems due to toxicity and carcinogenic property of dye. However, the dispose of dye into the environment can be treated by several alternatives. Agricultural waste is one of the alternative that is widely used for being a potential adsorbent in dyes removal. Researches and studies has been made and found out that the used of tea waste as adsorbent in the removal of MB dye proved to be more economical compared to other dye removal methods as the method of production is relatively easy. In this study, BTW activated carbon and raw BTW was investigated by comparing both samples using various parameters which were contact time, different concentrations, adsorbent dosage and pH to determine the optimum conditions and effectiveness of the adsorbent. The calibration curve of methylene blue dye was plotted. From the results obtained for BTW activated carbon, the optimum contact time was 50 minutes with the percentage removal of 97.95%, the optimum MB concentrations was 20 mg/L with percentage removal of 96.88%, the optimum adsorbent dosage was 0.8 g with percentage removal of 98.23% whereas the optimum pH of the solution was pH 9 with percentage removal of 99.88%. From the results obtained for raw BTW, the optimum contact time was 50 minutes with percentage removal of 97.23%, the optimum MB concentrations was 20 mg/L with percentage removal of 97.73%, the optimum adsorbent dosage was 0.8 g with percentage removal of 97.30% and for optimum pH of the solution there was no optimum point reached. The experimental data were analysed using percentage removal and efficiency of BTW activated carbon and raw BTW. Based on the study that has been made, BTW activated carbon has the potential to remove and adsorb MB dye that cause environmental problems and health effectively was proven.

ABSTRAK

Pewarna digunakan secara meluas dalam pelbagai industri membuat penyelidikan ke atas pengeluaran warna yang lebih penting. Walaupun begitu, pewarna adalah kelas penting untuk bahan pencemar di mana ia dialirkan ke dalam sumber air dan menyebabkan masalah utama alam sekitar daripada penyebab ketoksikan dan karsinogenik pewarna. Akan tetapi, pembuangan pewarna ke alam sekitar boleh dirawat dengan beberapa alternatif. Sisa pertanian adalah salah satu alternatif yang digunakan secara meluas untuk menjadi penjerap berpotensi dalam penyingkiran pewarna. Penyelidikan dan kajian telah dibuat dan mendapati bahawa penggunaan sisa teh sebagai bahan penjerap dalam penyingkiran pewarna metilena biru terbukti lebih menjimatkan berbanding dengan kaedah pewarna penyingkiran lain sebagai kaedah pengeluaran adalah agak mudah. Dalam kajian ini, BTW karbon yang diaktifkan dan BTW mentah telah diselidik dengan membandingkan kedua-dua sampel menggunakan pelbagai parameter yang merupakan masa yang digunakan, kepekatan yang berbeza, penjerap dos dan pH untuk memastikan keadaan dan keberkesanan bahan penjerap ditahap optimum. Keluk penentu ukuran pewarna biru metilena telah diplotkan. Daripada keputusan yang diperolehi bagi karbon BTW diaktifkan, masa sentuhan optimum adalah 50 minit dengan penyingkiran peratusan 97.95%, kepekatan MB optimum adalah 20 mg/L dengan penyingkiran peratusan 96.88%, penjerap dos yang optimum adalah 0.8 g dengan penyingkiran peratusan daripada 98,23% sedangkan pH optimum penyelesaian ini adalah pH 9 dengan penyingkiran peratusan 99.88%. Daripada keputusan yang diperolehi bagi BTW mentah, masa sentuhan optimum adalah 50 minit dengan penyingkiran peratusan 97,23%, kepekatan MB optimum adalah 20 mg/L dengan penyingkiran peratusan 97.73%, penjerap dos yang optimum adalah 0.8 g dengan penyingkiran peratusan 97.30 % dan bagi pH optimum penyelesaian tidak ada titik optimum yang tercapai. Data eksperimen dianalisis menggunakan peratusan penyingkiran dan kecekapan karbon BTW diaktifkan dan BTW mentah. Berdasarkan kajian yang telah dibuat, karbon diaktifkan BTW mempunyai potensi untuk mengeluarkan dan menjerap MB pewarna yang menyebabkan masalah alam sekitar dan kesihatan berkesan telah terbukti.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Three quarters of the Earth's surface is covered with water but 98 percent is salt water and not suitable for consumption. Less than 1 percent of all the water on Earth is freshwater that available for living things consumption which the humans, plants and animals are scarce in getting freshwater for daily life uses and consumption. Water is considered as one of the most vital natural resources for humans, plants and animals. In addition, it also essential to institutions, agriculture, industries and other purposes. Water is vital for keeping up a satisfactory nourishment supply and a profitable situation for the human population and for different creatures, plants, and organisms around the world. As human populations and economies increase, worldwide freshwater demand has been expanding quickly (Shiklomanov & Rodda, 2003). In addition to threatening the human nourishment supply, water deficiencies extremely reduce biodiversity in both aquatic and terrestrial ecosystems, while water contamination encourages the spread of serious human diseases or infections and reduces water quality (Postel *et al.*, 1996).

Unfortunately, the contributor of worldwide major water pollution is due to increase of uncontrolled disposal of industrial wastewater to the rivers and seas. Quality of water determines the quality of life. Quality of water also is firmly identified with water utilization and to the state of economic improvement. In addition, the procedure that involved in the industries are discharging of effluent containing chemical that may contaminated the environment. The plastics, leather, pharmaceutical, textile, rubber and food industries generally and usually used methylene blue as color. Disposal of polluted dye wastewater without appropriate treatment resulting in various environmental issues and problems such as chemical oxygen demand (COD) by the water body, and an increase in toxicity. There are around 10,000 different commercial dyes and pigments exist and more than 70,000 tonnes of synthetic dyes are produced annually around the world (Owamah *et al.*, 2013).

Several abatement technologies, including adsorption (Mohammed *et al.*, 2011), microbial degradation (Casaletto *et al.*, 2011) and advanced oxidation processes (Zuorro & Lavecchia, 2013), have been carried out for removal of methylene blue dye from textile effluents. Adsorption is one of the most effective methods and activated carbon is the most regularly used adsorbent. Despite its inherent advantages, for example, effectiveness and versatility, carbon adsorption remains costly process. This fact has prompted a developing enthusiasm into the production of low-cost alternatives to activated carbons (Gupta & Suhas, 2009). A low-cost adsorbent is characterized as one which is rich in nature, or is a by-product or waste from industry and requires practically zero capital or cost. In this contribution have been investigated for the suitability of STL to remove methylene blue dyes from aqueous solution. After water, tea is the most widely consumed refreshment in the world, as confirmed by that over 3,000,000 tons of tea leaves produced each year (Wan *et al.*, 2008). Although available in various assortments, for example, green, black or Oolong tea, all tea beverages are obtained from the same fundamental tea (*Camellia sinensis* L.) leaves. Once the beverage has been brewed, STL become a waste that must be disposed. Thus, like other biomass residues, STL represent one of the numerous waste materials destined for landfill and additionally an unused resource (Arvanitoyannis & Varzakas, 2008).

Studies over the last decade have demonstrated that STL can be adequately utilized for the removal of various types of pollutants from water, including arsenic (Murugesan *et al*., 2006), methylene blue (Hameed, 2009) and heavy metal ions such as zinc (Wasewar *et al*., 2009) and lead (Lavecchia *et al*., 2010). However, no report has so far been published on the use of STL to remove methylene blue dye from aqueous solutions.

1.2 Problem Statement

Methylene blue dye are commonly used in textile industries and the wastewater that been discharged to the natural water body system contains residue of the dye and untreated by an appropriate treatment. Besides that, the untreated methylene blue dye can harm the humans and the environment. The most significant impacts to the human being are through fresh water is contamination that can lead to allergic dermatitis, skin irritation, kidney dysfunction, liver, brain, reproductive and central nervous system (Khan *et al.*, 2013). In addition, the discharged of the methylene blue dye without proper treatment to the surrounding or nearby water bodies will pose threat to the aquatic life as it are non-degradable in nature. The methylene blue dye blocks sunlight and oxygen from penetrate into the river or water bodies. Therefore, eutrophication occur and curtails some photo-sensitive chemical reactions necessary to aquatic life (Robinson *et al.,* 2004). Furthermore, some of the methylene blue dyes are toxic even carcinogenic in nature (Boeningo, 1994). Moreover, the existing treatment technology to treat methylene blue dye wastewater is expensive. However, the selected treatment is one of the sustainable and very eco-friendly approach to treat the contaminated wastewater in a proper treatment with low cost.

1.3 Objective

i. To optimize the effect of adsorbent dosage, time, pH and concentration of activated carbon.
ii. To determine the effectiveness, efficiency and make comparison of the parameters between raw materials and activated carbon.

1.4 Significance of Study

The arisen to conduct this research because of the extensive volume of effluent leaving industries that includes dyes and pigments in its procedures to the water bodies without proper treatment. Due to the high cost of carbonaceous adsorbents, such as activated carbon (AC), numerous industries not performed any treatment procedures, thus, putting numerous individuals at risk along the procedure.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption Technology

Worch (2012) reported that, adsorption procedure have played as important and central part in water treatment for a long period but their significance is on the rise with the continuous revelations of new micro-pollutants in the water cycle (pharmaceuticals for instance). In addition, the traditional application in drinking water treatment, other application fields are drawing in expanding interest, for example, wastewater treatment, groundwater remediation, treatment of landfill leachate and others. Adsorption is a stage exchange prepare that is generally used as a part of practice to remove substances from liquid stages (gasses or fluids). It can also be observes as natural procedure in various natural compartments. The most general definition depicts adsorption as an enrichment of chemical species from a liquid stage on the surface of a fluid or a solid. In water treatment, adsorption has been proved as a very productive removal process for a variety of solutes. In this treatment, molecules or ions are removed from the aqueous solution by adsorption onto solid surfaces.

Strong surfaces are portrayed by active, energy-rich sites that can cooperate with solutes in the adjacent fluid stage because of particular electronic and spatial properties. Commonly, the active sites have various energies, or known as, the surface is enthusiastically heterogeneous. In adsorption theory, the solid material that provides the surface for adsorption is alluded to as adsorbent and the species that will be adsorbed are named adsorbate. By changing the properties of the liquid stage, such as, concentration, temperature and pH adsorbed species can be discharged from the surface and transferred back into the liquid stage. This reverse process is referred to as desorption (Worch, 2012).

2.2 Adsorbent

Adsorbent is known and defined as a material that has the ability to extract or separate certain substances which are atoms, ions or molecule from gases, liquids, or solids by causing the substances to adhere or stick to its surface without changing the physical properties of the adsorbent. Activated carbon, silica gel, and zeolites are the materials that are frequently used for this application (Jankowska *et* al., 1991).

2.2.1 Activated Carbon

Activated carbon is also known and called as activated coal, active carbon or activated charcoal. It is a type of carbon that has been prepared to an extremely porous and have a very large accessible surface area for adsorption and chemical reactions. AC generally derived from charcoal. Activated carbon is characterized as a carbonaceous material with an expansive internal surface area and highly developed porous structure resulting from the processing of raw materials under high temperature responses. AC made out of 87% to 97% carbon, however also contains different components relying upon the preparing processing procedure used and raw material it is alluded from. Activated carbon's porous structure permits it to adsorb materials from the fluid and gas stage (Jankowska *et* al., 1991).

Activated carbon is important for numerous of uses, for example, for gas purification, water purification, metal extraction, gold recovery, drug, sewage treatment, air filters in gas mask and filter masks, and filters in compacted air. In addition, activated carbon is very useful for the freshening up of closed spaces, for example, refrigerators and stockrooms, adsorption of ethylene to prevent untimely aging of fruits and vegetables, and discoloration of sugar, nectar, juices, and alcohol. Adequate activation for useful applications may come exclusively from the high surface region, however encourage chemical treatment regularly improves the adsorption capacity of the material (Jankowska *et* al., 1991).

2.3 Classification of Activated Carbon

Activated carbon materials are generally classified based on its preparation procedures or surface characteristics, for example, effective surface area per gram activated carbon, pore diameter and volume. It can also be classified based on its physical characteristics or attributes and these are some of the examples which are Powdered Activated Carbon (PAC), Bead Activated Carbon (BAC), Granulated Activated Carbon (GAC), Extruded Activated Carbons (EAC), Impregnated Carbon, Polymers Coated Activated Carbon and Spherical Activated Carbon (Bansal *et al.*, 1988).

2.3.1 Powdered Activated Carbon (PAC)

It is prepared as powders or fine granules with a size of less than 1.00 mm and the pore diameter is between 15 to 25 µm. That is the reason it has a small diffusion distance and a large ratio of surface area to volume. It is usually added directly and specifically to different procedures such as water treatment (Bansal *et al.*, 1988).

2.3.2 Bead Activated Carbon (BAC)

It is made with a size of 0.35-0.80 from petroleum pitch. It has spherical shape, which is suitable and appropriate for fluidized beds as a part of water filtration. It has high mechanical strength, low pressure drop and low dust content (Bansal *et al*., 1988).

2.3.3 Granulated Activated Carbon (GAC)

It can either be granulated or extruded. It has relatively larger size of particles compared to the powdered activated carbon. It has smaller external surface area/g hence it is suitable for gases and vapours with high diffusion rate. Granulated carbons are used for water treatment, separation of components of stream framework and aeration (Bansal *et al*., 1988).

2.3.4 Extruded Activated Carbons (EAC)

It is made by combining the powdered activated carbon with a binder which fuses together and give them a cylindrical or hollow shape with a diameter of 0.8 to 1.30 mm. It has high mechanical strength, low pressure drop and low dust content which make EAC be the best and preferable for gas-stage processes (Bansal *et al*., 1988).

2.3.5 Impregnated Carbon

It is porous carbons containing several types of the cations such as Al, Fe, Zn, Mn, Ca and Li impregnated by inorganic impregnates, for example, iodine and silver.

It has a bigger area of application both in gas-stage and liquid stage like drinking water treatment and air pollution control (Bansal *et al*., 1988).

2.3.6 Polymers Coated Activated Carbon

In this procedure a porous carbon can be coated with a biocompatible polymer to give a permeable and smooth coat without blocking the pores of the carbon. One of the application areas or territories for this kind of AC is for homo-perfusion which is a therapeutic or medical procedure used to remove toxic substances from a patient's blood (Bansal *et al*., 1988).

2.3.7 Spherical Activated Carbon

In this process, small spherical balls containing pitch is melted in the presence of tetralin or naphthalene and change into spheres or circles (Bansal *et al*., 1988). At that point, the naphtha solution extracts naphthalene and creates a porous structure. Subsequently in the presence of an oxidizing agent containing about 30% Oxygen by volume, the spheres or circles are oxidized in the temperature range of 100 to 400°C. Then, in the presence of ammonia the spheres are heated to introduce nitrogen into spheres. Finally the spheres are activated by CO_2 or steam. The characteristics with the spherical activated carbon are that it adsorb very well SO_2 and NO_2 and it has a high mechanical strength, which makes it suitable to use in high temperature processes (Bansal *et al*., 1988).

2.3.8 Physical Activation

Physical method consist of two stages that is carbonization and followed by activation (Martinez *et al.,* 2003). Carbonization is carried out under temperature of 400°C to 800°C while activation temperature ranges from 800°C to 1100°C (Gottipati, 2012). Carbonization is actually pyrolysis of carbon content raw material in the absence of oxygen with an inert atmosphere (Pradhan, 2011 and Foo, 2010). The mechanism of carbonization proceeds in such way that thermal decomposition takes place to eliminate non-carbon species and to produce fixed carbon mass (Hernandez-Montoya *et al.,* 2010). However, the produced charcoal is not an active product yet with low surface area (Cuhadaroglu & Uygun, 2008). One such disadvantage during the carbonization in physical method is the formation of tar that may block pores resulting in low surface area (Tiwari *et al.,* 2013). From Table 2.1, (Hernandez-Montoya *et al.,* 2010) described the advantages and disadvantages of physical activation of activated carbon.

Table 2.1 Advantages and Disadvantages of Physical Activation of Activated Carbon

Physical Activation	
Advantages	Disadvantages
Avoid incorporating of impurities coming from the activating stage	Activated carbon is obtained in two steps
The process is not corrosive	Higher temperature of activation
A washing stage is not required	Poorer control of porosity
Cheaper	

Source: Hernandez-Montoya *et al.*, 2010

2.3.9 Chemical Activation

Activated carbon chemical method is a single step process in which carbonization and activation takes place simultaneously (Gottipati, 2012). The raw material is impregnated with certain chemicals namely an acid, strong base or salt such as phosphoric acid (H_3PO_4), potassium hydroxide (KOH) or zinc chloride ($ZnCl_2$) (Pradhan, 2011). Impregnation in chemicals is done to destroy the structure of raw materials in low temperatures and then carbonization takes place in which carbon structure is restored and pore structure develops as surface area increases (Cuhadaroglu & Ugyun, 2008). According to Foo (2010), the temperature range used in chemical activation is much lower compared to physical activation. Chemical activation is responsible to reduce formation of taw and other by-products and thus increases the carbon yield (Martinez *et al.*, 2003). Tar formation is reduced in chemical activation because this activation acts as dehydrating agent to minimize the formation of tar (Foo, 2010). An important advantage of chemical activation is that process causes activated carbon with high surface area (Cuhadaroglu *et al.*, 2008). From Table 2.2, (Hernandez-Montoya *et al.*, 2010) described the advantages and disadvantages of chemical activation of activated carbon.

Table 2.2 Advantages and Disadvantages of Chemical Activation of Activated Carbon

Chemical Activation	
Advantages	Disadvantages
Activated carbon obtained in one step	Corrosiveness of the pore
Shorter activation time	Requires a washing stage
Lower temperature of pyrolysis	Inorganic impurities
Better control of textural properties	More expensive
High yield	
Well-developed microporosity	
Narrow microphone size distribution	
Reduction of the mineral matter content	

Source: Hernandez-Montoya *et al.*, 2010

2.4 Regeneration

Spent activated carbon is capable of being recycled by using the thermal and chemical reactivation techniques. Physical adsorption or physisorption is the main mechanism by which impurities can be removed from activated carbon. Physical adsorption is a reversible process. This makes the spent activated carbon capable to be regenerated. Regeneration of activated carbon is based on the fact that carbon is a stable material that is resistant to acidic and basic media and can withstand temperature changes. Activated carbons used in the chemical adsorption process are not suitable for regeneration because the formation of bonds between the carbon and the adsorbates makes the process non-reversible. There are several advantages of regeneration. It reduces the environmental impact of the disposal of the spent activated carbon and reserves the landfills. In some other cases the recovery of the adsorbed species is important and the regeneration of the activated carbon makes it possible. Some common regeneration methods are desorption by hot inert gas, desorption under vacuum and the use of a conventional liquid solvent. The most common method for the recovery of spent activated carbon is by passing a superheated steam flow through the activated carbon bed at a temperature lower than that which was used in the activation process (Shabanzadeh, 2012).

2.5 Black Tea Waste

Camellia Sinesis L. or tea plant is a member of the *Theaceae* family whose leaves are used to produce the ever-popular aromatic beverage, tea. Besides water, tea is the second most consumed fluid worldwide (Hopley *et al.*, 2005). This is simply due to the fact that tea contains many medicinal properties, such as its stimulating and detoxifying properties, improved blood and urine flow and joint-pain reliever (Dufresne & Farnworth, 2000). For the past several thousand years, tea is only harvested for their leaves. However, in more recent years, it is discovered that tea wastes, that consists of woody overgrown shoots are used as an alternative adsorbent for wastewater treatment (Malkoc & Nuhoglu, 2007). Since tea waste is classified as an agricultural waste, which often end up unused, it poses as a very good candidate in replacing the more costly synthetic adsorbents due to its natural abundance, renewability, cost effectiveness and its eco-friendly characteristics (Auta & Hameed, 2011).

2.6 Methylene Blue Dye

Methylene blue is a cationic thiazine dye as shown in Figure 2.1 with the chemical named tetra methyl thionine chloride. It has a characteristic deep blue colour in the oxidized state. But the reduced form is methylene blue is colourless. Methylene blue (MB) is also a cationic dye (Ghaedi *et al*., 2014). Experimented by Orth *et al*. (2000) MB has proven to be very effective in enhancing the percentage of tumor destruction in Photodynamic Cancer Therapy. Furthermore, MB has been the dye of choice for medical professionals in sample tissue staining for colonoscopic polypectomy (Munakata & Uno, 1994). In extend, MB also used in analytical chemistry as a Redox Indicator. In an oxidizing environment, the MB solution maintains a blue hue. However, once a reducing agent is added, the MB will decolorize, leaving a clear, transparent solution, easing differentiations between reducing and oxidizing reactions (Hulanicki *et al*., 1978). The textile industries also greatly benefits from MB as a colouring agent. Even here in Malaysia, the batik industry uses MB as a dye in their products. The problem arises when these dye-polluted effluents are released into the water streams. Even though MB is not highly toxic, the effects if inhaled or consumed may be quite severe, ranging from confusion all the way to vomiting and painful micturition (Hameed *et al*., 2007). In order to solve this problem, wastewaters must be treated before releasing into natural water streams. Furthermore, methylene blue are widely used worldwide for the evaluation of adsorbents as this dye can be 23 viewed as a model for visible pollution and as an indicator for mesoporosity (Bestani *et al*., 2008). Discharge of coloured wastewater without proper treatment can results in numerous problems such as chemical oxygen demand (COD) by the water body, and an increase in toxicity. Methylene blue, with an absorption maximum at 664 nm in visible light region, as shown in Figure 2.2, is usually used in mixed indicators or as a redox indicator. Hence, the amount of MB was measured quantitatively with the absorption of light at 664 nm (Whang *et al*., 2009).

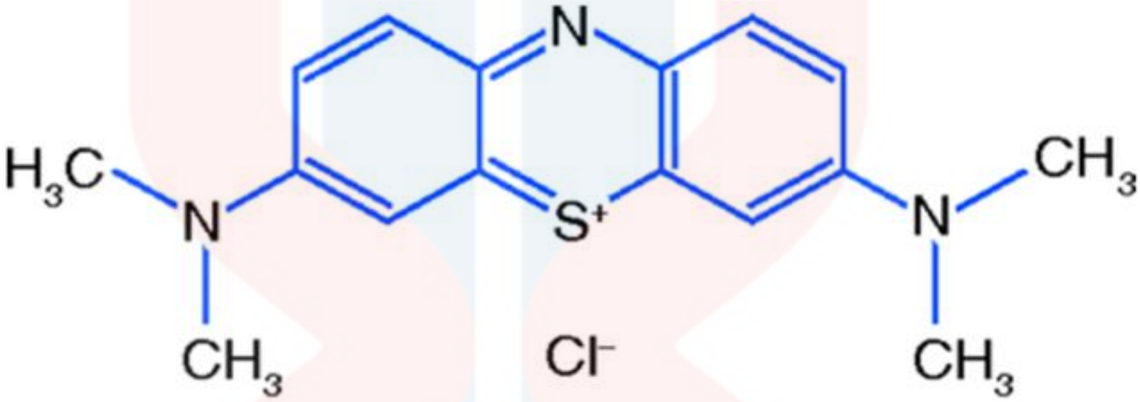

Figure 2.1: Molecular structure scheme of methylene blue or cationic thiazine dye (Vilca-Quispe *et al.*, 2010)

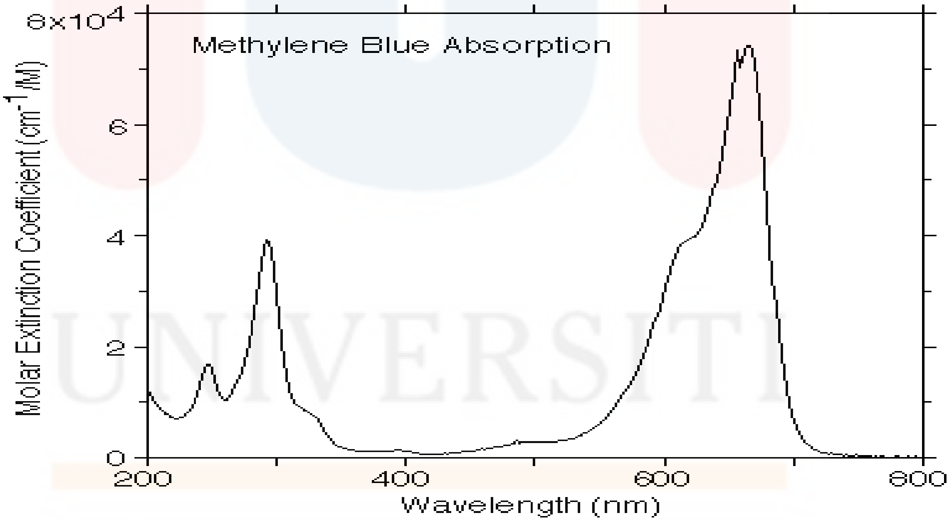

Figure 2.2: UV-Vis spectrum of methylene blue solution, with maximum adsorption at 664 nm (Whang *et al*., 2009).

2.7 Removal of Dye from Other Agricultural Waste

Biomass and other waste materials may also offer an inexpensive and renewable additional source of activated carbon. These waste materials have little or no economic value and often present a disposal problem. Therefore, there is a need to valorize these low-cost by-products. So, their conversion into activated carbon would add economic value, help reduce the cost of waste disposal and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbons. A wide variety of carbons have been prepared from biomass and other wastes, such as date pits, olive stones, furniture, sewage char and tyres, vermiculata plant, bamboo dust, coconut shell, groundnut shell, rice husk and straw, polyvinyldienefluoride fibers, jute fibre, zeolite, coconut husk, oil palm fiber, waste apricot, corncob, coir pith, pitch, olive-seed waste, fir wood, rattan sawdust, bio-plant of *Euphorbia rigida*, vetiver roots, durian shell, oil palm shell, sugars, wheat bran, *Hevea brasiliensis* seed coat, peach stones, almond shell, walnut shell, hazelnut shell and apricot stones and *Rosa canina seeds*.

The excellent ability and economic promise of the activated carbons prepared from biomass exhibited high sorption properties as shown in Table 2.3. Kanan and Sundaram (2010), reported the adsorption capacities of 472.10 mg/g of activated carbons made from straw. However, the adsorption capacities of carbons depend upon the sources of the raw materials used, the history of its preparation and treatment conditions such as pyrolysis temperature and activation time. Many other factors can also affect the adsorption capacity in the same sorption conditions such as surface chemistry (heteroatom content), surface charge and pore structure. A suitable carbon should possess not only a porous texture, but also high surface area. Recently, (Guo *et al.*, 2013) showed that the adsorption does not always increase with surface area. Besides the physical structure, the adsorption capacity of a given carbon is strongly influenced by the chemical nature of the surface. The acid and base character of a carbon also influences the nature of the dye isotherms. The adsorption capacity depends also on the accessibility of the pollutants to the inner surface of the adsorbent, which depends on their sizes. The specific sorption mechanisms through which the adsorption of dyes takes place on these adsorbents are still not clear. This is because adsorption is a complicated process and depends on several interactions such as electrostatic and non-electrostatic (hydrophobic) interactions. Although much has been accomplished in terms of sorption properties and kinetics, much work is still necessary to identify the sorption mechanisms clearly.

Table 2.3 Adsorption capacities for activated carbons derived from agricultural and industrial wastes

Adsorbents	Adsorption capacity (mg/g)
Polyvilnyldienefluoride activated carbon fibres	486
Straw activated carbon	472.10
Activated carbon (molasses/sulphuric acid)	454.20
Activated carbon prepared from coconut husk	435
Vetiver roots activated carbon-H_2O	434.78
Peach stines based activated carbon	423
Oil palm fiber-based activated carbon	412
Mesoporous carbons prepared by using alkaline-treated zeolite	400
Vetiver roots activated carbon P1.5	380
Rice husk activated carbon	375
HCl-treated oil palm shell-based activated carbon	343.50
Rattan sawdust-activated carbon	303.03
Activated carbon prepared from oil palm shell	243.90

Hevea brasiliensis seed coat-activated carbon	227.27
Activated tyre char	277
Jute fiber carbon	225.64
Mesoporous carbons prepared by using acid-treated zeolite	223
Activated furniture (850°C)	200
Chemically activated *Salsola vermiculata* plant	130
Activated sewage char (800°C)	120
Activated carbon prepared from a renewable bio-plant of *Euphorbia rigida*	109.98
Waste apricot-based activated carbon	102
Pyrolysed furniture	80
Coconut husk based activated carbon	66
Pyrolized *Salsola vermiculata* plant (PRSV)	53
Pitch/Y(OiPr)$_3$	52
Pitch/Y(naphthoate)$_3$	49
Activated *Rosa canina* seeds (500°C)	47.2
Pitch	33
Activated olive stones with 40 wt.% $ZnCl_2$ at 873 K in a nitrogen atmosphere	22.1
Activated date pits (900°C)	17.3
Activated olive stones with 40 wt.% $ZnCl_2$ at 873 K	16.1
Activated date pits (500°C)	12.9
Hazelnut shell-activated carbon 750°C	8.82
Coir pith carbon	5.87
Apricot stones-activated carbon 750°C	4.11

Walnut shell-activated carbon 750°C	3.53
Almond shell-activated carbon 750°C	1.33
Fir wood based activated carbon	1.21
Corncob based activated carbon	0.84

Source: Rafatullah *et al.*, 2010

2.8 Wastewater

Wastewater is defined as any water that has been adversely affected in quality by impact from human activities. Wastewater is the liquid waste discharged by domestic residences, business properties, industrial sites and agricultural farms, which often contains some contaminants those results from the mixing of wastewater from various sources. Industrial wastewaters, however, contain contaminants, for example, suspended solids, biodegradable organics, pathogens, heavy metals and more (Peavy *et al.*, 1985). Wastewater contaminants adversely affects the environment, human health and disturb daily activities. These contaminants are non-biodegradable and can spread easily and effortlessly by means of food, water and air. A further case of wastewater, which lies in the scope of this research are dyes and pigments. One of the dyes that often used in textile industries is MB and the discharged of the wastewater to water bodies did not have a proper treatment and affected the aquatic life. Therefore, there are several methods that could be employed when dealing with the treatment of wastewaters.

2.9 UV-Vis Spectrophotometry

Ultraviolet-visible spectroscopy or spectrophotometry which often is abbreviated to UV-Vis is a device used in measuring the adsorption or reflectance spectroscopy for the ultraviolet-visible spectral region. Between different compounds, an obvious difference normally would be the colour, such as green chlorophyll, yellow quinine and then some. Chemicals also varies in colours as the structures change (such as the difference is double bond conjugations), whereby colours for aldehydes and ketones range from bright yellow to deep red. As a general guideline for the visible spectrum, violet ranges from 400-420 nm, indigo from 420-440 nm and yellow from 570-585 nm. Wavelengths lower than 400 nm constitutes the ultraviolet range while a wavelength higher than 800 nm lies in the infrared range (William Reusch, 2013). The theoretical principle for absorbance, as stated in Beer Lambert's Law is absorbance is directly proportional to the path length and concentration of the species. Different molecules absorb radiation of different wavelengths. An absorption spectrum, such as UV-Vis will display a number of adsorption bands corresponding to structural groups within the molecule (Perkampus, 1992). The applications of UV-Vis spectroscopy include quantitative determination of concentrations in analytical chemistry, and also for determination of biological macromolecules (Haiss *et al.*, 2007).

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Chemicals

0.1 M NaOH (sodium hydroxide), 0.1 M HCl (hydrochloric acid), 10g methylene blue dye powder, distilled water, d`eionized water, raw black tea waste and black tea waste activated carbon were used in this study.

3.1.2 Apparatus

Beaker 1000 mL/1L, beaker 500 mL, conical flask 250 mL, measuring cylinder 5 mL and 10 mL, volumetric flask 100 mL, micropipette 1000 µL, spatula, glass rod, crucible, blender, drying oven, furnace, stopwatch, siever 3.0 µm, pH meter, pH litmus paper, aluminium foil, electronic weighing balance, air pump, rubber glove, dropper, ultraviolet-visible spectrophotometry, orbital shaker, cuvette, filter paper and wipe tissue were used in this study.

3.2 Methods

3.2.1 Sample Collection and Preparation of Raw Black Tea Waste

The inexpensive raw BTW was obtained from UMK Jeli cafeteria. Then, the raw BTW was washed with tap water and distilled water for 3 to 4 times to remove the impurities. After that, the raw BTW was dried under the sun for 5 days and in a drying oven for 30 minutes at 105° C. The raw BTW was weighed using electronic weighing balance to get the initial reading and was crushed using blender until it passed through 3.0 µm sieve to get the uniform particle size distribution of adsorbent. Next, the raw BTW powder was taken to weight for 100 g by using electronic weighing balance.

3.2.2 Preparation of Black Tea Waste Activated Carbon

After that, 200 g of raw BTW was placed in the crucible and the process of carbonization was started by placing it in furnace at 750°C for 2 hour and 30 minutes in order to get the raw BTW surface activated. The raw BTW powder which has been activated was prepared.

3.2.3 Preparation of Methylene Blue Dye Stock Solution

1000 mg/L of methylene blue dye solution was prepared. 1 g of methylene blue dye powder was weighed using electronic weighing balance and was added into 1000 mL of distilled water in 1000 mL beaker. After that, the solution was stirred and kept in 1000 mL reagent bottle.

3.2.4 Preparation of Calibration Standard

100 mg/L of methylene blue solution sample was prepared from dilution of 1000 mg/L stock solution. Then, further dilution with distilled water was carried out in order to get 2 mg/L, 4m g/L, 6 mg/L, 8 mg/L and 10 mg/L of methylene blue concentration. After that, the concentration for each dilution ranging from 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L sample was placed into the cuvettes and UV-Vis

spectrophotometer to get the absorbance value. The absorbance value was recorded to get the data. The concentration of the unknown sample was determined by using the developed calibration curve based on absorbance and concentration value.

This is the formula of the dilution of the methylene blue solution from 100 mg/L sample (Beer's Law formula) as mention in Equation 3.1:

$$M_1V_1=M_2V_2 \text{………………..Eqn. 3.1}$$

Where,

M_1 = Concentration in the molarity (moles/Litres) of the concentrated solution

V_1= Volume of the concentrated solution

M_2= Concentration in molarity of the dilute solution (after more solvent has been added)

V_2= Volume of the dilute solution

3.2.5 Optimization of Contact Time

100 mL of methylene blue dye solution with concentration of 20 mg/L was prepared in 5 different conical flasks. Then, 0.6 g of BTW activated carbon was weighed and was added in each 5 different conical flasks. After that, each 5 conical flasks was kept in an orbital shaker at a temperature of 35°C and vibrating at 115 rpm. The contact time for 5 different conical flasks were taken at 20 min, 30 min, 40 min, 50 min and 60 min. Lastly, the samples were collected and the absorbance at 664 nm

was determined using UV-Vis spectrophotometer for every samples. The steps was repeated using raw BTW sample.

3.2.6 Optimization of Concentration of Methylene Blue dye

100 mL of methylene blue dye solution with various concentrations of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L were prepared in each 5 different conical flasks. Then, 0.6 g of BTW activated carbon was weighed and was added in each 5 different conical flasks. After that, each 5 conical flasks were kept in an orbital shaker at a temperature of 35°C and vibrating at 115 rpm for 50 minutes. Lastly, the samples were collected and the absorbance at 664 nm was determined using UV-Vis spectrophotometer for every samples. The steps was repeated using prepared raw BTW sample.

3.2.7 Optimization of Adsorbent Dosage

100 mL of methylene blue dye solution with concentration of 20 mg/L was prepared in each 5 different conical flasks. The various dosage of BTW activated carbon that has been weighed which are 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1 g respectively and was added in 5 different conical flasks. Then, each 5 different conical flasks were put in an orbital shaker at a temperature of 35°C and vibrating at 115rpm for 40 minutes. After that, the samples were collected and the absorbance at 664 nm was determined using UV-Vis spectrophotometer for every samples. The steps was repeated using prepared raw BTW sample.

3.2.8 Optimization of pH

100 mL of Methylene blue dye solution with concentration of 20 mg/L was prepared in each 5 different conical flasks with various pH of 3, 5, 7, 9 and 11. The pH was maintained by adding required amount of 0.1 M NaOH to maintain basic in nature and 0.1 M HCl to maintain acidic in nature. Then, 0.6 g of BTW activated carbon was weighed and was added in each 5 different conical flasks. After that, each 5 different conical flasks were put in an orbital shaker at a temperature of 35°C and vibrating at 115rpm. Thus, the samples were collected and the absorbance at 664 nm was determined using UV-Vis spectrophotometer. The steps was repeated using prepared raw BTW sample.

3.2.9 Dye Wavelength Determination using UV-Vis Analysis

The UV-Vis spectrophotometer analysis is an instrument to measure the wavelength, λ of the dye. Firstly, the UV-Vis spectrophotometer wavelength's was set at fixed wavelength which was 664 nm. Then, the cuvette which was filled with methylene blue dye solution of the calibration was measured and the absorbance value was recorded. Then, the samples of raw BTW and BTW activated carbon that has been filtrated was measured by using UV-Vis spectrophotometer.

The amount of adsorbed methylene blue dye or efficiency (Q_e) was calculated according to the following expression (Zohre *et al.*, 2010) as mention in Equation 3.2:

$$Q_e = \frac{(C_0 - C_t)V}{m_s} \text{…………………..Eqn. 3.2}$$

Where,

c_o = Initial dye concentrations

c_t = Final dye concentrations

V = Volume of the solution

m_s= Mass of adsorbent.

Q_e = Efficiency adsorbent

The following expression was used to calculate the percentage of sorption (removal percentage) (Zohre *et al.*, 2010):

$$\%Sorption = \frac{(C_0 - C_t)}{C_0} \times 100 \text{………………..Eqn. 3.3}$$

Where,

C_0 = Initial concentrations of methylene blue

C_t = Final concentrations of methylene blue

%sorption = Percentage of sorption.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Standard Calibration Curve

In this study, methylene blue calibration curve was constructed using 100 mg/L dye concentration and absorbance readings were taken at 664 nm. 664 nm captures the reading the highest photons are mostly activated in that particular wavelength. Correlation coefficient, $R^2 = 0.9981$ shows the accuracy of the curve. The nearer the value of R^2 to 1, is the better. Absorbance reading increases according to the concentration of dye. The standard calibration curve data was shown in Appendix A. The concentration of methylene blue dye were determined using UV-Vis spectrophotometer. From 100 mg/L solution was diluted to 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L and 10 mg/L. The graph was plotted as shown in Figure 4.1.

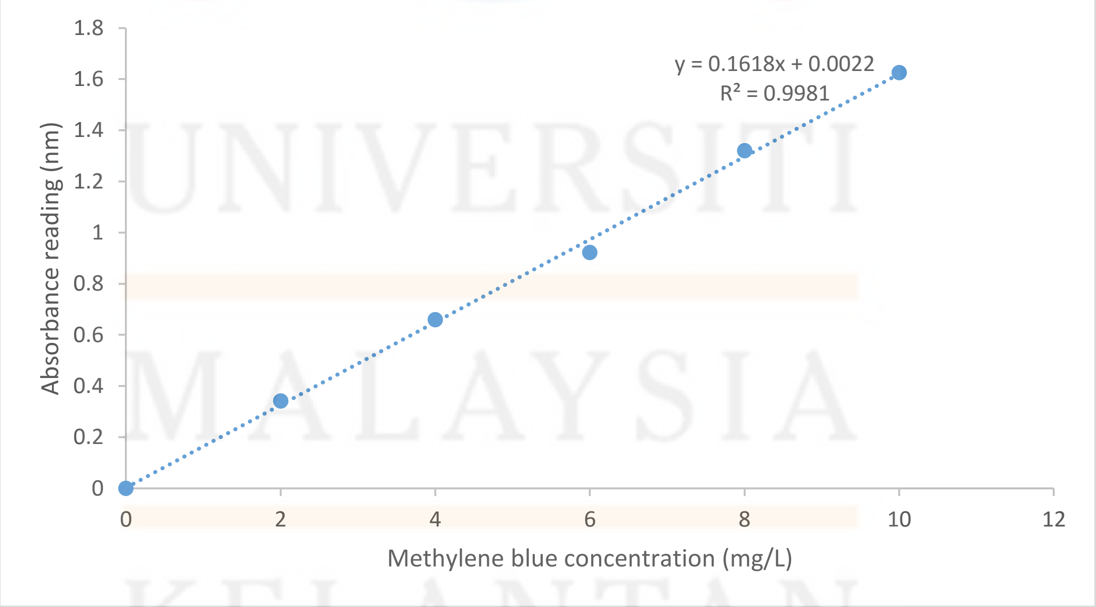

Figure 4.1: Calibration curve for methylene blue dye at 664nm at 35°C temperature

4.2 ADSORPTION STUDIES USING RAW (BTW) AND (BTW) ACTIVATED CARBON SAMPLE

4.2.1 Percentage Removal of Methylene Blue for Different Contact Time using Raw BTW and BTW Activated Carbon Sample

Based on Figure 4.2, the study was based on the uses of raw BTW by reacting with 100 mL and 20 mg/L of methylene blue and it clearly shows that the percentage removal of methylene blue increases with an increase in contact time. The contact time were varied at 20, 30, 40, 50 and 60 minutes. The data of the absorbance readings were shown in Appendix A. the optimization of contact time on percentage removal of methylene blue was shown in Figure 4.2.

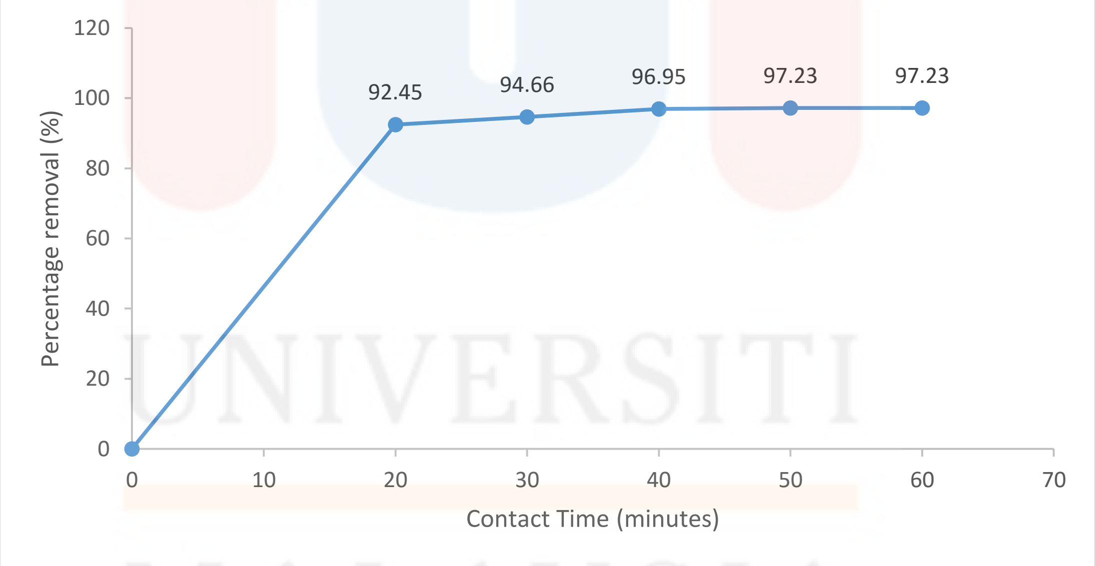

Figure 4.2: Optimization of contact time on removal of methylene blue using raw BTW at 664nm at 35°C.

Based on Figure 4.2, it clearly shows that the percentage of dye removal increased with an increase in contact time. An increase from 92.45% to 97.23% was observed when the time taken increased from 20 minutes to 60 minutes. The percentage of dye removal increased eventually from 20 minutes to 50 minutes which is from 92.45% to 97.23%. At this stage it indicates that the adsorption had completed at 50 minutes which is 97.23%. After 50 minutes to 60 minutes, the percentage removal remain constant which is 97.23% (refer Table A.2).

Thus, the optimum contact time obtained was at 50 minutes with the percentage removal of 97.23% and efficiency adsorbent value at 1.404 mg/g. Equilibrium of adsorption can be observed starting from 50 minutes. From Table A.2, it clearly shows that there was no significant difference between the optimum contact time, 50 minutes with the contact time of 60 minutes. The data for this study was shown in Appendix A.

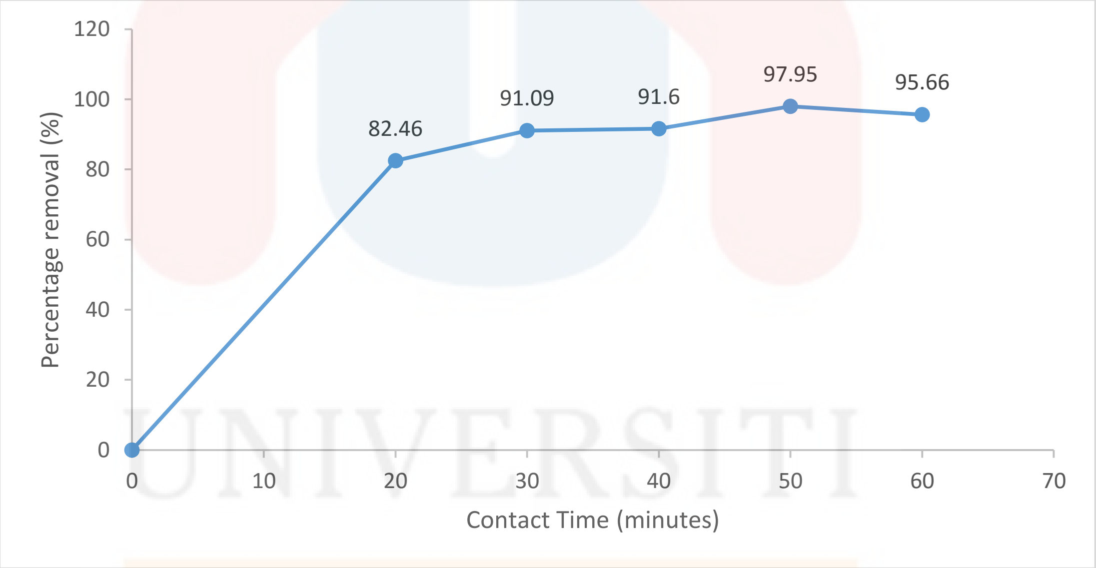

Figure 4.3: Optimization of contact time on removal of methylene blue using BTW activated carbon at 664nm at 35°C temperature.

Based on Figure 4.3, the research was based on BTW activated carbon and it clearly shows that the percentage removal of methylene blue increases with an increase in contact time. The variety of contact time for the study of using BTW activated carbon also the same which was at 20, 30, 40, 50 and 60 minutes. The data of the absorbance readings were shown in Appendix A. the optimization of contact time on percentage removal of methylene blue was shown in Figure 4.3.

Based on Figure 4.3, it clearly illustrates that the percentage of dye removal increased with an increase in time taken. An increase from 82.46% to 95.66% was observed when the time taken increased from 20 minutes to 60 minutes. The percentage of dye removal increased slightly from 20 minutes to 30 minutes which is from 82.46% to 91.09%. After that, there was an eventually increased from 30 minutes to 50 minutes with 91.09% to 97.95%. At this stage it indicates that the adsorption had completed at 50 minutes which is 97.95%. After 50 minutes to 60 minutes, the percentage removal remain constant which is 95.66% with efficiency adsorbent value at 1.414 mg/g (refer Table A.6). Thus, the optimum time taken obtained was at 50 minutes with the percentage removal of 97.95%. Equilibrium of adsorption can be observed starting from 50 minutes. From Table A.6, it clearly shows that there was significant difference between the optimum contact time, 50 minutes with the contact time of 60 minutes. The data for this study was shown in Appendix A.

4.2.2 Percentage Removal of Methylene Blue for Different Concentrations of Methylene Blue using Raw BTW and BTW Activated Carbon Sample

Figure 4.4 was based on raw BTW study, shows the optimization of methylene blue concentration at different dye concentrations which were 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L react with 100 mL volume of MB solution with 0.6 g of adsorbent dosage. The data of this study shown in Appendix A.

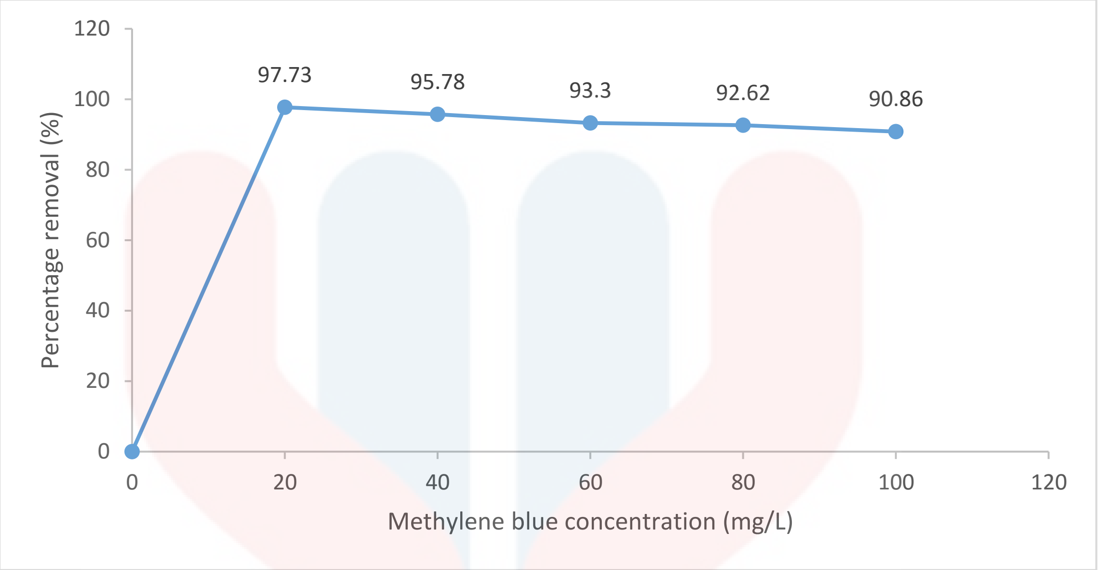

Figure 4.4: Optimization of methylene blue concentration on removal of methylene blue using raw BTW at 664nm at 35°C temperature.

From Figure 4.4, the graph shows that the percentage of dye removal decreased with increased of different methylene blue concentrations using raw BTW. The decreasing from 97.73% to 90.86% was observed when the methylene blue concentrations were increased from 20 to 100 mg/L. The percentage of dye removal decreased eventually from 97.73% to 90.86% which is from 20 mg/L to 100 mg/L. Therefore, the optimum methylene blue concentration obtained was at 20 mg/L with the percentage removal of 97.73%.

The equilibrium point was reached at 20 mg/L with the maximum percentage removal of 97.73%. But the percentage of methylene blue removal started to decrease from 95.78% to 90.86% at 40 mg/L to 100 mg/L. This is because there are no enough active sites available for the dye molecules to bind with resulting in more molecules present in the solution. The available active sites decrease and the amount of methylene blue dye being absorbed reduced. At higher concentration, adsorption sites of activated carbons are saturated, leading to the decrease in the adsorption efficiency (Mohamed *et al.*, 2012). Thus, the optimum methylene blue concentration obtained was at 20 mg/L with percentage removal of 97.73% and efficiency adsorbent value was 1.414 mg/g.

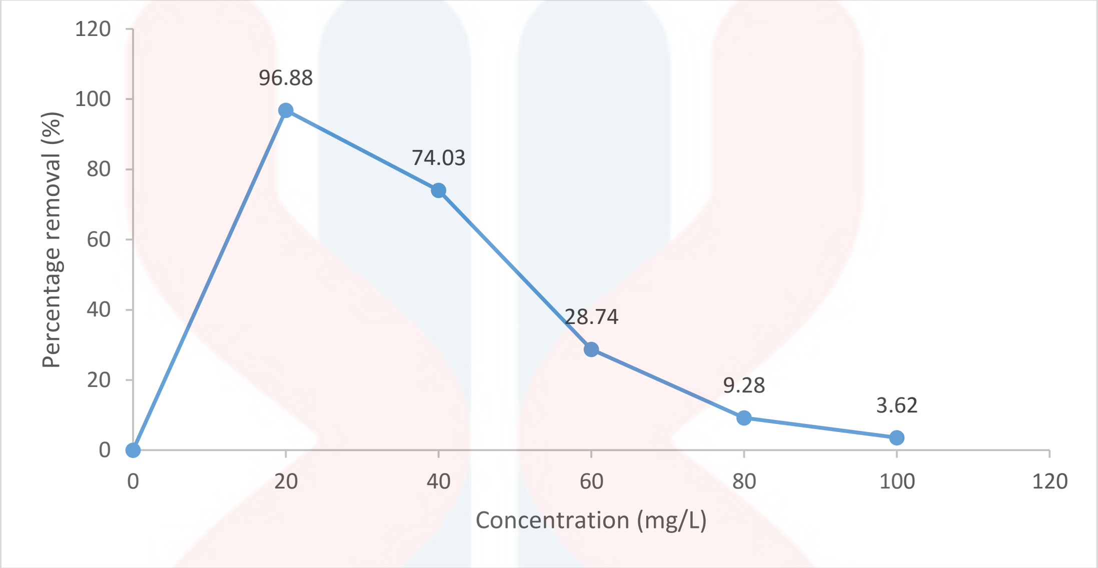

Figure 4.5: Optimization of methylene blue concentration on removal methylene blue using BTW activated carbon at 664nm at 35°C temperature.

Based on the above graph, it shows the study for the optimization of methylene blue concentration at different dye concentrations which are 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L by using BTW activated carbon react with 100 mL of volume MB solution. The data of this study shown in Appendix A and the graph shows inversely proportional based on Figure 4.5.

From Figure 4.5, it illustrates that the percentage of dye removal fluctuated with increased of different methylene blue concentrations. The fluctuation from 96.88% to 3.62% was observed when the methylene blue concentrations were increased from 20 to 100 mg/L. The percentage of dye removal fluctuated from 96.88% to 3.62% which is from 20 mg/L to 100 mg/L. Therefore, the optimum methylene blue concentration obtained was at 20 mg/L with the percentage removal of 96.88%. The equilibrium point was reached at 20 mg/L with the maximum adsorption of 96.88%. But the percentage of methylene blue removal started to decrease from 74.03% to 3.62% at 40 mg/L to 100 mg/L.

This is because there are no enough active sites available for the dye molecules to bind with resulting in more molecules present in the solution. The available active sites decrease and the amount of methylene blue dye being absorbed reduced. At higher concentration, adsorption sites of activated carbons are saturated, leading to the decrease in the adsorption efficiency (Mohamed *et al.,* 2012). Thus, the optimum methylene blue concentration obtained was at 20 mg/L with percentage removal of 96.88% and efficiency adsorbent value was 1.398 mg/g.

4.2.3 Percentage Removal of Methylene Blue for Different Amount of Adsorbent Dosage using Raw BTW and BTW Activated Carbon Sample

To study the optimization of adsorbent dosage, 5 dosages were used to react with 100 mL of 20 mg/L MB which is 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g. The data of the absorbance readings were shown in Appendix A. The optimization of adsorbent dosage on percentage removal of methylene blue using raw BTW was shown in Figure 4.6.

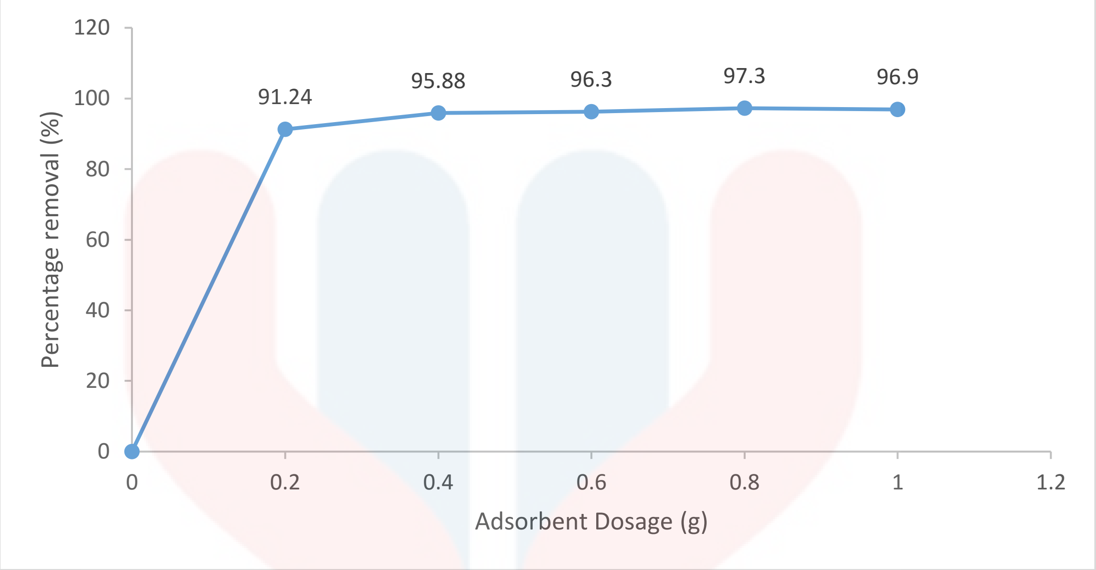

Figure 4.6: Optimization of adsorbent dosage on removal of methylene blue using raw BTW at 664nm at 35°C temperature.

Based on Figure 4.6, it can be said that the percentage of dye removal increased with an increase in adsorbent dosage. An increase from 91.24% to 97.30% was observed when the adsorbent dosages were increased from 0.2 g to 1 g. The percentage of dye removal increased slightly from 0.2 g to 0.4 g which is from 91.24% to 95.88%. The percentage of dye removal increased eventually from 0.4 g to 0.8 g which is from 95.88% to 97.30%. At this stage, it indicates that the adsorption had almost completed at 0.8 g which is 97.30%. There is a little bit difference of decreasing on the percentage of dye removal between 0.8 g to 1 g which is 97.30% to 96.90% (refer Table A.4).

Thus, the optimum adsorbent dosage obtained was at 0.8 g with the percentage removal of 97.30% and efficiency adsorbent value was 0.843 mg/g. The increase in adsorption with adsorbent dosage had contributed to the more adsorbent surface areas and increased the availability of the adsorption sites (Kumar & Ahmad, 2010). This is because the adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing adsorbent dosage (Yener *et al.*, 2006).

From Table A.4, it clearly shows that there was no significance difference between optimum adsorbent dosage which was 0.8 g with 0.6 g and 1 g that were obtained from the adsorption of methylene blue by raw BTW.

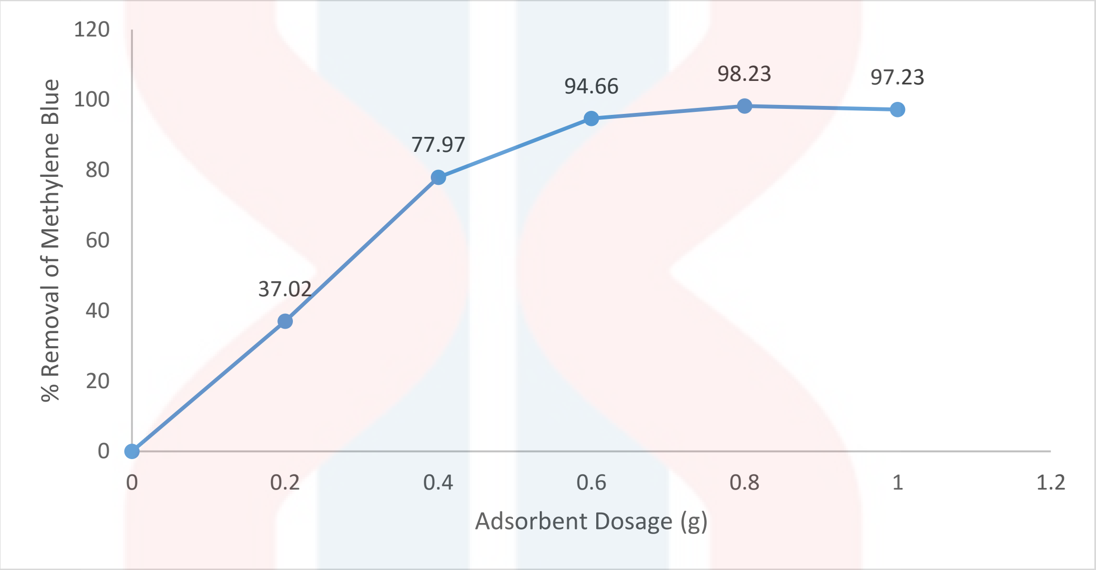

Figure 4.7: Optimization of adsorbent dosage on removal of methylene blue using BTW activated carbon at 664nm at 35°C temperature.

The adsorbent dosages were varied at 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g. The data of the absorbance readings were shown in Appendix A. The optimization of adsorbent dosage on percentage removal of methylene blue was studied by reacting all the dosages with 100 mL of 20 mg/L methylene blue. The graph was shown in Figure 4.7.

Based on Figure 4.7, it clearly shows that the percentage of dye removal increased with an increase in adsorbent dosage. An increase from 37.02% to 97.23% was observed when the adsorbent dosages were increased from 0.2 g to 1 g. The percentage of dye removal increased aggressively from 0.2 g to 0.6 g which is from

37.02% to 94.66%. The percentage of dye removal increased slightly from 0.6 g to 0.8 g which is from 94.66% to 98.37%. At this stage it indicates that the adsorption had almost completed at 0.8 g which is 98.37%. Thus, the optimum adsorbent dosage obtained. The adsorbent dosage reached its equilibrium at 0.8 g. After 0.8 g, the adsorbent dosage for BTW activated carbon decreasing slowly with percentage removal at 97.23%.

From Table A.8, it clearly states that the optimum percentage removal for adsorbent dosage obtained was 0.8 g for activated carbon and the value of efficiency adsorbent was 0.852 mg/g. This explains that adsorption occurs on the exterior surface of adsorbent first before penetrating into inner surface upon reaching equilibrium (Kushwaha *et al.*, 2014).

4.2.4 Percentage Removal of Methylene Blue for Different pH Value using Raw BTW and BTW Activated Carbon Sample

pH is defined as the degree of acidity or basicity of an aqueous solution (Bharathi & Ramesh, 2013). The magnitude of the electrostatic charges which are caused by the ionized dye molecules is control by the pH of the medium. Hence, the rate of adsorption will vary with the pH of an aqueous medium (Onal *et al.*, 2006). Methylene blue dye is a cationic dye. This means it is a dye where its surface charges are positive. pH plays a prominent role as it determines the chemistry of the solution and also binding of the reactive sites. Degree of dye ionization and surface adsorbent property is affected by hydrogen ion concentration (Shaibu *et al.*, 2014).

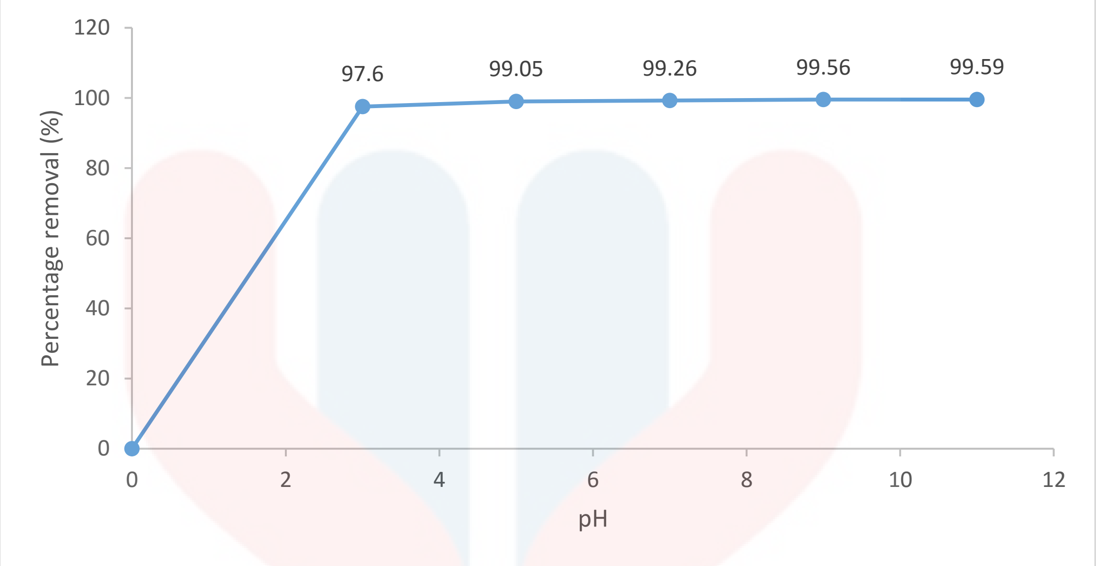

Figure 4.8: Optimization of pH on removal of methylene blue using raw BTW at 664nm at 35°C temperature.

From figure 4.8, the percentage removal of methylene blue increases from 97.60% at pH 3 to 99.59% at pH 11. In this study, there was no optimum pH obtained during the experiment conducted because the adsorption process can still undergo till higher pH. Since the adsorption process of methylene blue dye from wastewater is best from pH ranging in base from. (Khaled *et al.*, 2009). Therefore, the study of pH to adsorb the methylene blue dye can be done for future research ranging start from 12 till 15 and from Table A.5, it clearly shows that there was no optimum and efficiency of adsorbent of pH obtained from pH 3 until pH 11.

For optimization of different pH on removal of methylene blue BTW using activated carbon, different pH were prepared for 5 samples. Volume of methylene blue solution used was 100 mL, 0.6 g of adsorbent dosage and 50 mg/L of MB. The study of optimization of different pH using BTW activated carbon is shown in Figure 4.9. The pattern that can be observed from the graph shows in Figure 4.9 were very consistent. It clearly illustrates that the increase the number of pH the increase in percentage removal as well.

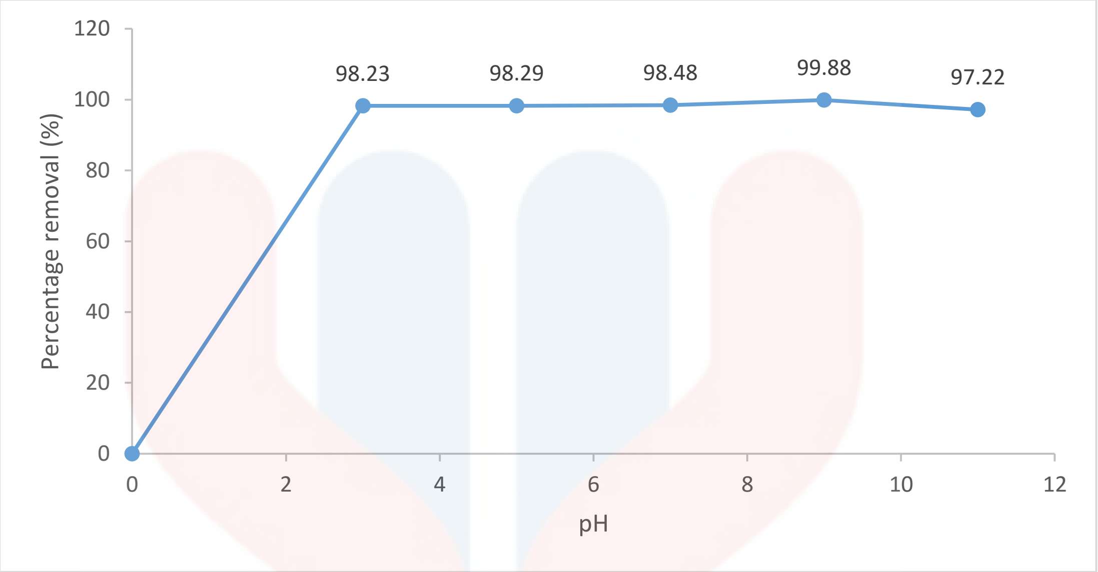

Figure 4.9: Optimization of different pH on removal of methylene blue BTW using activated carbon at 664nm at 35°C temperature.

Based on the graph above for BTW activated carbon, the percentage removal was found to be in the range of 97% to 99%. The removal percentage of MB in pH 3 was 98.23%. After that, there was a slow increase of percentage removal at pH 5 to pH 9 which was 98.29% to 99.88%. At pH 9, the percentage removal is the highest and the maximum adsorption of methylene blue dye occurred at pH 9 as can be seen in the data at Appendix A. The value decrease at pH 11 by obtaining 97.22% removal of MB.

Therefore, the condition which is neutral or almost neutral favours the adsorption. The main concept that can be explain this phenomenon is electrostatic attraction. In pH 7 and pH 8, the electrostatic force generated could have been more than sufficient for effective adsorption to take place or in other words in pH 8, it was a condition with maximum negative charge (Kushwaha *et al.*, 2014). From this study, it can be said that pH 9 was found to be the best pH for effective adsorption to take place as it was near to pH 8. Thus, the optimum pH for removal of MB was at pH 9 and the most efficient adsorbent was at 2.491 mg/g.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

In this research, the study on the adsorption of methylene blue using raw BTW and BTW activated carbon had been carried out. A few parameters that are important in the adsorption study including optimization of contact time, optimization of different concentration of methylene blue, optimization of adsorbent dosage and optimization of pH of the solution had been carried out.

From the results obtained for raw BTW, it clearly shows that the percentage of dye removal increased with an increase in contact time. The optimum contact time obtained was at 50 minutes with 97.23% percentage removal of methylene blue dye. Compared to BTW activated carbon, the result for activated carbon was the same which is 50 minutes but the difference is the percentage removal of methylene blue dye was 97.95%. From the comparison that can be made from raw BTW and BTW activated carbon, the removal using activated carbon is better than raw BTW. It is clearly shows from the significance difference of percentage removal of methylene blue from using both samples.

For the optimization of different concentrations of methylene blue, the optimum concentration of methylene blue from raw BTW obtained was 20 mg/L with percentage removal of methylene blue at 97.73%. For optimization of different concentrations of methylene blue, the optimum concentration of methylene blue by using BTW activated carbon obtained was 20 mg/L with percentage removal of methylene blue at 96.88%. Based on the observation that can be made from the comparison of optimization of different concentrations between raw BTW and BTW activated carbon that raw BTW resulted the best than BTW activated carbon.

In the study of the optimization of adsorbent dosage using raw BTW, the optimum adsorbent dosage obtained was 0.8 g with percentage removal of methylene blue which is 97.30%. For optimization of adsorbent dosage using BTW activated carbon was at 0.8 g with percentage removal of 98.23%. By comparing both samples, BTW activated carbon obtained its maximum adsorption compared to raw BTW.

From the result obtained for raw BTW, it clearly shows that the percentage of methylene blue removal increased with increase in pH. There is no optimum point for pH obtained. There was a slight increase of percentage methylene blue removal by using raw BTW. For BTW activated carbon, the result obtained for the percentage of methylene blue removal was 99.88% at pH 9. It can be observed at the data shown on Table A.9 in Appendix A. Therefore, to compare both samples BTW activated carbon is the most effective adsorbent for optimization of pH.

Last but not least, the objectives of this study to determine the optimum contact time, different concentrations of methylene blue, adsorbent dosage and pH was achieved. Besides that, the comparison of effectiveness and efficiency of both raw BTW and BTW activated carbon also was achieved. As a conclusion, based on final results the best method was by using BTW activated carbon.

5.2 Recommendation for Future Research

This research was able to identify the efficiency of raw BTW and BTW activated carbon. Besides that, through this research, it can be concluded that raw BTW is suitable and can be used to remove dyes especially methylene blue dye. In addition, the BTW activated carbon produced from physical activation is the best to adsorb dyes. However, within the scope of this research, there are a few recommendations that can be taken into future consideration in order to further understand the adsorption of dyes using BTW activated carbon.

Firstly, the structure of adsorbent has to be more porous to improve the adsorption process further. Porosity is one of the main driver for an adsorption to occur. Therefore, surface modification can be applied to enhance the porosity. Besides that, agitation used should be increase the rotational per minute because by increasing the rotation the number of possible collisions between the dye molecules and the adsorbent increase. Thus, physical force moves the dye molecules further into the adsorbent inner layer and this will increase the percentage removal and efficiency of the adsorbent. Other than that, adsorption at a higher temperature is more favourable as it may expand the adsorptive sites and allows more dye molecules to be adsorbed.

Last but not least, future research could focus on the surface area evaluation of BTW of raw material and activated carbon. Brunauere-Emmett-Teller (BET) could be used to identify the external and pore surface area of both raw material and activated carbon of BTW in which this would further support this research by explaining the reason behind high adsorptive capacity of BTW in dye adsorption.

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APPENDIX A

% REMOVAL OF METHYLENE BLUE AND ADSORBENT EFFICIENCY OF BLACK TEA WASTE

Table A.1 Calibration Curve Data

Concentration (mg/L)	Absorbance
0	0
2	0.341
4	0.659
6	0.922
8	1.320
10	1.625

Table A.2 Optimization of contact time on BTW adsorption using raw sample (35°C, 115 rpm)

Contact Time (min)	Absorbance Before Adsorption at 664 (nm)	Absorbance After Adsorption at 664 (nm)	% Removal of Methylene Blue	Adsorbent Efficiency (Q) (mg/g)
0	0	0	0	0
20	1.404	0.108	92.45	1.335
30	1.404	0.077	94.66	1.367
40	1.404	0.045	96.95	1.399
50	1.404	0.041	97.23	1.404
60	1.404	0.041	97.23	1.404
Blank	0	0	0	0

Table A.3 Optimization of concentration of methylene blue dye on BTW adsorption using raw sample (35°C, 115 rpm)

Different Concentration, (mg/L)	Absorbance Before Adsorption at 664 (nm)	Absorbance After Adsorption at 664 (nm)	% Removal of Methylene Blue	Adsorbent Efficiency (Q) (mg/g)
0	0	0	0	0
20	1.404	0.034	97.73	1.411
40	1.873	0.075	95.78	1.852
60	2.149	0.146	93.30	2.063
80	2.480	0.185	92.62	2.364
100	2.735	0.252	90.86	2.557
Blank	0	0	0	0

Table A.4 Optimization of adsorbent dosage on BTW adsorption using raw BTW sample (35°C, 115 rpm)

Amount Dosage (g)	Absorbance Before Adsorption at 664 (nm)	Absorbance After Adsorption at 664 (nm)	% Removal of Methylene Blue	Adsorbent Efficiency (Q) (mg/g)
0	0	0	0	0
0.2	1.404	0.125	91.24	3.952
0.4	1.404	0.060	95.88	2.076
0.6	1.404	0.054	96.30	1.391
0.8	1.404	0.040	97.30	0.843
1.0	1.404	0.045	96.95	1.049
Blank	0	0	0	0

Table A.5 Optimization of pH on BTW adsorption using raw BTW sample (35°C, 115 rpm)

Different pH Value	Absorbance Before Adsorption at 664 (nm)	Absorbance After Adsorption at 664 (nm)	% Removal of Methylene Blue	Adsorbent Efficiency (Q) (mg/g)
0	0	0	0	0
3	2.246	0.056	97.60	2.256
5	2.402	0.025	99.05	2.449
7	2.418	0.020	99.26	2.470
9	2.445	0.013	99.56	2.505
11	2.452	0.012	99.59	2.513
Blank	0	0	0	0

Table A.6 Optimization of contact time on BTW adsorption using activated carbon (35°C, 115 rpm)

Contact Time (min)	Absorbance Before Adsorption at 664 (nm)	Absorbance After Adsorption at 664 (nm)	% Removal of Methylene Blue	Adsorbent Efficiency (Q) (mg/g)
0	0	0	0	0
20	1.404	0.248	82.46	1.191
30	1.404	0.127	91.09	1.315
40	1.404	0.120	91.60	1.323
50	1.404	0.031	97.95	1.414
60	1.404	0.063	95.66	1.381
Blank	0	0	0	0

Table A.7 Optimization of concentrations of methylene blue dye on BTW adsorption using activated carbon (35°C, 115 rpm)

Different Concentration (mg/L)	Absorbance Before Adsorption at 664 (nm)	Absorbance After Adsorption at 664 (nm)	% Removal of Methylene Blue	Adsorbent Efficiency (Q) (mg/g)
0	0	0	0	0
20	1.404	0.046	96.88	1.398
40	1.873	0.488	74.03	1.427
60	2.149	1.532	28.74	0.636
80	2.480	2.250	9.28	0.237
100	2.735	2.636	3.62	0.102
Blank	0	0	0	0

Table A.8 Optimization of adsorbent dosage on BTW adsorption using activated carbon (35°C, 115 rpm)

Different Amount Dosage (g)	Absorbance Before Adsorption at 664 (nm)	Absorbance After Adsorption at 664 (nm)	% Removal of Methylene Blue	Adsorbent Efficiency (Q) (mg/g)
0	0	0	0	0
0.2	1.404	0.885	37.02	1.604
0.4	1.404	0.311	77.97	1.688
0.6	1.404	0.077	94.66	1.367
0.8	1.404	0.025	98.37	0.852
1.0	1.404	0.041	97.23	1.053
Blank	0	0	0	0

Table A.9 Optimization of pH on BTW adsorption using activated carbon (35°C, 115 rpm)

Different pH Value	Absorbance Adsorption at 664 (nm) (before shaking)	Absorbance Adsorption at 664 (nm) (after shaking)	% Removal of Methylene Blue	Adsorbent Efficiency (Q) (mg/g)
0	0	0	0	0
3	2.416	0.045	98.23	2.442
5	2.398	0.043	98.29	2.426
7	2.364	0.038	98.48	2.396
9	2.423	0.005	99.88	2.491
11	2.227	0.064	97.22	2.228
Blank	0	0	0	0

APPENDICES B

RAW MATERIALS

Figure B1 Raw sample of black tea waste

Figure B2 UV-Vis spectrophotometer

Figure B3 Furnace

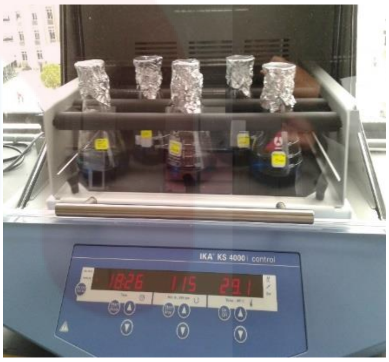

Figure B4 Orbital shaker

Figure B5 Used apparatus