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TITLE: PREPARATION AND CHARACTERIZATION OF WASTE EGGSHELL AS POTENTIAL NEW ADSORBENT

PREPARED BY:

SITI HAJAR A. HAMID

(13914)

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Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

Malaysia

CERTIFICATION OF APPROVAL

Preparation and Characterization of Waste Eggshell as Potential New Adsorbent

by

Siti Hajar A Hamid

13914

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Approved by,

____

(AZRY BORHAN)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(SITI HAJAR A HAMID)

ABSTRACT

As the contemporary worldwide development towards more strict environmental standards, technical applicability and cost-effectiveness has become the key factors in manufacturing adsorbents. Recently, more low-cost adsorbents have been derived from agricultural waste, industrial by-products or natural materials, since the development of value–added products from waste are highly recommended. On the other hand, the eggshells amount to large waste disposal problems for the food industry. The preparation of activated carbon from waste eggshell is considered one of the most environmental friendly solutions to this problem by transforming the waste material into a value-added product. The eggshell was first activated using potassium hydroxide and phosphoric acid at different impregnation ratio, activating time and temperature. The produced activated carbon is then characterized using Field Emission Scanning Electron Microscope (FESEM) and Micromeritics ASAP 2020. The optimal conditions to manufacture the activated carbon was found when the eggshell was activated at temperature of 400 °C for 60 minutes at impregnation ration of 1:3. Results proved that the BET surface area, total pore volume and diameter of activated carbon were 57.0687 m^2/g, 0.2796 cm^3/g and 18.68 nm respectively. Nitrogen adsorption desorption isotherm analysis shows that the activated carbon produced have mesopores present, making it suitable for adsorption process usage.

ACKNOWLEDGEMENTS

All praises go Allah, the gracious, for granting me the greatest health in order for me to complete this project without any hiccups. Not forgetting to mention, the man who has been guiding since day 1 of this project, none other than my supervisor, Mr. Azry Borhan. Besides that, my eternal gratefulness goes to my family, who has been my backbone, supporting me in completing my degree in anyways possible, be it in terms of morale or financial. In addition, I would like to express my gratitude to my fellow friends and classmates, who have been a great help for me to complete this project with a success. I would like to once again thank everyone who is involved in completing this project, whether directly or indirectly. Your kind cooperation is forever appreciated.

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CHAPTER 1: INTRODUCTION

1.1. BACKGROUND OF STUDY

At the present time, there are intensive researches done to look into low cost materials being transformed into alternatives to the commercial activated carbon. Materials such as coconut shell [1], wood sawdust [2] and limestone [3] are just a few examples of natural materials that have been studied to have the ability to substitute the commercial activated carbon.

Meanwhile, statistics have shown that the number of egg produced in Malaysia has exponentially increased. The eggs, which are mainly used in the food and beverage industry or household, recorded production of 10.3 million in 2011 increased to 10.7 million eggs in 2012 [4]. This number is not going to stop increasing in years as to cater the rate of consumption in the country as eggs are one of the staple foods for Malaysians. Despite the growing number of eggs produce, the more concerning issue is the amount of eggshells being disposed. One of the problems raised by landfill operators is that the waste eggshells attract vermin because of the attached membrane will expel foul smell. Hence, extensive studies have been conducted to explore the prospect of using waste eggshell as a new adsorbent in adsorption process.

High porosity activated carbons are manufactured through activation of carbonaceous materials aside from carbonization process. Besides the nature of the raw material, the activation process plays a major role in determining the porosity structure and the final properties of the activated carbon. There are two methods of activating the carbonaceous materials; the steam activation and the chemical activation. In the steam activation, activated carbons are produced in a two-stage process. First, the raw material is carbonized by heating in a low oxygen atmosphere to dehydrate and devolatile the material which in the end will produce coke or charcoal with pores that are either small or too restricted to be used as adsorbent.

Then, the activation takes place to enlarge the pore structure, increase the internal surface area and make it more accessible. On the other hand, the chemical activation involved mixing the carbonaceous raw material with an organic chemical compound, such as potassium oxide and zinc chloride, and carbonizing the resultant mixture. The chemical works as a support and prevents the charcoal produced to shrink in size. It dehydrated the raw material, causing the carbon to char and amortize, hence creating a porous structure and an extended surface area [5, 6].

With the objectives of this research is to prepare and characterize the waste eggshells as potential new adsorbent, optimization of different parameters is implemented to achieve the aim, therefore, producing the best activated carbon. For this research, the chemical activation method is chosen as the activated carbons produced have a suitable pore distribution. Effect on operating parameters such as activation temperature, time, activating agent and impregnation ratio of the raw material will be explained further in the report.

1.2. PROBLEM STATEMENT

Adsorption has been found to be a proficient and economical method for wastewater treatment to remove heavy metals, dyes and pigments as well as for controlling the bio-chemical oxygen demand. Inorganic oxides, minerals, activated carbon and natural adsorbents have been widely used as adsorbents to treat wastewater [7]

Even though the conventional adsorbents mentioned above are used abundantly in water and wastewater industries, they remain an expensive material. Despite that, other problems found to be associated with the use of carbon for pollutants adsorption process are;

(i) Incur relatively high cost to the operation
(ii) Regeneration and reuse of activated carbons are difficult due to the fragility of present types of activated carbon

(iii) Limitation of activated carbons towards the removal of non-polar materials [8].

Thus, many have seen the need to further search for materials that are more suitable and versatile than carbon for water treatment, be it for lesser preliminary price or potentially greater ease of regeneration. From the literature study done, waste eggshell is found to be an effective adsorbent to substitute conventional activated carbon in an adsorption process [9-12].

1.3. OBJECTIVES

The objectives of this project are as follows:

1) To prepare waste eggshell as activated carbon using chemical activation method
2) To characterize and find the optimum condition of the activated carbon from eggshells based on the activating agent, impregnation ratio, activation time and temperature
3) To study the capability of the activated carbon for oil and grease removal

1.4. SCOPE OF STUDY

The experiment will manufacture activated carbon using eggshell. The method of manufacturing is by chemical activation. The eggshell will be impregnated with activating agent at different ratio and will be put in the fixed bed activation unit at different operating activation temperatures and times. Upon completing the activated carbon, the sample will then undergo characterization using the Field Emission Scanning Electron Microscope (FESEM) to determine the element in the raw material and activated carbon and to analyze the surface structure and morphology of solids and Micrometrics ASAP 2020 to determine the specific surface area, pore size and pore volume of the activated carbon. Finally, the activated carbon from the eggshells will then be tested to prove the ability to remove traces of oil and grease in the wastewater

1.5. RELEVANCY OF PROJECT

The project is deemed as important as it is looking into new possibilities of finding alternative measures of the conventional type adsorbents. With the usage of waste eggshells does not only look into the potential of waste eggshells, it will also help with conserving the environment by implementing element of recycling waste material into something useful and profitable. Consequently, this project is very much relevant as the subject matter is not widely studied into its' maximum potential.

1.6. FEASIBILITY OF PROJECT

The project is feasible since it is dealing with a specified scope of experiment. In this experiment, the ability of adsorbent made from waste eggshells to remove oil and grease will be studied. It is within capability of the student to conduct the study with the guidance from the supervisor. It is positive that this project is able to be conducted and completed with the given time.

CHAPTER 2: LITERATURE REVIEW

2.1. ADSORPTION PROCESS

Adsorption is a surface phenomenon whereby a process of removing substances from either gaseous or liquid solutions by using solids undergoes. This procedure creates a layer of the adsorbate on the exterior of the adsorbent. Adsorption is not to be mistaken with absorption as it is a surface-based process while absorption involves the whole volume of the material. [13]

The process of adsorption involves separation of a substance from one phase accompanied by its concentration or accumulation on the surface of another. The main cause of physical adsorption is by electrostatic forces and van der Waals forces between adsorbate molecules and the atoms which make up the adsorbent surface. Therefore, the adsorbents are first categorized by surface properties, for example surface area and polarity.

2.1.1. Adsorbents

A large specific area of adsorbent is highly preferable due to the availability of large adsorption capacity. However, the manufacturing of large internal surface area in a limited volume unavoidably gives rise to large numbers of small sized pores between adsorption surfaces. The micropores size determines the ease of access of adsorbate molecules to the internal adsorption surface, so the distribution pore size of micropores is another significant characteristic to categorize the ability of adsorbents to adsorp. Materials such as zeolite and carbon molecular sieves can be particularly manufactured with precise distributions of pore size.

Adsorbents are used typically in the shape of spherical pellets, rods, moldings or monoliths with hydrodynamic diameters between 0.5 and 10mm. Besides that, they must also have high resistance of abrasion, high thermal stability as well as small pore diameters, which in turn will result in higher exposed surface area in addition to high surface capacity for adsorption. A distinct pore structure helps adsorbents to transport gaseous vapors faster.

Most industrial adsorbents are categorized into one of these three classes:

- **Oxygen-containing compounds –** Adsorbents are usually hydrophilic and polar, including materials such as silica gel and zeolites. This type of adsorbents is used for drying of process air and removal of heavy (polar) hydrocarbons from natural gas.
- **Carbon-based compounds –** Adsorbents are frequently hydrophobic and non-polar, including materials like activated carbon and graphite. These adsorbents are mainly used for adsorption of organic substance and non-polar adsorbates and in wastewater treatment. Activated carbon is the most widely used adsorbent as most of its chemical and physical properties can be customized according to what is required.
- **Polymer-based compounds –** Adsorbents are in polar or non-polar functional groups in a porous polymer matrix.

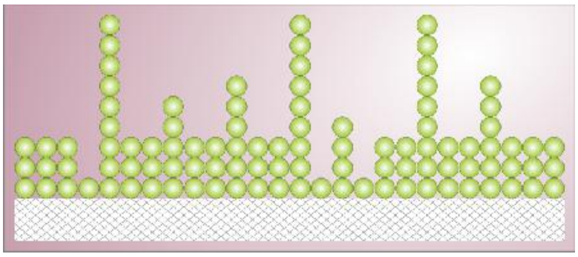


Figure 1: Brunauer, Emmett and Teller's model of multilayer adsorption on the material surface is a random distribution of molecules

2.1.2. Adsorption Isotherms

Isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure or concentration at constant temperature are usually used to describe adsorption. The amount adsorbed is almost always normalized by the mass of the adsorbent to allow comparison of different materials.

- **Freundlich Isotherm**

  Freundlich isotherm is an experimental model that takes heterogeneous adsorption on the adsorbent surface into consideration. The linearized equation for Freundlich isotherm is

  $$\log q_e = log k_F + \frac{1}{n} log C_e \quad (1)$$

  where q_e is the adsorption capacity at equilibrium (mg/g), k_F (L/g) is related to bond strength, n is the bond energies between metal ion and the adsorbent and C_e is the adsorbate concentration at equilibrium (mg/L) [12].

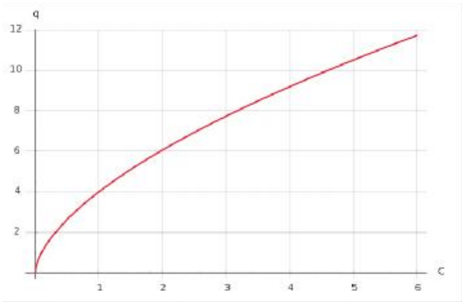


Figure 2: Freundlich Isotherm

- **Langmuir Isotherm**

  Langmuir isotherm relates the monolayer adsorbate coverage on the adsorbent surface to gas pressure or concentration of medium above solid surface at fixed temperature [14]. The linearized equation of Langmuir isotherm is

  $$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_n} \quad (2)$$

  where b is the adsorption equilibrium constant (L/mg) and q_m is the maximum adsorption capacity of adsorbent (mg/g) [12]

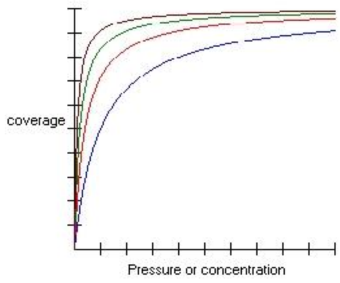


Figure 3: Langmuir Isotherm

2.2. EGGSHELL

2.2.1. Structure of Eggshell

Eggshell is composed of 94% to 97% of calcium carbonate crystals and the remaining is organic matter and eggshell pigment. It was found that an eggshell has as many as 8,000 microscopic pores in the shell itself. The external layer of the shell contains a mucous coating known as cuticle or bloom that is deposited on the shell prior to lay. This protein is required to shield the interior contents of the egg from bacterial contamination through the shell [15].

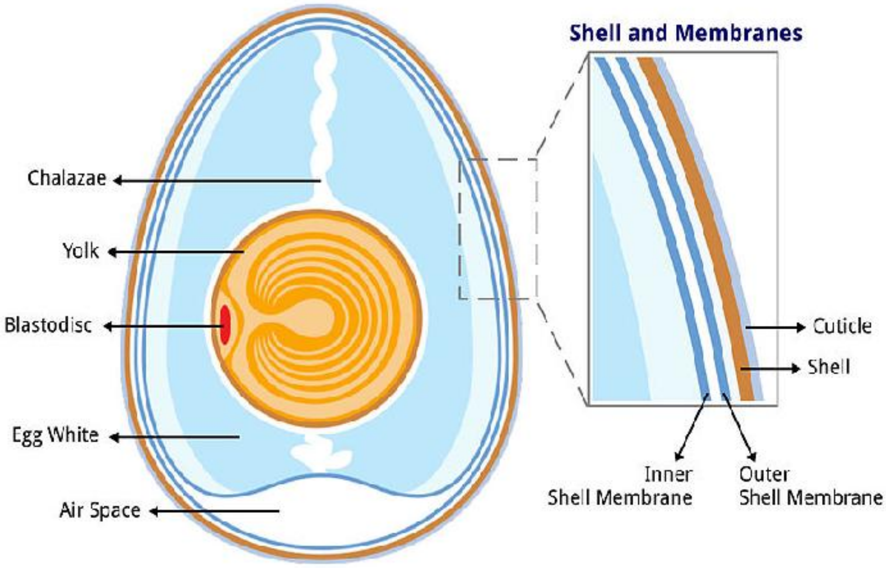


Figure 4: Anatomy of an Egg

2.2.2. Eggshell as Adsorbent

Various studies have found the capability of eggshell as a bio-sorbent, which is adsorbent made from bio-degradable materials due to its cellulosic structure and presence of amino acids. According to Bhaumik et al. (2012), eggshell can be used in removal of fluoride from aqueous solution with adsorption capacity of 1.09 mg/ [9]. Meanwhile, Zulfikar, Mariske, Djajanti (2012) found that eggshell is capable in removing lignosulfonate compounds with adsorption capacity at 93.46 mg/g [7]. Ngadi and Wan Jusoh (2013) discovered that eggshell can be utilized in dye removal and recorded removal of 64% of dye at 50 °C [11]. Besides that, Rohaizar, Abd. Hadi and Wong (2013) stated in their paper that eggshell is capable of removing Cu (II) in wastewater. The adsorption capacity recorded is 175.50 mg/g [12].

2.3. REMOVAL OF OIL AND GREASE

2.3.1. Physical Removal of Oil and Grease

The commonly used method of removing oil and grease from wastewater is by skimming devices. This method is viewed as a dependable and cheap, also able to achieve the desired level of water purity. Moreover, through skimming method, removal of oil before using membrane filters and chemical processes to be more cost-efficient. It prevents filters from blinding ahead of time and keeps chemical costs at low since there is not as much of oil to process.

All oil skimmers depend on the fluid properties of specific gravity as well as surface tension [16]. The majority of oil skimmers in the market employ a moving medium to remove floating oil from the fluid’s surface. The floated oil and grease will cling to the skimming media allowing the media more readily than water, in the shape of a belt, disk, drum, etc., to pass through the fluid surface and collect the floating oil while rejecting most of the water. The oil and grease accumulated is subsequently removed from the media by using the wiper blades or pinch rollers. An example of oil skimmer employing this design is API oil-water separator.

On the other hand, parallel plate separator is similar to API separator however parallel plate separator included tilted parallel plate assemblies, also known as parallel packs. However, the disadvantage of addition tilted parallel plates give more surface for suspended oil droplets to coalesce into larger globules. Otherwise, the parallel plates enhance the degree of oil-water separation resulting into a significantly less space required than a conventional API separator to achieve the same degree of separation.

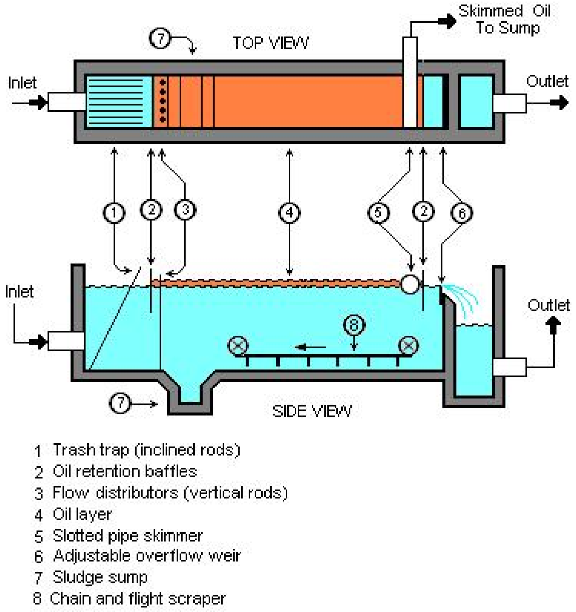


Figure 5: An API oil-water separator used in many industries

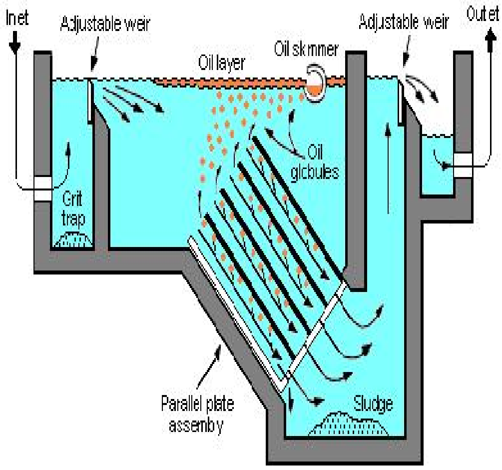


Figure 6: A typical parallel plate separators

2.3.2. Expected Results of Oil and Grease Removal Using Adsorption Method

A few researchers had looked into the efficiency of adsorbents in removing oil and grease from wastewater. Gimba & Turoti (2006) used coconut shell activated with iron chloride, calcium chloride, zinc chloride and potassium carbonate to test the efficiency of oil and grease removal. They found that the coconut shell based adsorbent manage to remove more 90% of oil and grease in the wastewater [17]. In addition, a research done by Ismail (2005) using walnut shell activated carbon achieved a removal of oil up to 96% [18]. Additionally, a research conducted by Ahmad, Bhatia, Ibrahim and Sumathi (2005) concluded that rubber powder accomplished 88% reduction in residual oil [19].

The table below summarized the results obtained by the researchers.

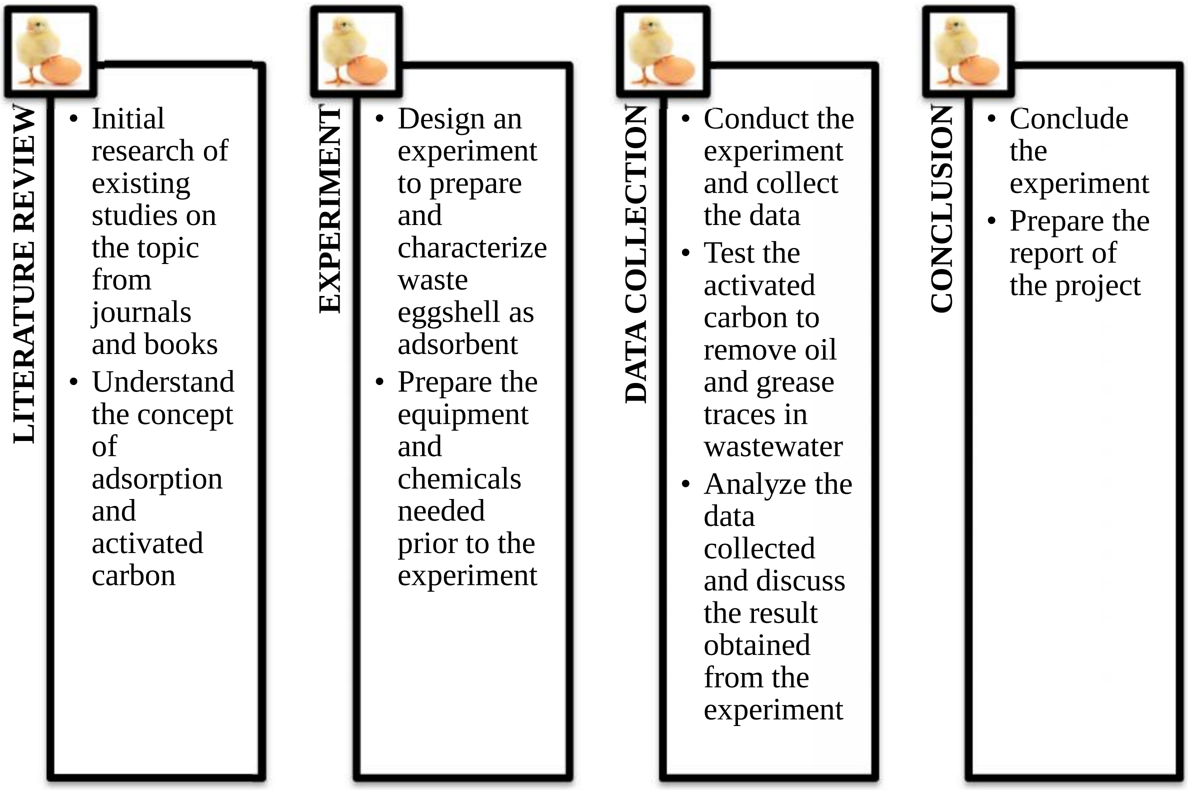
Table 1: Percentage of oil and grease removal using adsorbents

Adsorbents	Percentage of Removal of Oil and Grease (%)
Coconut Shell activated with:	
• K_2CO_3	90.2
• $CaCl_2$	91.0
• $FeCl_3$	94.3
• $ZnCl_2$	97.4
Walnut Shell	96
Rubber Powder	88

Based on the table above, coconut shell activated with zinc chloride has the highest percentage of removal of oil and grease at 97.4%. This proves that oil and grease can also be removed using adsorption process.

CHAPTER 3: RESEARCH METHODOLOGY

3.1. PROJECT ACTIVITIES



3.2. GANTT CHART AND KEY MILESTONE

3.2.1. Final Year Project (FYP I)

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project														
2	Preliminary Research Work														
3	Submission of Extended Proposal Defense														
4	Proposal Defense														
5	Commencement of Experimental Work														
6	Submission of Interim Draft Report to Supervisor														
7	Submission of Final Interim Report														

3.2.2. Final Year Project (FYP II)

No	Detail/Week	15	16	17	18	19	20	21	22	23	24	25	26	27	28
1	Project Work Continues														
2	Submission of Progress Report														
3	Project Work Continues														
4	Pre-SEDEX														
5	Submission of Report Draft														
6	Submission of Dissertation														
7	Submission of Technical Paper														
8	Oral Presentation														

3.3. EXPERIMENT METHODOLOGY

3.3.1. Tools and Equipment

Table 2: List of Tools and Equipment

No.	Equipment	Uses
1.	Oven	To remove moisture and dry the eggshells
2.	Furnace	To carbonize eggshells into activated carbon
3.	Desiccator	To keep the samples dehydrated
4.	Field Emission Scanning Electron Microscope (FESEM)	To provide magnified view of the activated carbon manufactured from eggshells
5.	Surface Area Analyzer and Porosimetry System (Micrometrics ASAP 2020)	To analyze the pore size distribution, porosity and specific surface area of the activated carbon from eggshells. Nitrogen gas is used in Micrometrics ASAP 2020 as the adsorbate that is set to flow at 350 °C for 2 hours.

3.3.2. Substance and Chemical

Table 3: List of Substances and Chemicals

No	Substance/Chemical	Purpose
1.	Eggshell	Used as raw material to be developed into activated carbon
2.	Potassium Hydroxide (KOH)	Used as impregnation agent for the eggshell to develop into activated carbon by chemical activation method

3.	Phosphoric Acid (H_3PO_4)	Used as impregnation agent for the eggshell to develop into activated carbon by chemical activation method
4.	Distilled water	Used for the purpose of washing and removing traces of pollutants and chemical on eggshell

3.3.3. Range of Variables

Table 4: Range of Variables

Variables	**Range of Values**		
Activating Agent	Potassium Hydroxide (KOH)	Phosphoric Acid (H_3PO_4)	-
Activation Temperature (°C)	400	500	-
Activation Time (minute)	60	90	-
Impregnation Ratio	1:1	1:2	1:3

3.3.4. Experiment Procedure

Sample Preparation

The waste chicken eggshells are obtained from local restaurants and bakeries. The waste eggshells are washed several times with distilled water to remove impurities and dried overnight at 40 °C. The eggshells are then grounded, sieved and kept in airtight and sterile container for further processes.

Figure 7 Eggshell being grinded

The ground eggshells are impregnated with different activating agent at different impregnation ratio. The impregnation is left overnight to let the impregnation agent to be absorbed into the eggshell.

$$IR = \frac{\omega_{activating\ agent}}{\omega_{eggshells}}$$

$$1:1 = \frac{10\ g\ of\ activating\ agents}{10\ g\ of\ eggshells}$$

$$1:2 = \frac{10\ g\ of\ activating\ agents}{20\ g\ of\ eggshells}$$

$$1:3 = \frac{10\ g\ of\ activating\ agents}{30\ g\ of\ eggshells}$$

The impregnated eggshells are first washed with distilled water to remove access impregnation agent, filtered and carbonized in a furnace at different operating activation temperatures and times.

Figure 8: Filtering the Impregnated Eggshells

The activated carbon is dehydrated in the oven overnight and finally it is placed in the desiccators to maintain the dryness.

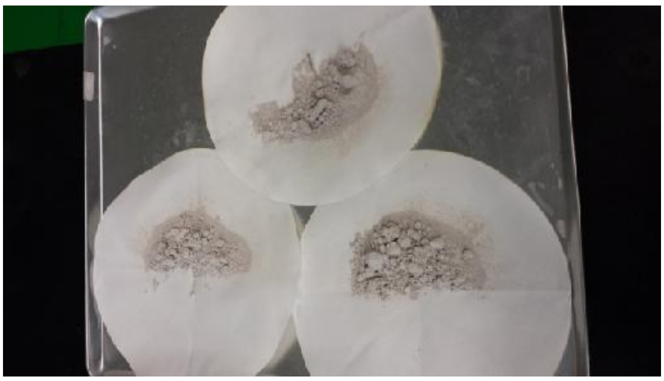


Figure 9: Carbonized eggshells

Sample Characterization

Field Emission Scanning Electron Microscope is used to analyze the carbonized eggshells to study the surface texture and the development of porosity. The analysis equipment is also used to determine the element present in the carbonized eggshell and the raw eggshell by undergoing the process of Energy Dispersive X-ray (EDX) Spectroscopy.

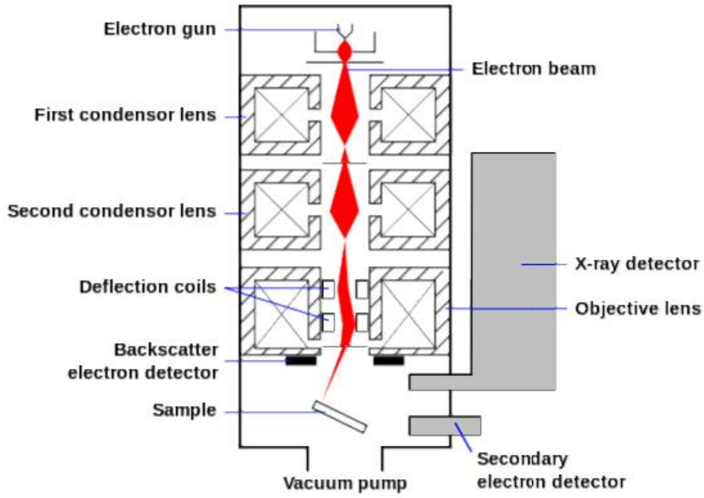


Figure 10: Schematic Diagram of an SEM

On the other hand, the pore size distribution, specific surface area and porosity of the carbonized eggshells were determined using nitrogen adsorption-desorption isotherms obtained using the Micrometrics ASAP 2020 equipment, employing nitrogen gas as adsorbate. Iniatially, the samples were degassed under N_2 gas flow at 350 °C for 2 hours in a vacuum at 22 °C. The Brunauer-Emmet-Teller (BET) method is used to estimate the specific surface area of the prepared activated carbons while using the nitrogen adsorption-desorption isotherm data. The pore volumes are calculated from the amount of nitrogen adsorbed at relative pressure of 0.98. Additionally, the pore size distribution is calculated using the Barrett-Joyner-Halenda (BJS) model [20] .

CHAPTER 4: RESULT AND DISCUSSION

The table below lists out the samples that were analyzed to determine the best operating condition to produce the best adsorbent:

Table 5: Sample Details

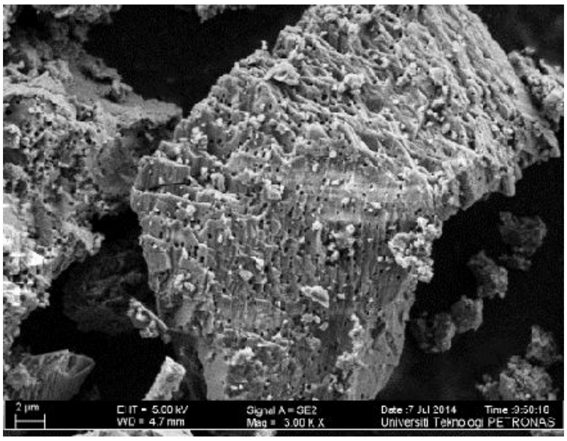
Sample Code	Impregnation Agent	Impregnation Ratio	Activation Temperature (°C)	Activation time (min)
A1	KOH	1:3	500	90
A2	KOH	1:2	500	90
A3	KOH	1:2	500	60
A4	KOH	1:1	500	60
A5	KOH	1:3	400	90
A6	KOH	1:3	400	60
A7	H_3PO_4	1:3	400	60
A8	H_3PO_4	1:3	400	90
A9	H_3PO_4	1:2	500	60

4.1. CHARACTERIZATION OF ACTIVATED CARBON

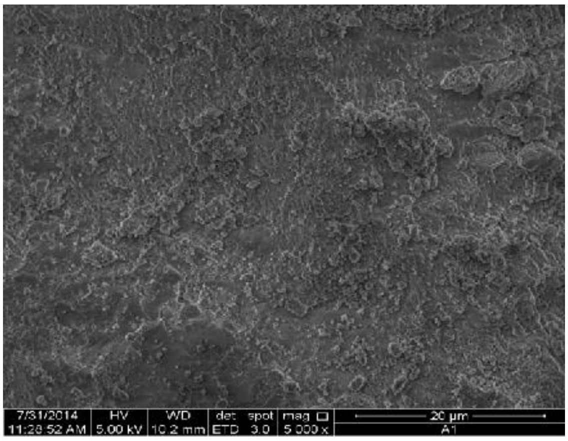
4.1.1. Field Emission Scanning Electron Microscope (FESEM) Analysis

Eggshell is known to be a semi per permeable bio-membrane with an intricate poly porous structure. Based on the figure below, the FESEM images showed that the eggshells have existing pores even before any impregnation is done. The existing pores will enable the impregnating agent to be fully absorbed by the eggshells to stimulate the carbon content inside it. According to I.M. Muhammad, U. A. El-Nafaty, S. Abdulsalam and Y.I. Makarfi, 2012, the eggshell consisted of pores from 8-17 µm in diameter and which is composed of interlaced protein fibers with an average diameter of approximately 2 µm [21].

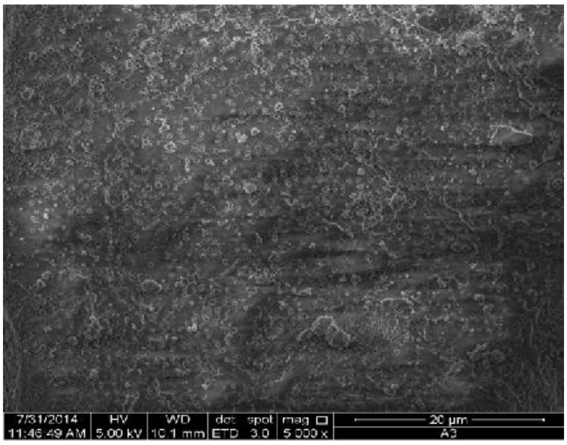
Eggshells are mostly composed of $CaCO_3$ by which takes up to 1/10 of the weight of an egg.



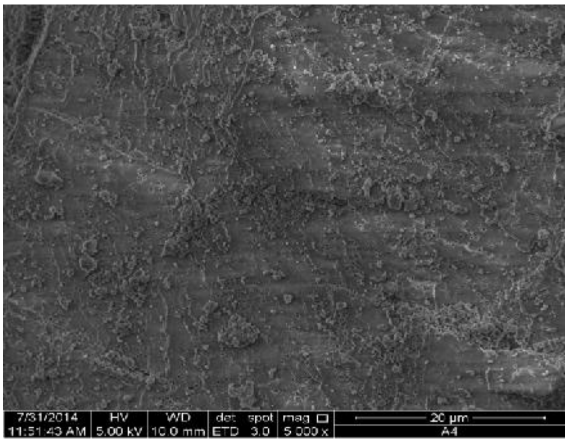
Raw Sample



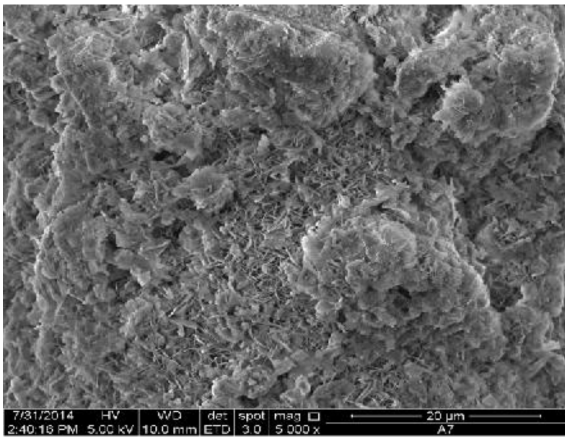
Sample A1



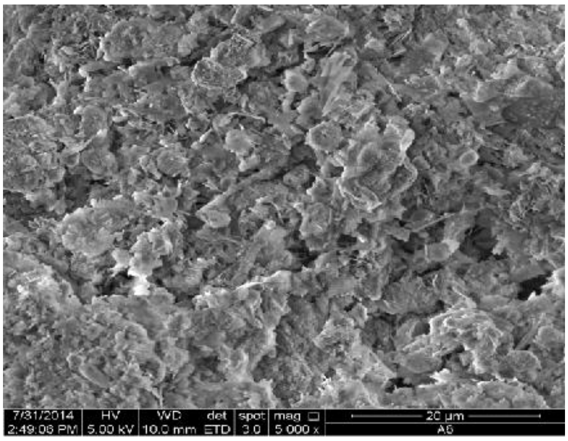
Sample A3



Sample A4



Sample A7



Sample A8

Figure 11: FESEM image of raw eggshell and carbonized eggshell

The FESEM images above are set at 5000x magnification. As observed, the carbonized eggshell has a rougher morphology, especially for sample A7 and A8. The samples A7 and A8 are carbonized at 400 °C, making the pores more structured and most probably make a better adsorbent compared to the raw eggshell. Nevertheless, for sample A1, A3 and A4, they are carbonized at 500 °C which resulted into smaller amount of pores due to the high heat breaking the porous wall slightly. Based on Li et al. (2007), porosity decrease as the temperature increase [22].

4.1.2. Energy Dispersive X-Ray (EDX) Analysis

The outcome of the Energy Dispersive X-ray (EDX) Analysis detected the element of carbon, oxygen and calcium which are present readily in raw eggshell. This is only evident because chicken eggshell is composed by 95-97% calcium carbonate ($CaCO_3$) [23] [24]. The presence of carbon also indicates that eggshell is suitable to be manufactured as activated carbon [5].

Table 6: Element Analysis of Raw Eggshell

Element	Weight (%)	Atomic (%)
C	26.13	38.01
O	45.42	49.60
Ca	28.44	12.40

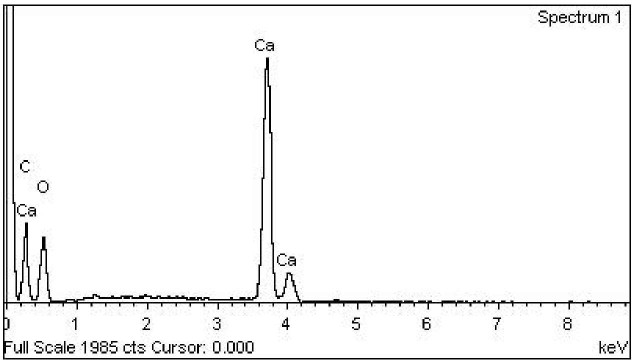


Figure 12: Electron Dispersion Spectrum of Raw Eggshell

Alternatively, the table below summarizes the result obtained from the Energy Dispersive X-ray (EDX) Analysis for the prepared samples

Table 7: Element Analysis of Carbonized Eggshell (weight %)

Elements	A1	A2	A3	A4	A5	A6	A7	A8	A9
C	18.78	27.43	21.81	12.07	10.11	22.47	3.90	10.05	9.35
O	55.04	72.29	62.31	40.37	32.03	64.82	20.73	54.37	47.58
Ca	32.55	32.46	34.01	30.33	21.31	33.32	22.85	32.97	33.02
P	-	-	-	-	-	-	7.79	16.97	17.96
K	0.42	0.47	0.44	0.21	0.27	0.65	-	-	-

As can be seen in the result tabulated above, some samples show additional elements like potassium (K) and phosphorus (P). This is due to traces from the impregnating agents are still in the activated carbon. However, the traces can be removed by washing the sample with distilled water thoroughly.

4.1.3. Surface Area And Porosity Analysis

Table 8: Surface Area and Porosity Analysis Result

Sample Code	BET Surface Area, S_{BET} (m^2/g)	Total Pore Volume, V_T (cm^3/g)	Average pore diameter, D (nm)
RAW	2.1384	0.0096	18.10
A1	3.1033	0.0067	10.58
A2	0.1505	0.0035	27.27
A3	3.5922	0.0087	14.30
A4	4.5075	0.0120	17.52
A5	0.2951	0.0139	36.46
A6	0.7447	0.0123	51.17
A7	57.0687	0.2796	18.68
A8	51.4612	0.2865	21.56
A9	38.8332	0.2883	25.88

The table above shows the result of the analysis obtained from Micromeritics ASAP 2020. The result shows that sample A7; which is prepared using phosphoric acid at impregnation ratio of 1:3 and activated at 400 °C and for 60 minutes; produces the largest BET surface area (S_{BET}) of **51.4612 m^2/g**, total pore volume (V_T**)** of **0.2865 cm^3/g** and pore diameter (D) of **18.68 nm**.

FACTORS AFFECTING SURFACE AREA AND POROSITY

Effect of Activating Time

In contrast, sample A8 which is prepared with the same conditions like sample A7 except that it is activated for 90 minutes shows a decrement in S_{BET}. This is probably caused by longer exposure to heat energy resulting in knocking and breaking of some porous wall [20]. Aside from that, prolonged activation will cause over activation, causing the surface erosion to accelerate. This is further supported by the samples like A2 and

A3and A5 and A6. Samples A2 and A5 are activated at longer time while maintaining the other activating conditions as compared to samples A3 and A6, which resulted to lower S_{BET} value.

Effects of Activating Agent

The effect of different activating agents can be seen through samples A5and A8, A6 and A7 and A3 and A9. These pairs of samples are activated at the same ratio, temperature and duration however, different activating agents, namely KOH and H_3PO_4. The results shown that the S_{BET} is higher for samples activated using H_3PO_4. This can be due to H_3PO_4 molecules are converted into phosphorus-containing constituents such as polyphosphoric acid ($H_{n+2}P_nO_{3n+1}$) and H_2O [25] that accelerate the carbonization of volatile components, resulting in the increment of porosity, as shown in the equations below [26].

$$nH_3PO_4 \rightarrow H_{n+2}P_nO_{3n+1} + (n-1)\,H_2O$$

$$\text{-----C---OH} + H_3PO_4 \rightarrow \text{------C----O-----PO}\,(OH)_2 + H_2O$$

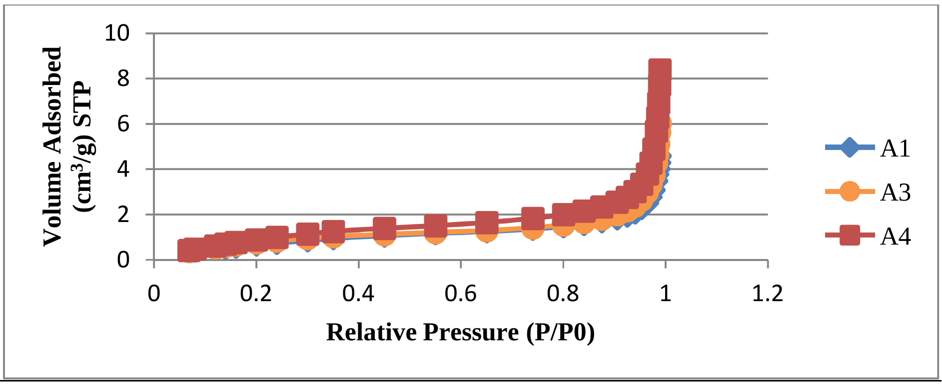
Effects of Activating Ratio

Activating ratio is an important aspect in the formation of pores. Due to the intercalanation of the metal atom into the carbon structure, the pores of the activated carbon are developed [27]. Although the higher the activating ratio will promote more pore formation [28], there is a maximum amount of metal atom that can be uptake by which when the limit is reached, the pore formation will reduce. In the case of activating carbon impregnated with KOH, the excessive amount of KOH will generate excessive reaction between KOH and carbon, hindering the pore formation [29]. This can be proven with samples A1 and A2 and A7 and A9.

Effects of Activating Temperature

In the experiment, the activating temperature is varied by 400 °C and 500 °C which has been reported to be the range of optimum activation temperatures [30]. At activation temperature of 400 °C, the developing rudimentary of activating carbon pores were formed by removing the low molecular weight volatile compounds from the matrix structure. When the temperature is increased to 500 °C, the removal of molecular is further enhanced and new pores are created which finally results into the acceleration of porosity development of the activated carbon [20]. This is evident in the case of samples A1 and A5. The surface area of sample A1 is higher compared to A5 when the temperature is increased. However, when the activating temperature is further increased, results into knocking and breaking of some porous wall, consequently preventing the formation of pores.

N_2 ADSORPTION DISTRIBUTION



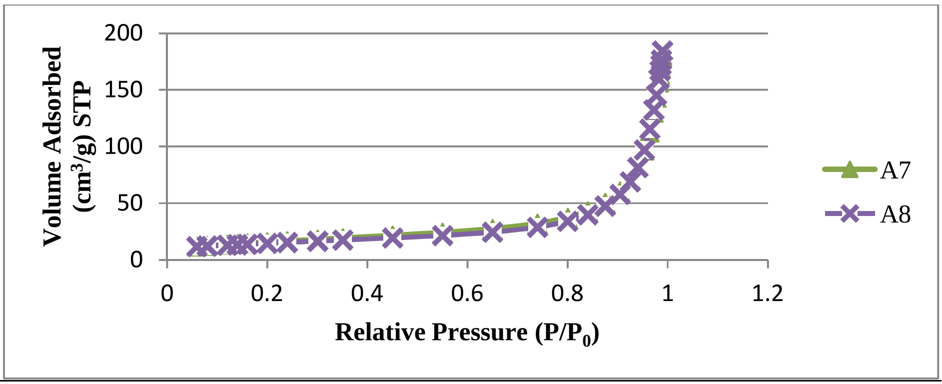


Figure 13: Nitrogen Adsorption-Desorption Isotherm for Samples A1, A3, A4, A7& A8

Figure 13 above displays the nitrogen adsorption-desorption isotherms for samples A1, A3, A4, A7 and A8. The volume of N_2 adsorbed is plotted against the relative pressure (P/P_0) of N_2. The isotherm obtained will be compared with the IUPAC classification of adsorption isotherm to find the fit in order to satisfy the adsorption analysis. The rule is that the adsorption isotherm should at least fit one or combination of the six distinct isotherm graphs [31].

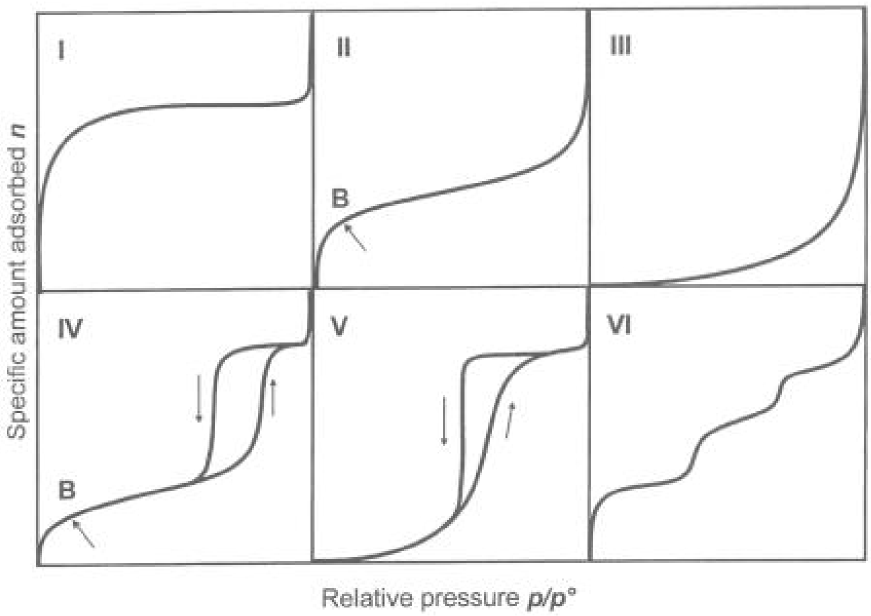


Figure 14: Classification of Adsorption Isotherms Defined by IUPAC

From the graph, it can be observed that samples A1, A3 and A4 fit a combination of type II and type III isotherms. Type II isotherm specifies that unlimited layer formation after completing the monolayer is observed with various pore dimensions in the adsorbent. Furthermore, the isotherm also refers to adsorption in non-porous adsorbents, but type II does not show saturation limit.

Isotherm type III, on the other hand, also displays characteristics of non-porous materials and materials which have the weak interaction between the adsorbent and adsorbate. As a result, isotherm types II and III are closely related to the gas-solid adsorption of carbon based material with meso- to macro porosity in which samples A1, A3 and A4 fall into.

For samples A7 and A8, the adsorption isotherms begin to change considerably, adopting type III isotherm. At this condition, the mesopores have been developed, observing from the upward increment which is often associated with presence of slit-shaped mesopores [32].

4.2. COMPARATIVE ANALYSIS: ADSORPTION OF OIL AND GREASE USING EGGSHELL

Based on previous studies [33] of oil and grease removal using adsorbents, the following results were obtained to compare the characteristics to the activated carbon produced from eggshell.

Table 9: Adsorption Capacities of Bio-adsorbents

Adsorbents	Surface area (m^2/g)	Porosity (%)	Adsorption Capacity (%)
M. rouxxi	20.55	85	93
A. coerulea	0.68	60	91

It can be seen from the figures tabulated in Table 9 that M.rouxxi has the highest adsorption capacity. It was found out that adsorbent with higher surface area is able to facilitate the adsorption of oil [34]. Besides that, high content of chitosan was found in the composition of M.rouxxi which is found to assist the oil removal.

When the surface area of adsorbents obtained from this previous study is compared to the result obtained by this study, it can be deduce that eggshell also have the capability of removing oil. The surface area obtained with the activated carbon from eggshell is in the range of the surface area values of the previous study.

Besides that, the adsorption capacity can also be manipulated by varying the parameters like pH, quantity of adsorbent loading, mixing speed, and mixing time [35].

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1. CONCLUSION

In a nutshell, this project deals with finding alternative method of producing adsorbant using bio-degradable materials which is more environmental friendly and cost efficient. Manufacturing activated carbon using eggshell can also be seen as a method of reusing waste product and turning it into a value-added product. Aside from that, eggshell also is found to be suitable to be made into activated carbon due to carbon readily present in it.

Parameters for instance, activation time, activation temperature, impregnation ratio and impregnation agent play a major role in the porosity of the eggshell. It was found that the impregnation done using H_3PO_4 produces larger surface area due to conversion of H_3PO_4 molecules into phosphorus-containing constituents accelerates the carbonization process. The higher ratio of impregnation is also preferable since it will promote pore formation. Additionally, the best temperature range to use when producing activated carbon is between 400 °C to 500 °C.

Based on the analysis done, it was found that activated carbon A7, which has been impregnated with H_3PO_4 at ratio of 1:3, and activated at temperature of 400 °C for 60 minutes yield the largest surface area and pore volume at **51.4612 m^2/g** and **0.2865 cm^3/g** respectively. Besides, sample A7 also fit into type III adsorption isotherm which indicates mesoporosity.

5.2. RECOMMENDATION

As a recommendation, more waste materials or biomass should be studied to examine the feasibility to be generated into activated carbon. Activated carbon that is made from different waste materials will result into different adsorption capacity and preference in adsorbant. Therefore, it can be an interesting to manufacture something out of waste material and producing a valuable material.

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