Eggshell as Adsorbent for Bromophenol Blue Dye Removal

by

NIK NABILA SHUHADA BINTI NIK GHAZALI

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THESIS DECLARATION

I declare that this thesis entitled Eggshell as Adsorbent for Bromophenol 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 : Nik Nabila Shuhada Binti Nik Ghazali

Date : 2 January 2017

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LIST OF SYMBOLS AND ABBREVIATION

g	Gram
mg/L	Milligram per liter
ml	Mililiter
M	Molarity
kg/year	Kilogram per year
L	Liter
µm	Micrometer
ppm	Parts per million
rpm	Revolution per minute
H_3PO_4	Phosphoric acid
NaOH	Sodium hydroxide
HCL	Hydrochloric acid
dH_2O	Distilled water
^oC	Degree Celcius
%	Percentage

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ABSTRACT

Water pollution is one of the main pollution in the worldwide due to increase of industry of textile, food and agriculture. The water pollution becomes negative impact to human and ecosystems. As the pollution rise and cost for treatment of water pollution is expensive the worldwide has find solution by using waste from agriculture to produce adsorbent. The adsorbent from agriculture waste was used widely for wastewater treatment because it contains highly removal capacity. Hence, the agriculture waste also low cost and can continuously been investigated. This research attempt to study the adsorption of Bromophenol Blue dyes removal by using eggshell as adsorbent. The objective of the research is to provide activated carbon from eggshell. Hence, the adsorption was determine by using ultra violet visible (uv-vis) of Bromophenol Blue is 465nm. The result shows that the adsorption process increased with the increased of time (10, 20, 30, 40 and 50 minute), the adsorption process decreased with the increased of concentration of dyes (20,40,60,80 and 100mg/L), the adsorption process of adsorbent dosage shows decreased (1,2,3,4 and 5 gram) and pH (2,4,6,7,8 and 10). This results shows that eggshell can be used as a suitable adsorbent for removal dyes.

Kulit telur sebagai penjerap untuk pewarna bromophenol biru disingkir

ABSTRAK

Pencemaran air adalah salah satu pencemaran utama di seluruh dunia disebabkan oleh peningkatan industri tekstil, makanan dan pertanian. Pencemaran air telah memberi kesan negatif kepada manusia dan ekosistem. Pencemaran meningkat dan kos untuk merawat pencemaran air adalah mahal menyebabkan dunia sekarang mencari jalan penyelesaian dengan menggunakan sisa daripada pertanian digunakan sebagai penjerap. Kaedah penjerap telah digunakan secara meluas untuk rawatan air sisa kerana ia mengandungi kapasiti penyingkiran yang sangat tinggi. Disebabkan itu, bahan dari sisa pertanian digunakan kerana kos murah dan boleh dikaji secara berterusan. . Oleh itu, kajian ini dilakukan untuk mengkaji penjerapan pewarna Bromophenol Blue. Objektif kajian ini adalah untuk menyediakan karbon diaktifkan dari kulit telur untuk dijadikan penjerap. Penjerapan ditentukan dengan menggunakan ultra ungu (uv-vis) daripada Bromophenol Blue adalah 465nm. Hasil kajian menunjukkan bahawa proses penjerapan meningkat dengan peningkatan masa (10, 20, 30, 40 dan 50 minit), proses penjerapan menurun dengan peningkatan kepekatan pewarna (20,40,60,80 dan 100mg / L) , proses penjerapan bahan penjerap menunjukkan dos menurun (1,2,3,4 dan 5 gram) dan pH (2,4,6,7,8 dan 10). Keputusan ini menunjukkan bahawa kulit telur boleh digunakan sebagai bahan penjerap untuk menyingkir pewarna dalam air sisa buangan.

CHAPTER 1

INTRODUCTION

1.1 Background Of Study

Pollution is one of the processes that making land, water, air and other parts of the environments become polluted and unsuitable for living things to use it. The pollution occurred because of human activities to the natural environments. Nowadays the main problem that concerned people around the world is water pollution. It is because water is one of a basic source of life and regarded as the most essential of natural resources. According to Agarwal (2009), most of the surface of the world is covered by water which is 98% of water is seawater and is unusable for drinking because of the high concentration of salt. While, about 2% of the planet's water is fresh, but 1.6% is locked up in polar ice caps and glaciers. Another 0.36% is found underground in aquifers and wells. Meanwhile, only about 0.036% of the planet's total water supply is accessible in lakes and rivers (Lee, 2012).

Water pollution occurred when chemicals or any dangerous foreign substances are introduced to water including chemicals, sewage, pesticides and fertilizers from agricultural runoff or metals like lead or mercury (Jodeh *et al.*, 2016). The clean environments need to maintain for the survival of aquatic and terrestrial lives including human beings is in critical condition and it increasing concern to the environmentalist. The water pollution might be caused by several of agents such as heavy metals, rubbish, leftover food and dyes. Among the list of agents, heavy metals and dyes are stated as main cause for environment harmful and serious health problem to the living thing in the world (Ali *et al.*, 2012).

The discharge of textile effluents to the water bodies has raised much concern because of potential health hazards associated with the entry of toxic components into the food chains of humans and animals. Synthetic dyes are extensively used for dyeing and printing in a variety of industries (Bhoi *et al.,* 2010). The removal of colour from textile effluents has targeted attention over the last few years, not only because of its toxicity, but mainly due to its visibility.

Conventional treatment facilities are often unable to remove certain forms of colour, particularly those arising from reactive dyes as a result of their high solubility and low biodegradability thus methods for decolourizing textile effluents are on the horizon (Vijayaraghavan *et al.,* 2009). Dyes are widely used in industries such as textiles, rubber, plastics, printing, leather, cosmetics, to colour their products. As a result, dyes generate a considerable amount of coloured wastewater. Among various industries, textiles industry ranks first in usage of dyes for coloration of fabric. The total dye consumption of textile industry worldwide is in excess of 107kg/year and estimated 90% of this ends up on fabrics (Singla *et al.*, 2016). Consequently, 1000 tones/year or more of dyes are discharged into waste streams by the textile industry worldwide (Singla *et al.*, 2016).

On the other hand, the dye that was charge into stream and river will cause negative impacts to aquatic life and economy. It is because population of aquatic life will be decrease due to light cannot penetrate to the bottom of oceans. Economy will be affect because the fisherman cannot goes to oceans to catch the fish to supplies to customers. The economy also will decrease because the cost of treatment for contaminated water is expensive. People do not care about the negative impact to the environment and do not think the issues related to the wastewater are responsible of communities.

There are three main methods used for wastewater treatment to remove dyes which is physicochemical, chemical and biological methods. According to Jodeh *et al*., (2016) due to proof of efficiency in the removal of pollutants, adsorption has gained favour in recent years. The adsorption is well known as a low cost of physical and chemical method for dyes removal.

The efficiency of adsorption process depends on the physical and chemical properties of the adsorbents and adsorbate. Adsorbent selectivity is based on the adsorption capacity, surface area, availability and total cost. Various adsorbents was used such as commercial activated carbon, mineral, clay, agricultural solid wastes and agricultural solid waste based activated carbon have been used in the removal of dyes from wastewater (Singla *et al.*, 2016). Activated carbon like many other removal dye treatments is well suited for one particular waste system and ineffective in another. The carbon also has to be reactivated otherwise disposal of the concentrates has to be considered (Robinson *et al.*, 2001). The activated carbon that based on agricultural waste is more effective, low cost, green technology and eco-friendly for the environment (Bhaumik *et al.*, 2012). This treatment can reduce the waste and not harmful for human health. Through this treatment, the waste agricultural was introduced as adsorbent material for dyes removal.

Eggshells are expected to be a good adsorbent because it contains amino acid and has a cellulosic structure (Bhaumik *et al.*, 2012). The large amount of eggshells can be used to another purpose because of its enrichment of carbonate materials. The chemical composition of eggshell are 94% calcium carbonate, 1% magnesium carbonate, 1 % calcium phosphate and 4 % organic material, as well as the porous nature of eggshell structure are 7000-17000 pores (William and Owen, 1995) makes it an attractive material to serve as an adsorbent agent. Eggshell was choosing as adsorbent because of it low cost and ease of regeneration. By this research, the effectiveness of eggshell for adsorbent of dyes removal and the optimization of contact of time, concentration of dyes, dosage and pH will be determine.

1.2 Problem Statement

Nowadays, water has become a threat to environment. This is because, the population of people growth rapidly among the years which is demand of various industry become high and disposal of waste throw in water without treatment. The demand from human and development make the three industries (food industry, chemical industry and textile industry) activities growing rapidly without realise the effect of pollution to environment and human.

The industrial activities are increase rapidly and it uncontrolled amount are led to the rivers. The disposal of industrial water and wastewater is a bigger problem to the world. Hence, the dumping site of wastewater from industry will be destroying the sustainable development approach. Pure water normally is colourless but water in nature often coloured by foreign substances. Highly colour water is unsuitable for laundry, dying, paper making, dairy production and other industries.

Thus the colour in water affects its marketability for both domestic and industrial use (Peavy, 1986). It consequently will be cause polluted and harm to all biotic living and environment. The biotic living population and habitat will loss through this problem. The human will also be affected from water pollution issues. This is because people did not get clean water for daily life such drink, cook and wash. The oceans, rivers and seas will be polluted and make the tourist do not want to visit Malaysia.

To prevent the water pollution problem become more serious, the researchers and scientists come out with idea of using agriculture waste as adsorbent. Recently, various low-cost adsorbents derived from agriculture waste, industrial by-products or natural materials have been intensively investigated. According to Kumar, *et al* (2013), the eggshells from egg breaking operations constitute significant waste disposal problems for the food industry, the development of value added by products from this waste is to be welcome. The egg processing industry is very competitive with low profit due to global competition and cheap imports. The costs associated with the eggshell disposal on landfill sites are significant and expected to continue increasing as landfill taxes increase.

1.3 Objectives

The aim of this research is to:

- Produce Activated Carbon from eggshell
- Optimize four parameters which are contact of time between adsorbent and dye, concentration of dyes, dosage of adsorbent and pH level towards the effectiveness of the eggshell as the adsorbent.
- To determine the efficiency of adsorbent by using eggshell for Bromophenol Blue dye removal.

1.4 Significance Of Study

The optimization and efficiency of eggshell as adsorbent will be determine to provide the benefit of eggshell and replacing costly adsorbent.

CHAPTER 2

LITERATURE REVIEW

2. 1 Bromophenol Blue

According to Baker (1958) bromophenol blue has recently come into general use as histo-chemical reagent for the recognition of protein. It purpose is to inquire whether a microscopically object that is coloured by Bromophenol blue dye necessarily contain protein. Bromophenol blue usually use as an acid indicator, colour maker and dye. There are various types of application classes for dye and it chemical. The application of different classes of dye and it chemical can be obtained in Table 2.1.

Table 2.1: Application Classes of Dyes and Their Chemical Types (Yasmin, 2004)

Class	Substrate	Method of Application	Chemical types
Acid	Nylon, wool, silk, paper, inks and leather	Usually from neutral to acidic bath	Azo (including premetallized), anthraquinone, tryphenylmethane, azine, xanthene, nitro and nitroso
Basic	Paper, polyacrylonitrile, modified nylon, polyester and inks	Applied from acidic dye baths	Cynanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine and anthraquinone
Reactive	Cotton, wool, silk and nylon	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and Ph	Azo, anthraquinone, phthalocyanine, formazan, oxazine and basic
Direct	Cotton, rayon, paper,leather and nylon	Applied from neutral or slightly alkaline baths containing additional electrolyte	Azo, phthalocyanine, stilbene and oxazine
Disperse	Polyester, polyamide, acetate, acrylic and plastics	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye maybe padded on cloth and baked on or thermo fixed.	Azo, anthraquinone, styryl, nitro and benzodifuranone.
Solvent	Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils and waxes	Dissolution in the substrate	Azo, triphenylmethane, anthraquinone, and phthalocyanin
Sulphur	Cotton and rayon	Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fiber	Indeterminate structures

The Bromophenol blue dye will be adsorbs red light most strongly and transmits to blue light when it achieve neutral pH and when the blue light at low pH, it will adsorbs ultra violet visible. The ultra violet visible for Bromophenol blue dye is 465nm. Bromophenol blue also has characteristics of green red colour that apparent as shift colour with depends on the concentration or path length through the solution is observed. There are various colour classes of dye and each of classes has disadvantage. Table 2.2 shows the disadvantage of different dyes classes.

Dye class	**Disadvantages**
Azo groups	Their reductive cleavage of azo linkages is responsible for the formation of toxic amines in the effluent
Anthraquinone-based dye	It is most resistant to degradation due to their fused aromatic ring structure and thus remains coloured for a longer time in wastewater
Basic dyes	It has high brilliance and intensity of colours and is highly visible even in a low concentration

Table 2.2: Disadvantage of different dye class (Yasmin, 2004)

Without any pH adjustment the Bromophenol blue can dissolved in water and this phenomenon is called as dichromatic colour. From this phenomenon, it proved that the Bromophenol blue dye has the largest change in colour appearance parameters when the thickness or concentration of observed sample increase or decrease. It is well known that bromophenol blue is one of a powerful acid dye and it capable for making direct links with basic groups in tissues constituents (Baker, 1958)

Based on Baker (1958) the bromophenol blue is an acid phthalein dye that is commonly used as pH indicator and will be used for colouring proteins in paper-electrophoresis. According to Columbia Chemical Industries (2013), the Bromophenol blue dyes need to handle with care. This is because it can cause eye irritation, harmful if inhaled, absorbed through skin and harmful if swallowed. It can cause respiratory tract irritation and causes skin irritation. The bromophenol blue dye also known as tetrabromophenolsulfonphthalein ($C_{19}H_{10}Br_4O_5S$). The structure of bromophenol blue dye is shown in figure 2.1 as follow:

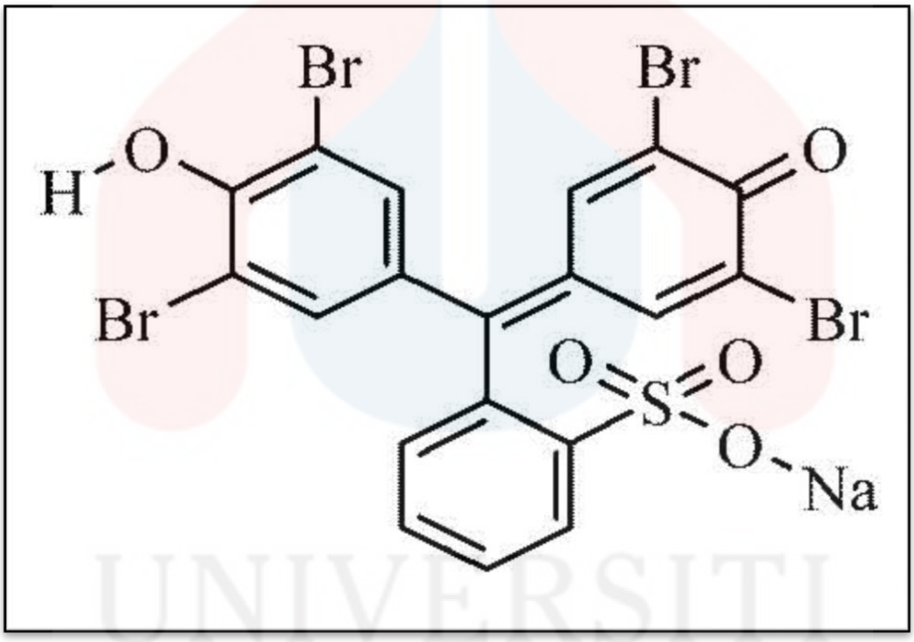

Figure 2.1: Structure of Bromophenol Blue Dye (Source: Sigma,201

2.2 Treatment of Dyes

Nowadays, the public has become more sensitive towards the protection of the environment and general awareness has now increased about the potential adverse effects of industrial effluents contaminate with various pollutants, including dyes on the environment (Karthik *et al.*. 2014). Dyes are mainly engaged in the textile, food, pharmaceutical, cosmetics, and plastics, photographic and paper industries. Although the rapid industrialization is the best way to achieve economic growth, it affects human health directly and indirectly by escaping wastes into water bodies (Alqaragully, 2014). Unfortunately, most of dyes escape into conventional wastewater treatment process. Though dye effluent escape into water bodies from various sources, textiles plant is classified as the most polluting industrial sector. It is noteworthy that some dyes are highly toxic, mutagenic, carcinogenic and also decrease light penetration, photosynthetic activity, causing oxygen deficiency and limiting downstream beneficial uses such as recreation, drinking water and irrigation (Alqaragully, 2014). It is known that 40,000 different of synthetic dyes and pigments are used industrially while 450,000 tons of dyestuffs are produced worldwide (Zengin *et al.*, 2012). The largest and versatile class of dyes is Azo dye for up to 50% of the annual production (Zollinger, 1987). According to Robinson, (2001), the treatment for removal dyes was divided into three categories which are physical methods, chemical methods and biological methods. Although this treatment was used worldwide it also has it pros and contras.

From the three treatments, based on Karthik, *et al.* (2014), biological process is cheaper than other methods. When compared to chemical methods, for biological process investment cost is 5-20 times less and operating costs are 3-10 times less than chemical methods (Karthik, *et al*., 2014). It is because biological treatment uses biodegradation methods such as fungal, biomass and bioremediation that was commonly used in treatment of industrial. This treatment uses many microorganisms such as bacteria, yeasts and fungi that are able to accumulate and degrade different pollutants (Robinson *et al.*, 2001). This application often restricted because of technical constraint. The biological treatment need a large area and constrained by sensitivity towards toxicity of some chemicals and the area must less flexibility in design and operation (Bhattacharyya, 2003).

Various biological, chemical and physical methods are adopted for the treatment of dyes which is discharged as effluent from industries. Different methods are reviewed for the removal of dyes. The large area is requiring for biological treatment and this method still not unsatisfactory in colour eliminated with current biodegradation processes (Karthik *et al.,* 2014). According to different oxygen demand, the biological treatment methods are classified into two treatments which is aerobic and anaerobic treatment. According to Yadav *et al.,* (2012), chemical method which is filtration, precipitation, electro floatation, and electro kinetic coagulation, conventional oxidation methods by oxidizing agents such as ozone, irradiation or electrochemical processes can remove dyes completely. Hence, this method is so expensive and also accumulation of concentrated sludge creates a disposal problem. The chemical are used in this process is excessive chemical that are used generate secondary pollution problem. Recently, new emerging techniques known as advanced oxidation process, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for the pollutant degradation. This new methods are costly and commercially unattractive. This method also has it disadvantage which is the high electrical energy demand and the consumption of chemical reagents (Karthik, *et al.,* 2014).

Meanwhile the physical methods used commonly are membrane filtration process which is nano filtration, reverse osmosis, electro dialysis and adsorption techniques (Karthik *et al.*, 2014). The adsorption technique is one of the most popular methods for removal of dyes that has used worldwide to treat water pollution. Adsorption need proper design to produce a high quality treated effluent in a dye removal. Through this method it will provide an attractive alternative for treatment of contaminated of water. The physical method has use worldwide for adsorption techniques to treat water in textile industry.

2.3 Adsorption

Among various physical method which are adsorption, activated carbon and chemical methods, adsorption has shown better decontamination efficiencies. Adsorption is now viewed as a superior method for wastewater treatment and water reclamation. Recently solid phase extraction technique using organic modified polysiloxane has become known as a powerful tool for separation and enrichment of various inorganic and organic analytic (Jodeh *et al.*, 2016). Adsorption is commonly used in wastewater treatment for removal of toxic or recalcitrant organic pollutants, inorganic pollutants or any substances that will accumulation the water. On the other hand, adsorption is known as polishing step before final discharge in wastewater. Every day, the tonnes of dyes that are released to the oceans, seas and rivers are increased. From this problem, the adsorption processes have been demonstrated as a potential technique for the removal of dyes from wastewater. The adsorption of dyes is a process that transfer dye molecules from bulk solution phase to the surface of the adsorbent. The most common biological adsorbents or material from which the scientist produced in the process of adsorption include activated carbon, coconut shell, tree bark, lignin, shellfish shells, cotton, zeolites, fern and compounds contained number of minerals and microorganisms (Dhananasekaran *et al.*, 2016).

Based on van der Waals interaction (physical adsorption, physisorption) or the character of a chemical process (chemical adsorption, chemisorption) it can shows the result of adsorption. The strength of interaction forces that responsible for adsorptive bonds can be established in Table 2.3. Chemisorption occurs as monolayer which is opposites form physisorption. Hence, the physical adsorption can be compared to the condensation process of the adsorptive. According to its rules, it is a reversible process that occurs at a lower temperature or close to the critical temperature of an adsorbed substance (Dabrowski, 2001). Adsorption is highly effective, economical, promising and is widely applied for scavenging the metal bearing wastewaters. The conventional and non-conventional adsorbents have been used for the heavy metals and dyes removal (Gupta *et al.*, 2009).

Table 2.3: Strength of interaction forces responsible for adsorptive bonds (Klaus Christmann, 2011)

Properties	**Physisorption**	**Chemisorption**
Bonding	Weak, long range Van der Waals interactions (e.g. London dispersion, dipole-dipole)	Strong, short range Chemical bonding involving orbital overlap and charge transfer
Enthalpy	5-50kJ mol^{-1}	40-800kJ mol^{-1}
Saturation	Multilayer	Monolayer
Surface Specificity	No	Yes
Nature	Reversible	Mostly Irreversible

2.4 Activated Carbon

Activated carbon are widely known for their high adsorption capacity however, high operating cost hamper their use in large scale applications. This has prompted many researchers to search for cheaper substitutes such as barley husk, sunflower stalks, peel of cucumis sativa fruit, orange peel and lemon peel were use as adsorbent (Ladhe & Patil, 2014). The raw material that used to produce the activated carbon mostly comes from agriculture waste. The agriculture waste is under the Joint Expert Committee for Food Additives (JECFA). JECFA is an international expert scientific committee that is administered jointly by the Food and Agriculture Organization of the United National and the World Health Organization. JECFA , also known as the re-evaluation of the safety of vegetable carbon when used as a food colouring substances.

Based on JECFA (2003), it stated that the activated carbon is a solid, porous, carbonaceous material prepared by carbonizing and activating organic substances. The raw materials that were used is from agro waste such as sawdust, peat, lignite, coal, cellulose, residues, coconut shells and petroleum coke may be carbonized and activated at high temperature with or without the addition of inorganic salts in a stream of activating gases such as steam or carbon dioxide. JECFA (2003) also stated that carbonaceous matter may be treated with a chemical activating agent such as phosphoric acid or zinc chloride and the mixture carbonized at an elevated temperature followed by removal of the chemical activating agent by water washing. The activated carbon is the most widely used as adsorbent for dye removal because of its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity and very effective for adsorbing cationic, mordant and acid dyes (Carvalho *et al.*, 2011).

The effectiveness of activated carbon is depending on the type of raw materials used and the characteristics of the wastewater. By using massive doses of carbon, the removal rates can be improved. Like many other dye removal treatments, activate carbon is well suited for one particular waste system and ineffective in another. Although activated carbon is used commonly in the worldwide but it the process of activated carbon is expensive. The carbon also has to be reactive otherwise disposal of the concentrates has to be considered. The reactivation process results in 10-15% loss of the sorbent (Ladhe *et al.,* 2014).

Previous study done by Ademiluyi *et al.,* (2009), the more efficient of activated carbon is granular activated carbon. It is because the granular requires an understanding of the adsorption process as well as the pre-calculation of the concentration curves. The researchers come out with production of activated carbon from low cost and renewable precursors. According to Din *et al.,* (2008), it stated that the coconut shell is a potential precursor for the production of activated carbon. It is because it corresponds to 35% of the fruit mass. The coconut shells generates a large amount of waste from it fruit and it currently profit equivalent to 6% of world. Brazil has advantage because it is the fourth largest producer of coconut in the world. Mostly, the characteristics of activated carbon is black, amorphous solid containing major portion of fixed carbon content and other materials such as ash, water vapour and volatile matters in smaller percentage. The large surface area results in a high capacity for absorbing chemicals from gases or liquids. The adsorptive property stems from the extensive internal pore structure that develops during the activation process (Ani, 2004).

2.5 Eggshell

The calcareous egg is produced by all birds and most reptiles. The eggshell has been shaped through evolution to resists physical and pathogen challenges from the external environment, while satisfying the metabolic and nutritional needs of the developing embryo by regulating gas and water exchange and serving as a calcium reservoir (Hincke & Martel, 2013). Based on Salman, *et al*., (2012), eggs are used by enormous number of food manufactures and restaurants and the eggshell as a by-product represents approximately 11% of the whole egg weight is discard as waste.

In Taion, for example the annual generation of eggshell waste from the food processors was estimated to be over $1.3x10^4$ tons from $1.7x10^9$ chicken eggs (Salman *et al.,* 2012). According to Marinamarican (2015), in Malaysia food waste from eggshells is very limited compared to European countries. It also revealed that the dumping site in Malaysia has increased in dangerous rate due to the abandoned of waste of eggshell in dumping site. Because of this concern, the government make a solution to open more of dumping site and it was too costly.

Many researchers have been done to make use of eggshell in different applications such as fertilizers, feed additive and adsorption heavy metals and organic compounds from wastewater (Salman *et al.,* 2012). From previous research that study in eggshell components (Kumar *et al.,* 2013), the eggshell is mainly composed of calcium carbonate 94.03% and it also contains calcite and calcareous soil. Eggshell has a cellulosic structure and also contains amino acids. Because of this component, the eggshell is expected to be a good bio-sorbent and it was reported that large amounts of eggshells are produced in some countries as waste products and disposed in landfills annually. Kumar *et al.,* (2013), also state that the porous nature of eggshell makes it an attractive material to employ as an adsorbent. Each eggshell has been estimated to contain between 7000-17000 pores (William *et al.,* 1995) Table 2.4, shows the type of agriculture waste used as adsorbent.

Table 2.4: Agriculture waste used as adsorbent (Kumar *et al*., 2013)

Low cost adsorbents	Adsorbate	References
Rice husk (water washed)	Cd(II)	Grassi M et al., 2012
Walnut sawdust	Acid green 25 and acid red 183	Grassi M et al., 2012
Rice husk ash	Methylene blue	Grassi M et al., 2012
Jack fruit peel	Methylene blue	Grassi M et al., 2012
Papaya seed	Cr(VI)	Grassi M et al., 2012
Bael fruit shell	Cu	Grassi M et al., 2012
Hazelnut shell	Ni(II)	Grassi M et al., 2012
Sawdust (acid activated)	Lurazol Brown pH (LBP) dye	Talokar AY, 2011
Orange peel	Direct red 23	Grassi M et al., 2012
Bagasse	Chromium	Wan Ngah WS et al., 2008
Peanut husk(treated with Sulfuric acid)	Pb(II)	Rane NM et al., 200
Jute fibres(treated with Reactive Orange 13)	Zn(II)	Rane NM et al., 200
Sugarbeet pulp(treated with Hydrochloric acid)	Cu(II)	Rane NM et al., 200
The lemon, orange and sweet lime skin powder	Cr(VI)	Soto ML, 2008

The porous nature of eggshell makes it an attractive material to be employed as an adsorbent. The eggshell typically consists of ceramic materials which are arranged in a three layered structure, namely the cuticle on the outer surface, a spongy (calcareous) layer and inner lamellar (mammillary) layer (Carvalho *et al.*, 2011). Through this layers it form a matrix composed of protein fibers bonded to calcite (calcium carbonate), which representing more than 90% of the material. The utilization of the eggshell has started over 1970 with the development of several studies aiming at the calcium supplement and other nutrition sources from the albumin, membrane and matrix of the eggshell, which was processed by crushing and miling to obtain fine particles for animal use (Tsai *et al.,* 2006).

2.6 Ultraviolet Visible Spectrophotometer (UV-Vis)

Ultraviolet Visible Spectrophotometr (UV-Vis) is comprise only a small part of the electromagnetic spectrum, which includes such other forms of radiation as radio, infrared (IR), cosmic and X rays. The UV-Vis function is to monitor the relative response of the sample signal to the blank (Tony, 2000). In Figure 2.2, diagram of UV-Vis was shown as below. The components of UV-Vis may not useful for all wavelength ranges. It is because the wavelength ranges is limits components. The UV-Vis was first public at 1979 with name diode-array spectrophotometers and it characteristics were not well-understood. The primer was very well received and many thousands of copies have been distributed. After a few decades, the world is changed with new technologies. The UV-Vis was improved from the previous and produces a new primer. The new UV-Vis is used computer to evaluate data and to read the data about the test. The UV-Vis also has many sources in it. The Uv range, visible range and emission spanning is the important sources to read and record the data.

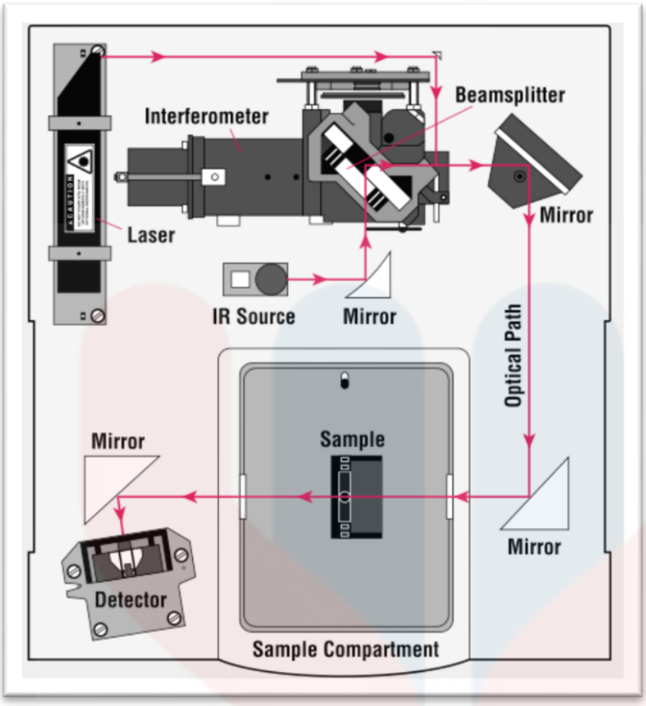

Figure 2.2: Diagram of UV-Vis (Sigma, 2013)

The concentration of Bromophenol blue dye was analysed by using UV-Vis. The wavelength that was obtained to the experiment was 465nm. From the wavelength, it will be benchmark to maximum concentration of Bromophenol blue dye. When, the concentration at higher level and over the benchmark, it no longer behaves independently of one another. The reasons it occur like that because the absorptivity and molar absorptivity is depend on the sample of refractive index. The calibration curve can be done through the analysis of value change for absorptivity and molar absorptivity.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Chemical	Brand	Purity
Bromophenol blue	Merck KCGA, Germany	95%-97%
Phosphoric acid (H_3PO_4)	Sigma, Germany	38%
Hydrochloric acid (HCl)	Sigma, Germany	38%
Sodium hydroxide (NaOH)	Sigma, Germany	47%
Distilled water	RPI	> 95%
Raw material (eggshell)	Gred A	-

3.2 Apparatus

Instrument	Brand	Model
Air pump	-	¾ HP
Crucible	Procelain Crucible	JGC030
Spatula	Ajax Scientific	LA 162-000
Dropper	Katito White	Standard
Filter paper	Grade 1	FPR009
Rubber glove	Latex Glove	SKU:XSA537-19
Aluminium foil	Diamond, USA	25SF
Oven	Panasonic, Japan	MOV-112
Sterile container	Runlab, China	231501-2316
Zip plastic bag	MDS	-
Quartz cuvettes	-	-

Instrument	Brand	Model
Blender	Elba, Italy	ELB-EBLD1552GBL
Sieve (425 um)	Impact, UK	BS410-1:2000
Beaker 1000ml	Schott Duran, Germany	Pyrex style
Conical flask 250ml	Schott Duran, Germany	Pyrex style
Measuring cylinder 10ml	Schott Duran, Germany	Pyrex style
Volumetric flask 100ml	Schott Duran, Germany	Pyrex style
Orbital shaker	AZ-Tech Sinar, Pulau Pinang	SI-600R
Electronic weighing balance	Cimarec,China	B3002-S
Pipette micro meter 100ml	Watson Nexty, Japan	-
pH meter	Hanna, China	pH 213
UV-Vis	PMT	V-760

3.3 Method

3.3.1 Raw material collection and preparation

Eggshell were collected from cafeteria UMK Jeli and washed with distilled water to avoid contamination or any other bacteria that will affect the adsorbent and experiment. After that, the eggshells were dried under sunlight for 8 hours. The dried eggshells were grinded with blender and sieved with sieve 425µm. (Bhaumik *et al.*, 2012).

3.3.2 Preparation of activated carbon

About 50g of eggshell that was blender into powder and sieved was put into beaker 1000ml. The eggshell powder was mixed with phosphoric acid (5ppm) and stir continuously for 30 minutes. After that, the activated eggshell was carbonized in furnace at 500°C for 2 hours. By using hot and cold deionized water, the activated eggshell were washed until it become pH 7 before drying in oven at 100°C for 2 hours. After that, the activated carbon was stored in sterile container before further use. (Abechi *et al*., 2013).

3.3.3 Preparation of bromophenol blue dye stock solution

Stock solution of bromophenol blue dye was prepared by dissolving 0.22g of bromophenol blue powder in 1L distilled water. The required concentration of bromophenol blue solution was prepared by serial dilution of 1000mg/L bromophenol blue stock solution. The 1000mg/L of bromophenol blue stock solution was diluted to get 100mg/L. 10ml of bromophenol blue stock solution were pipetted into the 100ml volumetric flask for 10 times. After that, the distilled water was poured into the volumetric flask until reach the 100ml mark. The stopper was placed in the volumetric flask and it was inverted to mix. (Bhaumik *et al.*, 2012).

3.3.4 Preparation of calibration curve

Preparation for calibration curve was done by dilute the dye solution. About 10ml of bromophenol blue dye solution was taking from stock solution by using micropipette. After that, the distilled water was poured into volumetric flask until the water up to the 100ml mark and the volumetric flask was shaken for 2 minutes. Then, the solution in volumetric flask was put into beaker and the solution was dilute with different concentration (0, 2, 4, 6, 8 and 10 mg/L) to get the calibration curve. From the solution, the 2mg/L was pipette and put into the volumetric flaks and the distilled water were put into the volumetric flask until the water level reach to 100ml. The volumetric flask was shaken for 2 minute and by using dropper the solution was put into cuvette and the reading was analysis with ultra violet visible (uv-vis). After the reading was recorded by uv-vis, the data was used to perform calibration curve. However, the calibration the calibration curve (Figure 4.1) does not reflect on the result due to procedure error in the beginning of the experiment.

3.3.5 Preparation of blank solution

The blank solution of the adsorbent was determined by using 50ml of bromophenol blue dye solution transferred into a series of 100ml conical flask. The flask were then placed into a constant temperature 35 ^{o}C orbital shaker at 300 rpm and shaken for 24 hours. The reading that was obtained from blank solution was used as benchmark for optimization of adsorption. The value of standard pH for blank was 7. The obtained reading that was expected from blank solution is zero. (Bhaumik *et al.*, 2012).

3.3.6 Preparation for effect of concentration on dye adsorption

About 2g eggshell of activated carbon were mixed with 50ml of bromophenol blue solution for different concentrations (0, 20, 40, 60, 80 and 100 mg/L) in beaker 1000ml and the mixtures were agitated 35 ^{o}C at 300 rpm for 30 minutes in orbital shaker. The final reading was analysis by UV-Vis and the step was repeated to the eggshell of raw material experiment. On Figure 3.3 it has shown the step of experimental.

Put 2g eggshell of activated carbon in 5 conical flask and mixed with 50ml of bromophenol blue dye with different concentration (0,20,40,60,80 and 100 mg/L)

↓

Then, the mixture was agitated at 35 ^{o}C at 300 rpm for 30 minutes in orbital shaker.

↓

Analysis the data by using UV-Vis

↓

The step was repeated for raw material

Figure 3.3: Step for experiment to determine effect concentration of dye (Salman *et al*.,2012)

3.3.7 Preparation for effect of pH on dye adsorption

The 50 ml of bromophenol blue dye was put into 6 conical flasks and was measured with different pH (0, 2, 4, 6, 7, 8 and 10) by adjusted with 0.1M HCl or NaOH. After that, put 2g of activated carbon of eggshell in each of conical flasks. The mixtures were incubated at 35 ^{o}C at 300 rpm for 30 minutes in orbital shaker and record the data by using UV-Vis. The step was repeated to the raw material of eggshell. The step of this experiment was shown in Figure 3.4

By using 6 conical flasks, put 50ml solution of dye and measured the pH (0, 2, 4, 6, 7, 8 and 10) by adjusted with 0.1M HCl or NaOH

↓

After that, put 2g of activated carbon of eggshell in each conical flasks

↓

Then, the mixture were incubated at 35°C at 300rpm for 30 minutes in orbital shaker

↓

By using UV-Vis, the data was analysis

↓

The step was repeated for raw material of eggshell

Figure 3.4: The step experimental for determine effect of pH (Salman *et al*.,2012)

3.3.8 Preparation for effect of adsorbent dosage on dye adsorption

By using 5 conical flasks, 50ml of bromophenol blue dye solution was put into the flasks and were mixed with different dosage of adsorbent (0, 1, 2, 3, 4 and 5g). By using orbital shaker, the solutions were agitated for 35 °C at 300 rpm for 30 minutes. The concentration dyes was determined by measuring absorbance of solution at 465 nm by using uv-vis. The method was repeated for eggshell of raw material. Figure 3.5 were obtained the step of the experiment.

50ml of bromophenol blue dye solution were mixed with different dosage of adsorbent (0,1,2, 3, 4 and 5g) into 5 conical flasks

↓

By using orbital shaker, the solution was agitated with orbital shaker at 35 °C at 300 rpm for 30 minutes

↓

Final data was recorded using UV-Vis and the step was repeated for eggshell raw material

Figure 3.5: The step of determine dosage of adsorbent for dye removal (Salman *et al*.,2012)

3.3.9 Preparation for effect of contact time on dye adsorption

The activated carbon of eggshell was weight for 2g and was mixed with 50 ml of dye solution in 5 conical flasks. After that, the conical flasks were put in the orbital shaker and were shaken with different time (0, 10, 20, 30, 40 and 50 minute) by constant temperature 35 °C at 300 rpm. The mixture was put into UV-Vis to record the final reading. The same methods were used for raw material of eggshell. The step of experimental was shows in Figure 3.6 as follow:

The activated carbon of eggshell was weight for 2g and were mixed with 50 ml solution of dye into 5 conical flasks

↓

At constant temperature 35 ^{o}C and 300 rpm, the mixture was shaken using orbital shaker for different time (0,10,20,30,40 and 50 minutes)

↓

For every 10 minutes the conical flasks was remove from orbital shaker

↓

The mixtures was filter and the analysis of dye was record by using uv-vis

Figure 3.6: Step experimental for determine the effect of contact of time (Salman *et al*.,2012)

3.3.10 Preparation of Dilution Series

A series of dilution was made up to get 2,4,6,8 and 10 mg/L as the series of bromophenol blue stock solution. 1 ml from 100mg/L of solution is pipetted and poured into the 50ml volumetric flask to get 2mg/L. The distilled water was poured into the volumetric flask until it reaches the 100ml mark. The solution is inverted to mix and the stopper is placed in the volumetric flask. Through this experiment, the equation 3.1as follow is used (Habeeb *et al*., 2014):

$$M_1V_1 = M_2V_2 \text{ -------------------- equation 3.1}$$

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

3.3.11 Preparation of analysis for UV-Vis

Before used UV-Vis, self-check should be 100% accurate. The solution was poured into Quartz cuvettes (UV transparent) and was wiped with soft tissues. The Quartz cuvettes need to be wiped to avoid the error occurs while analysis was measured. The 465nm value of wavelength was entered and the protective cover was opened. The cuvettes were inserted into UV-Vis and the transparent side must parallel with the arrow. Then, the lid was closed and the reading was recorded. This step was repeated for other experiment.

3.3.12 Calculation of adsorption efficiency

The adsorption capacity and efficiency of eggshell as adsorbent was estimated by using this formula equation 3.2 (Habeeb *et al*., 2014) :

$$qe = \frac{v}{m} x\ (Co - C) \text{ --------------- equation 3.2}$$

Where, v = volume of solution (ml)

m = mass of adsorbent (mg)

Co = initial concentration

C = final concentration

Meanwhile, the calculation for percentage of removal dye was calculated by using the equation 3.3 (Basu *et al*., 2014):

$$E = \frac{Co - C}{Co} x\ 100\% \text{ ------------------ equation 3.3}$$

CHAPTER 4

RESULT AND DISCUSSION

4.1 Calibration Curve

Calibration curve is the key for accurate data in the research and the good calibration cannot be emphasized. According to Das *et al.*, (2014), the relationship between instruments and concentration usually is linear and only one corresponding concentration. Sample with different concentration was identifying by using ultraviolet visible (uv-vis). After the reading was analysis by uv-vis, the data was used to perform calibration curve. From the data, it can expressed the equation of straight line, y = mx + c. The correlation coefficient must not be less than 0.998. The correlation coefficient of graph was shown in Figure 4.1 which is R^2 = 0.9981.

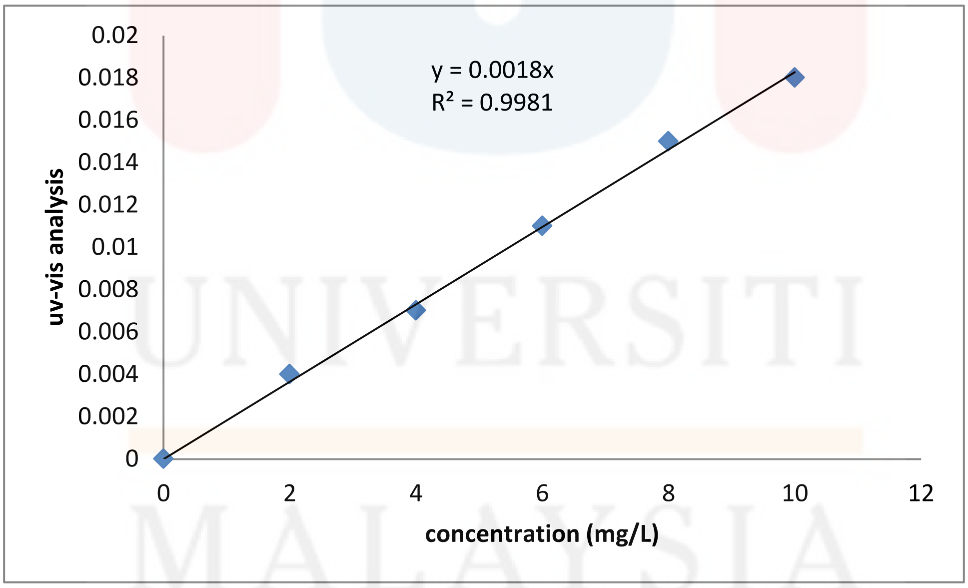

Figure 4.1 Calibration Curve

From the graph, it shows that equation of this research is y = 0.0018x + 0. Through this equation, the initial and final reading of the result from this research was calculated. The initial value is constant value for while the final value is changes according to the uv-vis recorded. The graph also shows that the linearity between the concentration and adsorbents.

4.2 Adsorption of Raw Material and Activated Carbon

4.2.1 Effect of concentration on dye adsorption

The effect of concentration on dye adsorption of activated carbon and raw material of eggshell was illustrated in Figure 4.2. From the result, it was obtained that the adsorption capacity of eggshell decreases with the increases of concentration of Bromophenol Blue dye. The percentage of removal Bromophenol Blue at initial concentration 20mg/L for both adsorbent was the highest which were 80.00% for activated carbon and 77.78% for raw material. This result shows that the percentage of removal for activated carbon decreases from 80.00% to 53.79% while for raw material the result declined from 77.78% to 57.10% as the dye concentration was increased from 20mg/L to 100mg/L.

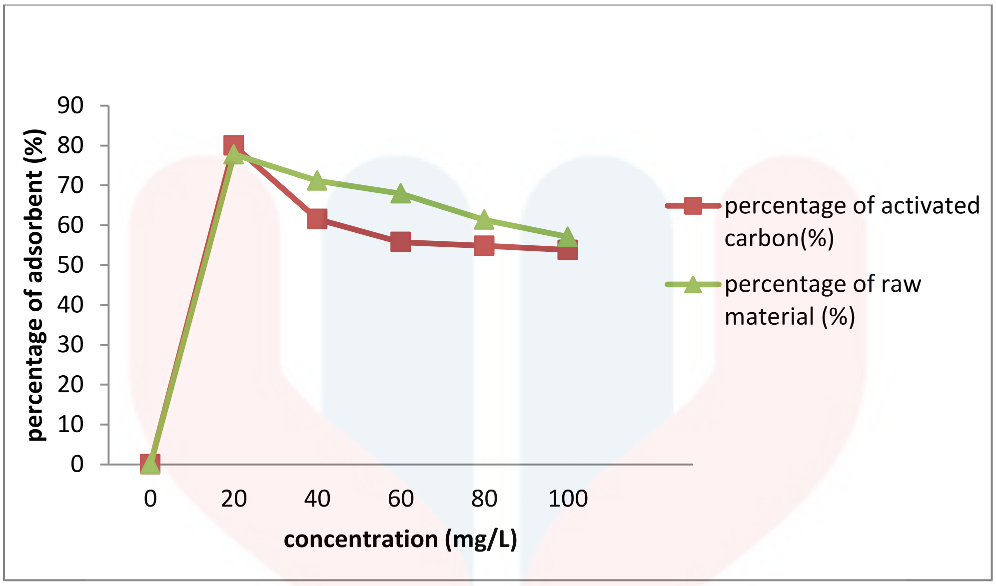

Figure 4.2 Effect of concentration on dye adsorption

This may be occur due to all sorbate ions that present in the sorption medium might interact with binding site. On the other hand, at higher level of concentrations, the percentage removal of dye decreases because of saturation of sorption sites. According to Zulfikar *et al.*, (2013), to overcome all resistance of the dye between the aqueous and solid phase, an important driving forces by increase in the initial concentration.

The optimum value of concentration was 20mg/L that stated the highest percentage for both adsorbent. This is because the gradient concentration between adsorbent and dye was increased and the percentage of removal was high until the system reaches its equilibrium (Dhananasekaran *et al.*, 2015).

4.2.2 Effect of pH on dye adsorption

The effect of pH on dye adsorption of activated carbon and raw material eggshell as adsorbent at 35 °C and 300 rpm are showed in Figure 4.3. The result indicates that the adsorption capacity of eggshells decreases with the increases of pH. The highest adsorption occurs at pH 2 for both adsorbent which for activated carbon 82.66% and for raw material was 61.82%. Meanwhile the lowest adsorption capacity occurs at pH 10 for activated carbon the result obtained 1.96% while for raw material was 5.89%.

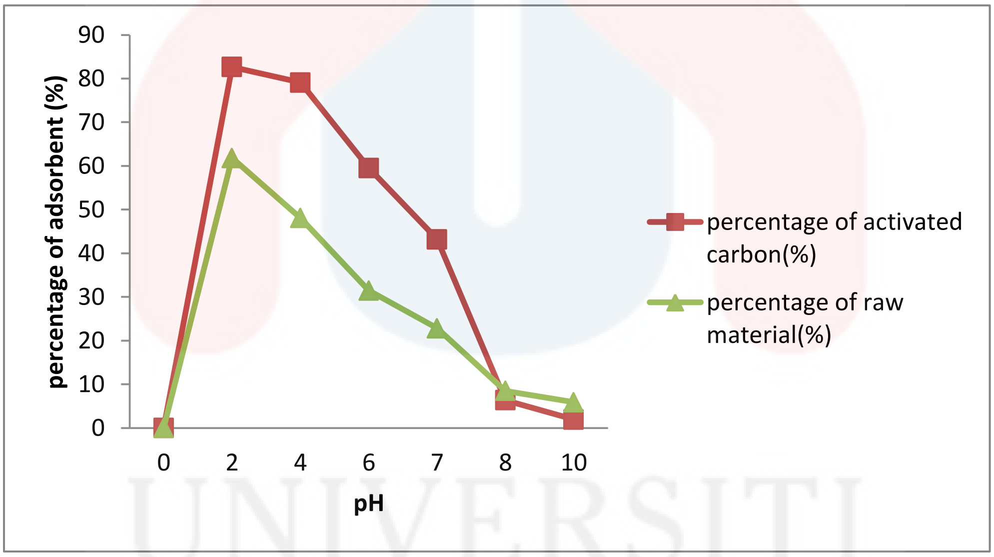

Figure 4.3 Effect of pH on dye adsorption

According to graph, from pH 2 is the optimum value for adsorption. This is because from pH 4 to pH 10, the adsorption decreases. The changes in the initial pH would affect the dissociation of the functional group of adsorbent. According to Dhananasekaran *et al.*, (2015), pH influences the adsorption process very less.

The maximum adsorption was observed at pH 2. According to Dhananasekaran *et al.*, (2015), this situation occurs because of the physical interactions such as formation of hydrogen bond and pore diffusion.

4.2.3 Effect of adsorbent dosage on dye adsorption

Based on Figure 4.4, the graph was illustrated the percentage removal of Bromophenol Blue by activated carbon and raw material of eggshell at different dosage which is from 1g to 5g. The graph showed that the adsorption capacity was slightly increased from 1g to 3g for activated carbon which are 66.33% to 70.96% while for the raw material it rose from 1g to 2g which result as 69.30% to 69.96%. Meanwhile, from 3g to 5g the graph showed decreased adsorption from this experiment which is 70.96% to 68.64% for activated carbon. The percentage for raw material started to fall from 3g to 5g which is 68.98% to 66.01%.

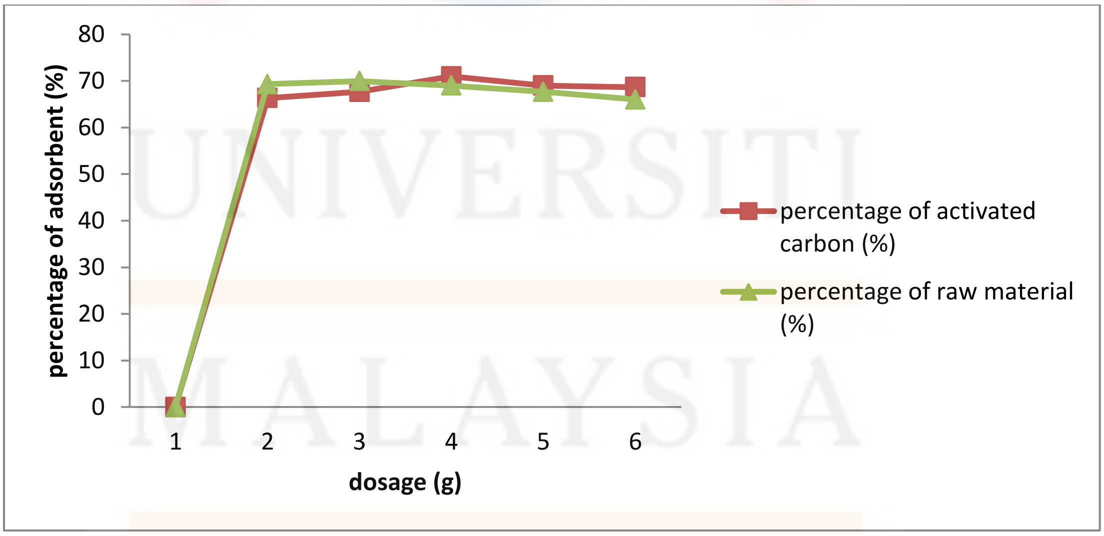

Figure 4.4 Effect of adsorbent dosage on dye adsorption

From the observation, the optimum value of activated carbon percentage removal is during 3g and for raw material it optimum is at 2 g. This situation happens because of the saturation that occurs at the dosage.

4.2.4 Effect of contact time on dye adsorption

The variation of adsorption capacity of activated carbon and raw material of eggshell over times towards Bromophenol Blue dye was illustrated in Figure 4.5. From the result obtained, it was shown that there are slightly increase of adsorption from minute 10 to 50 for both adsorbent. However, the adsorption capacity highest removal was at minute 50 which are 69.96% for activated carbon and 68.98% for raw material.

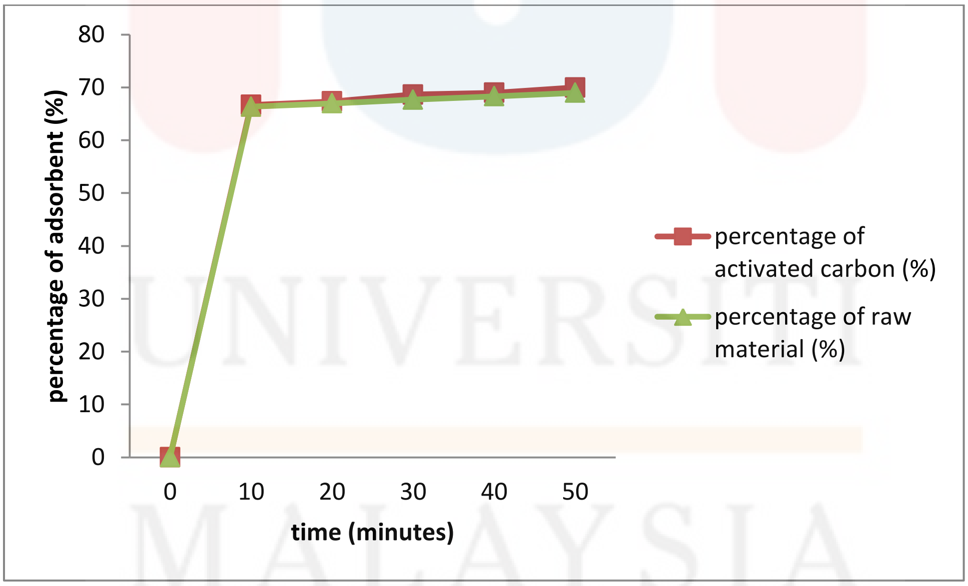

Figure 4.5 Effect of contact time on dye adsorption

This stage was known as dynamic equilibrium. According to Seidmohammadi *et al*., (2015), this occurs due to the fact that during the adsorption process, the mass of dye molecules are received to boundary layer. From this process, it slowly released from boundary layer to the absorber surface.

According to Salman *et al.*, (2012), the relationship between contact of time and percentage removal was proportional and the percentage of removal increase within the increase of time. This is because of the pore diffusion become largest and adsorbed many dyes.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Based on the finding, the study has successfully produce activated carbon from the eggshell. The eggshell has been succeeding to be used as adsorbent for dye removal. The adsorbent was proven significantly affected by the concentration of dye, pH of dye, dosage and contact time of dye used.

The result shows that the higher concentration of dye the lower percentage of removal. This occurs because of the saturated dye at the site of adsorption. The highest percentage removal was formed in this study was 82.66% at the optimum condition of pH 2 under concentration 20mg/L at 50 minutes using 3g of adsorbent for activated carbon.

However, for the raw material the highest percentage of removal was recorded 77.78% at the optimum circumstance of concentration 20mg/L at 50 minutes under pH 2 using 2g.

5.2 Recommendation

There are a few recommendations that can be done in further research. The researcher can carry out different parameters in this study which were the effect of size particle, initial concentration and the different type of eggshell.

On the other hand, the researcher can further investigate the uses of eggshell as adsorption kinetics and use different type of dye. The researchers also can use wastewater from industry of textile to proof the efficiency of eggshell as adsorbent.

The different type of chemicals was recommended to be done in this experiment for further studied and be used to mix into eggshell before produced activated carbon.

The researcher also can provide desorption of eggshell to be reuse over time. The eggshell is suitable for low concentration and in wastewater. To get more accurate result of experiment, the distilled water needs to be replacing with ionized water. It is because the ionized water more accurate pH.

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APPENDICES A

EXAMPLE CALCULATION OF INITIAL, FINAL CONCENTRATION, PERCENTAGE REMOVAL AND EFFICIENCY

Figure A.1 Calculation of initial concentration

$R^2 = 0.9981$

$y = 0.0018x$

Initial = 0.303

Substitute y = 0.303

$y = 0.0018x + 0$

$0.303 = 0.0018x$

$$x = \frac{0.303}{0.0018}$$

$x = 168.33$

Therefore, initial concentration = 168.33

Figure A.2 Calculation of final concentration

$R^2 = 0.9981$

$y = 0.0018x$

Final = 0.102

Substitute y = 0.102

$y = 0.0018x + 0$

$0.102 = 0.0018x$

$$x = \frac{0.102}{0.0018}$$

$x = 56.67$

Therefore, final concentration = 56.67

Figure A.3 Calculation of Percentage removal

E = $\frac{Co-C}{Co}$ $X\ 100$

E = $\frac{168.33-56.67}{168.33}$ $X\ 100$

E = 66.33 %

Figure A.4 Calculation of efficiency

qe = $\frac{v}{m}$ x $(C\text{o} - C)$

qe = $\frac{50}{2000}$ x ($168.33 - 56.67$)

qe = 2.79 mg/g

APPENDICES B

FINAL CONCENTRATION OF RAW MATERIAL AND ADSORPTION CAPACITY OF BROMOPHENOL BLUE DYE REMOVAL

Table B.1 Effect of contact time on dye adsorption

(35 ^{o}C, 300 rpm)

Time (minutes)	Final Concentration (mg/L)	qe (mg/g)	Percentage Removal (%)
0	0	0	0
10	0.102	2.79	66.33
20	0.100	2.82	66.99
30	0.098	2.85	67.66
40	0.096	2.88	68.32
50	0.094	2.90	68.98

Table B.2 Effect of concentration on dye adsorption

(35 ^{o}C, 300 rpm)

Concentration (mg/L)	Final concentration	qe (mg/g)	Percentage removal (%)
0	0	0	0
20	0.020	0.97	77.78
40	0.030	1.03	71.15
60	0.050	1.47	67.94
80	0.117	1.82	61.39
100	0.130	2.40	57.10

Table B.3 Effect of adsorbent dosage on dye adsorption

(35 ^{o}C, 300 rpm)

Dosage (g)	Final concentration	qe (mg/g)	Percentage removal (%)
0	0	0	0
1	0.093	2.91	69.30
2	0.091	2.94	69.96
3	0.094	2.90	68.98
4	0.098	2.84	67.66
5	0.103	2.78	66.01

Table B.4 Effect of pH on dye adsorption

(35 ^{o}C, 300 rpm)

pH	Final concentration	qe (mg/g)	Percentage removal (%)
0	0	0	0
2	0.152	3.08	61.82
4	0.149	1.72	48.08
6	0.122	0.070	31.46
7	0.125	0.046	22.84
8	0.086	0.10	8.50
10	0.096	0.08	5.89

APPENDICES C

FINAL CONCENTRATION OF ACTIVATED CARBON AND ADSORPTION CAPACITY OF BROMOPHENOL BLUE DYE REMOVAL

Table C.1 Effect of contact time on dye adsorption

(35 ^{o}C, 300 rpm)

Times (minutes)	Final concentration	qe (mg/g)	Percentage removal (%)
0	0	0	0
10	0.101	2.80	66.67
20	0.099	2.83	67.33
30	0.095	2.89	68.64
40	0.094	2.90	68.98
50	0.091	2.94	69.96

Table C.2 Effect of concentration on dye adsorption

(35 °C, 300 rpm)

Concentration (mg/L)	Final concentration	qe (mg/g)	Percentage removal (%)
0	0	0	0
20	0.018	1.00	80.00
40	0.040	0.89	61.54
60	0.069	1.21	55.77
80	0.112	2.49	54.84
100	0.140	2.26	53.79

Table C.3 Effect of adsorbent dosage on dye adsorption

(35 °C, 300 rpm)

Dosage (g)	Final concentration	qe (mg/g)	Percentage removal (%)
0	0	0	0
1	0.102	2.79	66.33
2	0.098	2.85	67.66
3	0.088	2.99	70.96
4	0.094	2.91	68.98
5	0.095	2.89	68.64

Table C.4 Effect of pH on dye adsorption

(35 ^{o}C, 300 rpm)

pH	Final concentration	qe (mg/g)	Percentage removal (%)
0	0	0	0
2	0.069	4.11	82.66
4	0.060	2.84	79.10
6	0.072	1.33	59.55
7	0.092	0.88	43.21
8	0.088	0.07	6.38
10	0.100	0.02	1.96

APPENDICES D

MATERIAL AND EQUIPMENT

Figure D.1 Bromophenol Blue Powder

Figure D.2 Eggshell

Figure D.3 Furnace

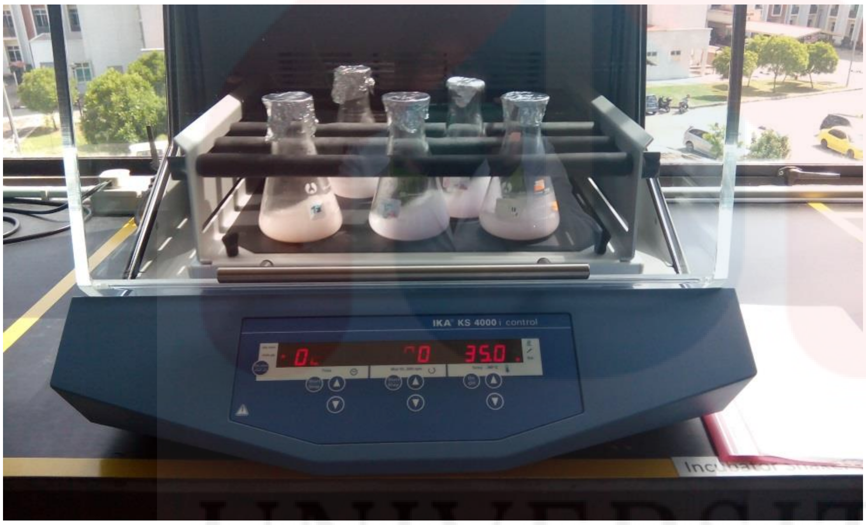

Figure D.4 Orbital Shaker

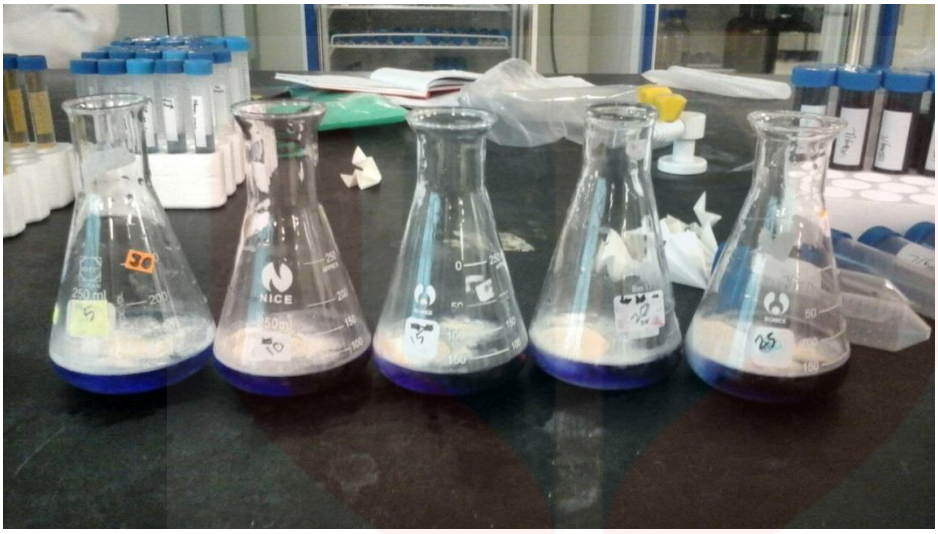

Figure D.5 Before experiment

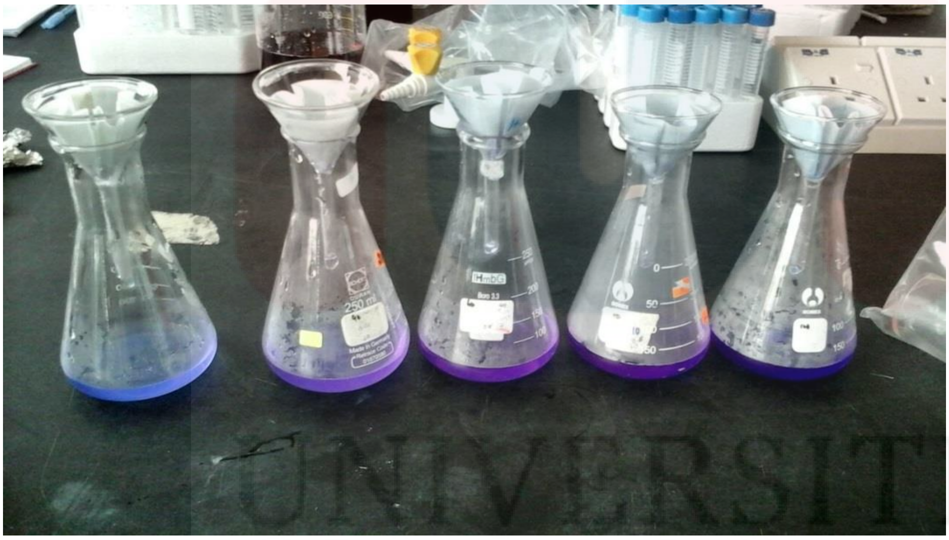

Figure D.6 After experiment