

**SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING  
UNIVERSITI SAINS MALAYSIA**

**Reactivation, oxidation and surface functionalization of spent  
activated carbon for glycerin decolourization.**

By

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**Dissertation submitted in fulfillment  
of the requirements for the degree of Bachelor of Engineering with  
Honours**

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## DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Reactivation, oxidation and surface functionalization of spent activated carbon for glycerin decolourization**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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## LIST OF ABBREVIATIONS

AC	Activated Carbon
SAC	Spent Activated Carbon
RAC	Reactivated Carbon
OSAC	Oxidized Spent Activated Carbon
ORAC	Oxidized Reactivated Carbon
FORAC	Functionalized Oxidized Reactivated Carbon
FRAC	Functionalized Reactivated Carbon
DI	Deionized water
VF	Volumetric Flask
RT	Room Temperature
FTIR	Fourier transform infrared spectroscopy
XRD	X-ray diffractometry
SEM	Scanning electron microscopy

## LIST OF SYMBOLS

$2\theta$	Angle of Diffraction
%	Percentage
wt %	Weight Percent
$^{\circ}\text{C}$	Unit of Temperature on Celsius Scale
g	Gram
kg	Kilogram
mg	Milligram
L	Liter
nm	Nanometer
SG	Specific Gravity

# **PENGAKTIFAN SEMULA, PENGOKSIDAAN DAN FUNGSIONALISASI PERMUKAAN KARBON YANG DIBUANG UNTUK PENJERAPAN WARNA GLISERIN.**

## **ABSTRAK**

Selepas penggunaan berterusan dalam proses penjerapan, karbon teraktif (AC) yang habis diguna akan menjadi tepu. Ini menyebabkan AC tidak dapat menjerap dengan berkesan. Dalam penyelidikan ini, karbon teraktif yang tepu akan diguna semula menjadi penyerap yang berguna melalui proses pengaktifan semula, diikuti dengan proses pengoksidaan dan fungsionalisasi kepada karbon-karbon tersebut. Pengoksidaan permukaan karbon teraktif semula untuk meningkatkan kapasiti penjerapan dari karbon yang diaktifkan semula (RAC) . Pengoksidaan karbon teraktif dilakukan dengan menggunakan kimia pengoksidaan  $\text{HNO}_3$ . Pengfungsian karbon dari karbon diaktifkan semula dan karbon dioksidasi diperkenalkan melalui rawatan hidrofobik, untuk pembentukan dekolourisasi gliserin yang lebih baik. Etilamina (EA) digunakan dalam rawatan hidrofobik. FTIR dilakukan terhadap karbon yang disediakan untuk menlampirkan bon  $\text{COO}^-$  dan  $\text{CN}$  berfungsi terhadap karbon. Penjerapan gliserin dinilai sebelum dan selepas karbon menjalankan pengfungsian hidrofobik. Fungsionalisasi terhadap karbon meningkatkan penjerapan karbon terhadap produk gliserin sekitar 2.1%. Selain itu, perbandingan prestasi dekolourisasi gliserin dilakukan antara sampel industri dan sampel makmal yang dilakukan. Sampel makmal menunjukkan hasil yang lebih baik daripada sampel industri sebanyak 4.6%.

# REACTIVATION, OXIDATION AND SURFACE FUNCTIONALIZATION OF SPENT ACTIVATED CARBON FOR GLYCERIN DECOLOURIZATION.

## ABSTRACT

After continuous use in adsorption process, the spent AC will be saturated and unable to remove targeted adsorbate effectively. In this research, spent activated carbon was reconverted into useful adsorbent via a re-activation process, followed by oxidation and functionalization process to the carbon materials. Oxidation of the surface of reactivated carbon was carried out to further improve the adsorption capacity of the reactivated carbon. Oxidation of activated carbon was done with using chemical oxidation of  $\text{HNO}_3$ . Functionalization of the reactivated and oxidized carbon was introduced through hydrophobic treatment, for better glycerin decolourization. Ethylamine (EA) was used in the hydrophobic treatment. FTIR was done toward all carbon material to conclude the presence of functional group of  $\text{COO}^-$  and CN bond. The adsorption of glycerin product was evaluated before and after the hydrophobic functionalization. Functionalization improved carbon adsorption of glycerin product by around 2.1%. Besides, performance comparison of was decolourization was conducted between industrial sample and lab sample was done. Lab RAC shows better result then industry sample by 4.6%.

# CHAPTER 1

## INTRODUCTION

### 1.1 GENERAL INTRODUCTION

Spent activated carbon (SAC) is produced from AC that has remove targeted contaminant through continuous adsorption process. After certain duration of services, eventually AC will become saturated and unable to remove targeted contaminant effectively (Guo and Du, 2012). SAC is considered a waste and has very little commercial value. The accumulation of the spent activated carbon causes serious environmental issues and huge amount of money is spent on the proper disposal of this waste. Therefore, conversion of SAC into useful adsorbent via reactivation process (Siemens Water Technologies, 2007). This is a more economical and eco-friendly solution to handle the waste.

Reactivation is the best option to produce cost-effective AC adsorbent. The reactivation of SAC is usually done using physical, chemical or both physicochemical regeneration methods. The effect of reactivation temperature, time and flow rate can be studied, in order to obtain best-reactivated carbon (Samonin et al., 2013). Although reactivation is very useful and cost-effective, however, reactivation causes mass loss, volume loss, and loss of apparent density to the SAC (Chestnutt et al., 2007). Moreover, not all metals and organic halogens can be completely burnt off in reactivation process (Cabotcorp, 2016). These would eventually affect the adsorption functionality and capacity of the reactivated carbon (RAC).

Oxidation of RAC an effective approach is to improve adsorption functionality of reactivated carbon. Oxidation of reactivated carbon is to introduce oxidation surface onto the RAC (Jaramillo et al., 2010). Oxidation methods involve many different methods, such as utilization of variation oxidizing gases. However, the oxidation may also produce changes toward porous structure of RAC which may affect its adsorption behavior. Therefore research aiming at oxidizing the surface chemistry of RAC may need to obtain the knowledge of the porous structure.

On top of RAC oxidation of RAC, other functional group can be added to the RAC before and after oxidation. Functionalization of AC to produce AC with hydrophobic surface (HAC) might improve the glycerin decolourization performance compare to basic RAC. HAC is mechanically robust with highly hydrophobic characteristic, molecules with large hydrophobic groups can be strongly adsorbed onto carbon surface (Bhatnagar et al., 2013). From other studies, basic RAC adsorption is different from removing organic compounds. Superior contaminant removal rates and the adsorption capacities can be substantially boosted by functionalization of the AC with suitable functional group. For this reason, functionalization techniques were applied to improve the adsorption rate and waste removal capacity. Functional group is added selectivity to AC.

## **1.2 PROBLEM STATEMENTS**

Huge amount of SAC had generated annually and disposed of as a waste (Hjaila et al., 2013). As an environmental concern, changing regulations of the environmental problem and increasing cost of AC are the factors that cause reusing of AC. Reactivation



of SAC rather than traditional disposal methods, such as landfilling is done. Reactivation is generally considered cheaper than disposal. It is considered more environmentally friendly. Most importantly, reactivation is done toward SAC and forming a closed loop of AC chain. This will eliminate concerns of future liability. SAC can be converted into useful and efficient adsorbent via reactivation process. If reactivation is not done disposal of hazardous SAC might cause serious environment problem (Hamilton et al., 2012).

### **1.3 SCOPE OF RESEARCH**

In this study, recycling of SAC into new AC is carried out through reactivation. CO<sub>2</sub> gas reactivation process was studied to regenerate useful AC. Parameters such as temperature, time and CO<sub>2</sub> flow rate was controlled to obtain the best reactivation process. Characterization methods such as Iodine number test, Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA), X-ray Diffractometer (XRD), and Scanning Electron Microscope (SEM) were applied to study characteristics of the samples.

After determining the optimal parameter of reactivation carbon, oxidation and functionalization of the RAC were performed to improve the adsorption behaviour. The targeted functional group is embedded on the RAC surface. Oxidation and functionalization were performed to obtain the desired adsorption. Then SAC, RAC, ORAC, FORAC and FRAC were evaluated via glycerin decolorization adsorption process.

## **1.4 OBJECTIVES**

The overall objective of this study is to evaluate different types of carbon material as stated below.

1. To reactivate the SAC and characterize the SAC.
2. To carry out surface oxidation and functionalization to reactivated spent carbon.
3. To evaluate all the carbon samples with glycerin decolourization and compared with industrial RAC.

## **CHAPTER 2 LITERATURE REVIEW**

### **2.1 ACTIVATED CARBON (AC)**

Activated carbon (AC) is a special material filled with holes, voids, spaces, sites, pores, and etc (H Marsh and Rodríguez-Reinoso, 2006a). AC is an extraordinary porous carbonaceous solid material. AC had pores volume and large surface area. Although these pores are spaces of zero electron density, they possess strong van der Waals forces from the near proximity of carbon atoms that responsible for adsorption process. AC is used for adsorption purposes such as heavy metal removal, wastewater treatment, dye removal and air filtration (Harry Marsh and Rodríguez-Reinoso, 2006).

AC is carbon with a lot of porosity or can be explained by space being enclosed by carbon atoms. Carbon activation means the carbon atoms had been through activation processes such as thermal activation, chemical activation or etc. Activation is a process of making something operational on adsorption. The common structure in activated carbons is that they are all assemblies of defective graphene layers (H Marsh and Rodríguez-Reinoso, 2006b).

Fixed carbon come from everywhere in this world of flora. That is suitable for providing a porous carbon on carbonization in an inert atmosphere. However, most of the synthesized activated carbon is not capable of performing with the requirement of the industrial need (H Marsh and Rodríguez-Reinoso, 2006a). Commercial activated carbons are the result of continuous and intensive research and development towards applicable activated carbon. The availability of raw materials are very important to the availability

of internal pore volumes that associated with the right kind of porosity and surface chemistry (H Marsh and Rodríguez-Reinoso, 2006b).

AC is produced in different forms which are powdered activated carbon (PAC), granular activated carbon (GAC) and activated carbon fibers (ACF). The difference between them is the size and shape. PAC is a pulverized carbon with a particle size less than 0.18 mm. This results in the large external surface area with a small diffusion distance. GAC has irregular shapes of particle and sizes range from 0.2 to 5.0 mm. GAC is usually used in fixed bed adsorbers in continuous processes for the adsorption of gases and vapors (Wan Nik et al., 2006). ACF is a light porous carbon in fiber form with diameter ranged from 10-40  $\mu\text{m}$ . ACF has several advantages compared to PAC and GAC. These advantages are a large surface area, the high adsorption capacity of liquid and gas phase of adsorbates (Ko et al., 2002).

## **2.2 ACTIVATION PROCESS (THERMAL OR CHEMICAL)**

Activated carbon is produced by synthesized of carbon material by various method. The porosities of a carbon, as firstly done by traditional carbonization, are not sufficient enough to develop for most applications. Some improvement of carbon is a required step. This can be done in multiple ways involving the creation of further porosity, or even widening of existing porosity. Some modifications to the surfaces of porosities and also modifying the carbonization process may lead to further improvement. All activation reactions are heterogeneous use is made of either carbon dioxide or steam or mixtures of these two gases. The classical chemical kinetics of these gasification reactions are applicable and are set out.

### **2.3 SPENT ACTIVATED CARBON**

SAC is AC that is continuously used in adsorption application until it becomes exhausted and saturated. AC is “spent” when it has adsorbed so much contaminant that its adsorptive capacity severely depleted (Awaleh and Soubaneh, 2014). Depending on the situation, SAC is most likely to be dumped as a waste or used as a low-grade fuel to heat kilns (Chestnutt et al., 2007). Improper disposal of the spent activated carbon would cause serious environmental issues and affect the quality of lives. For examples from past research, improper disposal of spent activated carbon had caused environmental impacts. These impacts of SAC includes acidification potential (62%), ozone depletion potential (44%), human toxicity (64%), freshwater aquatic ecotoxicity (90%) and terrestrial ecotoxicity (92%), eutrophication (96%). One of the highest impacts is found to be the global warming potential (11.096 kg CO<sub>2</sub> eq/kg AC) (Hjaila et al., 2013). Thus, the spent activated carbon has to be disposed off with care to prevent pollution. One of the effective alternatives to handle the spent activated carbon is to reuse and recycle via reactivation process.

### **2.4 REACTIVATED CARBON**

Carbon reactivation is restoring spent activated carbon to a state of the adsorbent material bring back the adsorbing power to the carbon. Carbon reactivation usually causes carbon regeneration, by regenerating the pores in the carbon to restore the adsorbing power. There are various methods to reactivate spent activated carbon. SAC can be processed through various types of treatments to improve its physicochemical properties. All SAC waste can be regenerated using a chemical and thermal reactivation, which

enable organic contaminants to be removed as well as reactivate the carbon for reuse. This reactivation process can help the industry to minimize their waste disposal management to dispose off their SAC (Samonin et al., 2013).

Prior to reactivation, SAC is washed at intense agitation and the mixture is separated at regular time intervals by decantation modeling the industrial carbon washing process. SAC is regenerated by washing the carbon with an aqueous solution containing from 1 to 15 % by weight hydrochloric acid and from 0.5 to 3% by weight ammonium bi-fluoride for a period of time to enable removing the waste in carbon (Smith, David W. and Baadsgaard, Marinus J, 1979). In thermal reactivation process, the SAC is heated to temperatures around 800°C (Guo and Du, 2012). Adsorbed organics are thermally destroyed at high temperature. The RAC may have lower of adsorption capacity compared to fresh AC. This might be due to metals and organic halogens in the SAC that do not burn off in reactivation process that acts as an impurity (Cabotcorp, 2016).

For most reactivation process, the SAC is dried to remove excess moisture content. Drying is done around 150°C to remove excess water from the spent carbon (Gu et al., 1999). When the SAC achieve the desired moisture content, the SAC is then ready to heat up to the desired temperature. Moisture content is around 10-25% still left in the SAC. At this point, steam or CO<sub>2</sub> is injected into the system through pressure to remove the remaining water vapor and to “reactivate” the carbon. During this process, it is common to have carbon losses between 5-10% (Directo, 1980). Besides thermal reactivation, microwave regeneration of spent activated carbon is also used (Fang and Lai, 1996).

In the past research, carbon dioxide and steam reactivation develop the difference in microporosity. ACs prepared by carbon dioxide reactivation will exhibit a larger pores

volume. It will also have a narrower pores size distribution compare to steam activation carbon material. For carbons with high yield, there is some molecular sieving effect for 0.5-0.6 nm. However for AC, with around 80%yield the molecular sieving is lower in comparison to carbons prepared by steam activation (Molina-Sabio et al., 1996). As in lab scale, AC with larger micropore shows a better result in testing.

For chemical reactivation process, alkaline such as NaOH solution can be used to treat the spent activated carbon prior to reactivation. Then, the yield RAC is with cold distilled water to neutralize its pH and dried in a desiccator at 100–110°C. (Samonin et al., 2013).

Using RAC significantly reduces the volume of fresh AC is needed (Berner, 1999). The benefits of carbon reactivation are to the reduction of raw materials, transportation, cost, and eliminate handling.

## **2.5 REACTIVATION PROCESS**

### **2.5.1 Chemical Reactivation**

Chemical reactivation of AC is one of the methods to reactivate Spent activated carbon (SAC). These chemical reactivations of SAC involve in the co-carbonization with a chemical. There are multiple type chemicals, which often seen and frequently used, include phosphoric acid, zinc chloride and traditional method of alkaline salts.

Reactivation or activation using phosphoric acid ( $H_3PO_4$ ) (Molina-Sabio et al., 1995) are able to prepared by bulk carbon (particle size around 2.5 mm). Using bulk carbon with solutions of phosphoric acid of different concentrations to activate or reactivate the carbon. This degree of carbon reactivation is defined by the amount of

phosphorus that able to penetrate into the carbon. The phosphorus impregmented carbon is then heat treated under a flow of nitrogen gas at 450 °C. After heating, the carbon is washed until no reactant is present (Almansa et al., 2004).

There is some reactivation or activation process using zinc chloride( $ZnCl_2$ ) for activation (Caturla et al., 1991). Start with prepared bulk carbons of around 2 mm particle size by chemical activation of peach stones with zinc chloride. This degree of activation is evaluated from the amount of Zn impregmented into the carbon. Some heat treatment is carried out using nitrogen at 500 °C(Almansa et al., 2004).

Alkaline salts chemical reactivation process is a traditional method to co-carbonization of an organic carbon material, such as SAC. Alkaline salts such as potassium hydroxide or potassium carbonate result in enhanced porosity within the carbon material, leading to having good adsorption capacity. This chemical reactivation method is done on a mostly industrial scale with fast heating of carbon and alkaline salts mixture to about 750 °C. This leads to the explosive removal of the metal, with the production of extremely low density with high surface area due to the total destruction of structure in the spent AC. The carbon is as if the graphene layers of the structure had been individually separated, the carbon will form a good reactivated carbon.

### **2.5.2 Thermal or Physical Reactivation**

Thermal or physical reactivation mechanisms are most widely using carbon dioxide and water vapor relationships between carbon structure. Although SAC is mostly organic macromolecular system (H Marsh and Rodríguez-Reinoso, 2006b). Therefore, thermal reactivation will have carbonized to microporous carbons. That carbon might need to widen existing porosity to include wider micropores and some mesoporosity.



Furthermore, porosity within the carbon, which is closed to a specific adsorbate, can be improved to allow more access to larger adsorbate molecules (Bansal et al., 1970).

Carbon dioxide and steam are types of activating agents used in physical reactivation. It is advisable to compare the porosity developed by each one. Carbon dioxide and steam reactivations develop differences in microporosity. RACs prepared by carbon dioxide reactivation exhibit a larger micropore volume and a narrower micropore size distribution than those prepared by steam activation. For carbons with high yield, there is a molecular sieving effect for 0.5-0.6 nm, but for carbons, with around 20% burn-off the molecular sieving is much lower for carbons prepared by steam activation (Molina-Sabio et al., 1996). As in lab scale, activated carbon with larger micropore shows a better result in testing (Molina-Sabio et al., 1996).

For physical reactivation process, the SAC is dried to remove excess moisture content. Drying is done around 150°C to remove excess water from the spent carbon (Gu et al., 1999). When SAC achieve the desired moisture contents, it is then ready to be heated up to the desired temperature. Moisture content is around 10-25% left in the SAC after drying. At this point, steam or CO<sub>2</sub> is injected or inserted into the furnace through pressure to remove the remaining water vapor. This is to “reactivate” the carbon. During this process, it is common to have carbon losses between 5-10% (Directo, 1980). Besides thermal reactivation, microwave regeneration of spent activated carbon is also used (Fang and Lai, 1996).

## 2.6 ACTIVATED CARBON OXIDATION

Oxidation method is one of the most traditional modifications to made changes to carbon material into the oxidized state. Oxidation method is used to introduce carbon-oxygen functional groups in carbon material. There are many types of oxidation methods, such as utilizing of oxidizing gases. For example, gas such as oxygen, steam and carbon dioxide are used in oxidation, or sometime oxidizing solutions such as nitric acid, hydrogen peroxide and chlorine water. However, the oxidation of carbon material from the gas phase or liquid phase may produce changes in the porous structure of the material which may also affect its adsorption behavior. Besides, research aiming at oxidizing the surface chemistry of activated carbon must be coupled with a parallel study of the porous structure (Jaramillo et al., 2010).

The surface chemistry of carbon types materials is determined by the acidic and basic character of their surface. There is two type of oxidation method, dry method, and wet method. Wet method is more effective compared to dry method as the result of Jaramillo research with 2 co-workers (2010). Their oxidation methods involve the utilization of concentrated nitric acid ( $\text{HNO}_3$ ). However, the oxidation of AC from the gas phase or liquid phase may produce changes in the porous structure of the material which may also affect its behavior.

Using nitric acid is due to some excellence result past research that concentrated nitric acid is the most used oxidant. This is because oxidizing specifications can be controlled by both concentration and temperature (Boehm, 2002). Frequently, not only a single oxidant but more oxidants have been used in the treatment of a given carbon material. From past experiment, the treatments of carbon material with  $\text{HNO}_3$  result in the

formation of mostly carboxylic acid groups and most effectively. The content of basic sites greatly decreases for HNO<sub>3</sub> showing effective oxidation (Jaramillo et al., 2010).

## **2.7 OXIDIZATION METHOD**

Wet oxidation was the method that was using. The method to oxidize carbon material is used about 1 g of carbon material is oxidized with 100 mL of 5 N HNO<sub>3</sub> aqueous solutions until the HNO<sub>3</sub> dry up. In the case of the HNO<sub>3</sub> treatment, the solid and liquid known as oxidizing solution in the containing system will cause continuous agitation. This is only available with maintained under a reflux at boiling for a period of time. After the oxidation treatment, the mixture is separated by centrifuge and the residual solid is washed thoroughly with distilled water, oven-dried at 110 °C for 12 h, and stored in glass bottles (Jaramillo et al., 2010).

## **2.8 ACTIVATED CARBON FUNCTIONALIZATION**

Functionalization towards carbon material will attach different functional groups on its surface that include carboxyl, phenol, lactone, carbonyl, quinones and etc. The adsorption properties of these functionalized carbons are strongly influenced by the type and amounts of functional groups on its surface. The presence of these functional groups on carbon surface depends on the precursor materials, types of preparation conditions and activation methods used while functionalizing the carbon (Bhatnagar et al., 2013).

In general, the surface functionalization of carbon material is carried out after the activation or reactivation step, meaning that only after the carbon is activated. The modification can be classified into three categories, that is chemical functionalization,

physical functionalization and, biological functionalization. Before performing any surface functionalization to the carbon material, knowledge of various factors which influence the adsorption power of carbon material is studied. This functionalization step will help to tailor their specific physical and chemical characteristics to enhance its affinities towards a different type of adsorbing material present in aqueous solution (Bhatnagar et al., 2013).

## **2.9 FUNCTIONALIZATION METHOD**

Method of functionalizing is an ongoing process due to there is an infinite amount of way to produce various kind of functionalize AC material. Several conventional functionalization methods which have been studied to improve the adsorption power of carbon material for adsorbing the various type of material. These functionalize methods have been found to alter the pore structure of carbon in little or large extent. Furthermore, in those research acidic treatment of carbon material has been found promising for the higher uptake of metal ions, while base treatment of carbon material has shown good uptake of anionic species from aqueous solutions. However, some of the new functionalization methods include the treatment costs involved in the process, and leaching of the chemicals used in the functionalization process in the aqueous material that is being treated (Bhatnagar et al., 2013). Table 2-1 show the type of conventional functionalization method that had been researched.

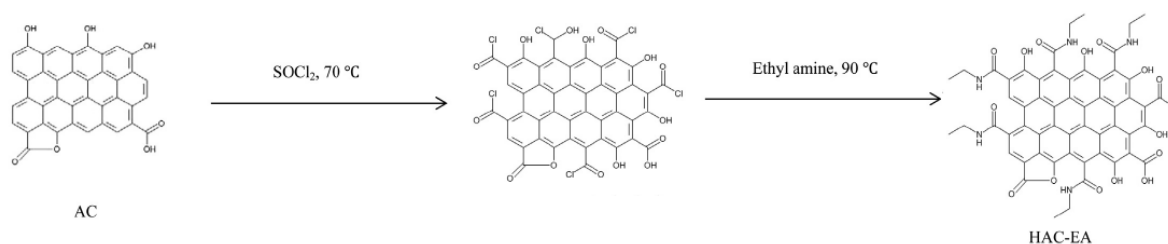
Table 2-1 Type of conventional functionalization method (Bhatnagar et al., 2013).

Treatment step	Main Results
Modified with tetrabutyl ammonium iodide (TBAI) and sodium diethyl dithiocarbamate (SDDC)	A total $\text{CN}^-$ removal was achieved using the TBA-carbon column with uptake capacity of 29.2 mg/g. Using SDDC-carbon column, Cu, Zn and Cr metal ions were removed with uptake capacity of 38, 9.9 and 6.84 mg/g, respectively
Oxidized with nitric acid, ammonium persulphate and hydrogen peroxide in the solution phase and with gaseous oxygen at 350 °C. The activated carbons were also degassed at different temperatures between 400 °C and 950 °C	Adsorption of Cr(III) increased on oxidation and decreased on degassing, while the adsorption of Cr(VI) decreased on oxidation and increased on degassing
Oxidized with a saturated solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 1 M $\text{H}_2\text{SO}_4$	Decrease in surface area and carbon porosity after oxidation, but Zn(II) uptake greatly increased
Oxidation with $\text{HNO}_3$	Carboxylic acid groups were the major surface species incorporated and phenol and quinone groups were introduced during oxidation process. Cadmium adsorption was dramatically enhanced after the carbon was oxidized
Heat treatment (1200 K) in nitrogen ( $\text{N}_2$ ), air oxidation (693 K), and nitric acid (6 N)	Oxygen surface complexes, possibly lactone and carbonyl groups, were the active sites for $\text{Hg}^0$ uptake
Heating from ambient temperature to 900 °C in $\text{SO}_2$ ; treatment at ambient temperature in $\text{SO}_2$ ; or successive treatments in $\text{SO}_2$ and $\text{H}_2\text{S}$ at ambient temperature	The amount of sulphur introduced was high when heated to 900 °C in $\text{SO}_2$ . Heating to 900 °C was found to be the most effective treatment, and the adsorption in this case was 70.3%.
Oxidation with nitric acid	Surface area and pore volume were reduced after oxidation treatment. The modified sample displayed cation-exchange properties over a wide range of pH values and exhibited polyfunctional nature.
Treated with $\text{HNO}_3$ and NaOH	Nitric acid oxidization produced positive acid groups, and subsequently sodium hydroxide treatment replaced $\text{H}^+$ of surface acid groups by $\text{Na}^+$ , and the acidity of activated carbon decreased. Adsorption capacity of Cr(VI) increased from 7.61 mg/g to 13.88 mg/g.
Treated with 1.0 M citric acid, followed by an optional step of reaction with 1.0 M NaOH	Surface modification reduced the specific surface area by 34% and point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of the carbon by 0.5 units but increased the Cu(II) adsorption capacity to 14.92 mg/g, which was 140% higher than the unmodified carbon
Ammonia-modification	Increased adsorption capacity for 2,4-DCP from 232.56 to 285.71 mg/g (22.86% higher)
Treatment with gaseous ammonia from 400 to 800 °C	Adsorption capacity toward phenol was enhanced by as much as 29% at the optimum treatment temperature (700 °C)
Modified by high temperature helium or ammonia treatment, or iron impregnation followed by high temperature ammonia treatment	Iron-impregnated and ammonia-treated activated carbons showed significantly higher dissolved organic matter uptakes than the virgin activated carbon
Impregnation of AC with iron followed by high temperature ammonia treatment	DOM uptake enhanced about 50–120%
Impregnation with an aluminium nitrate solution, followed by calcinations in an inert environment at temperatures above 300 °C	Fluoride adsorption capacity increased of three to five times higher than that of virgin AC
Microwave treatment under $\text{N}_2$ atmosphere	Enhanced adsorption of methylene blue caused mainly by the enlargement of the micropores
Ozone treatment	Mercury sorption increased
Oxygen plasma treatment	Oxygen functional groups were increased after the plasma treatment, however, a slight decrease of specific surface area was shown
Modified with tris(hydroxymethyl)aminomethane	Adsorption capacity of Au(III) onto AC-TRIS was 33.57 mg/g at pH 1.0

In this research, hydrophobic functionalization is done on AC is the most productive way to produce effective functionalized AC. By checking different type of conventional method and availability of chemical, hydrophobic functionalization using ethylamine are reliable toward glycerin decolourization.

To prepare hydrophobic activated carbons (HACs) via functionalization method, dry carbon material is allowed to react thionyl chloride in toluene under reflux. The product is immediately mixed ethylamine (EA) and the mixture is kept under reflux. The mixtures are then purified via Soxhlet extraction followed by washing with deionized water and HCl is carried out to remove residual amines from carbon surface. Finally, the carbon is thoroughly washed with deionized water to remove residual acid. The carbon is allowed to dry in an oven under vacuum until constant weight is reached (El-Shafey et al., 2016). Figure 2-1 shows the chemical structure change in this functionalization.

Figure 2-1: The chemical structure change in this functionalization (El-Shafey et al., 2016).



## 2.10 GLYCERIN COLOUR AND FUNCTIONAL GROUP

Colour of the glycerin compound is due to carotenoids and some other pigments. Usually a little of beta-carotene will show the oranges color. In nature beta-carotene is a type of precursor to vitamin A. carotenoids adsorb wavelengths from the range 400-550 nanometers (violet to green light). Carotenoids then showed deeply colored yellow, orange, or red. Carotenoids are a type of pigment that provides yellow pigment that as shown in the Figure 2-2 (Armstrong and Hearst, 1996). There are over 600 known carotenoids, mostly the carotenoids are separated into two classes, xanthophylls (which contain oxygen) and carotenes (which are purely hydrocarbons and contain no oxygen). Therefore, carotenoid in glycerin compound will give a bridge colour. As using reactivated carbon, the carotenoids is the targeted compound to be removed. In the glycerin decolourization test, carotenoids is the key for AC to removed. Figure 2-2 shows the pigment that forms in carotenoids that enable us to see yellowish orange color (Chichibabin, 1957).

In the industry, glycerin and fatty acids and other components, of the crude glycerol were reduced by adsorption with commercial activated carbon. Next, the AC was dried to eliminate free moisture, In the adsorption stage, activated carbon was mixed with refined crude glycerol and then subjected to vacuum filtration to remove the AC. Then the decolourized glycerin is produced (Manosak et al., 2011).

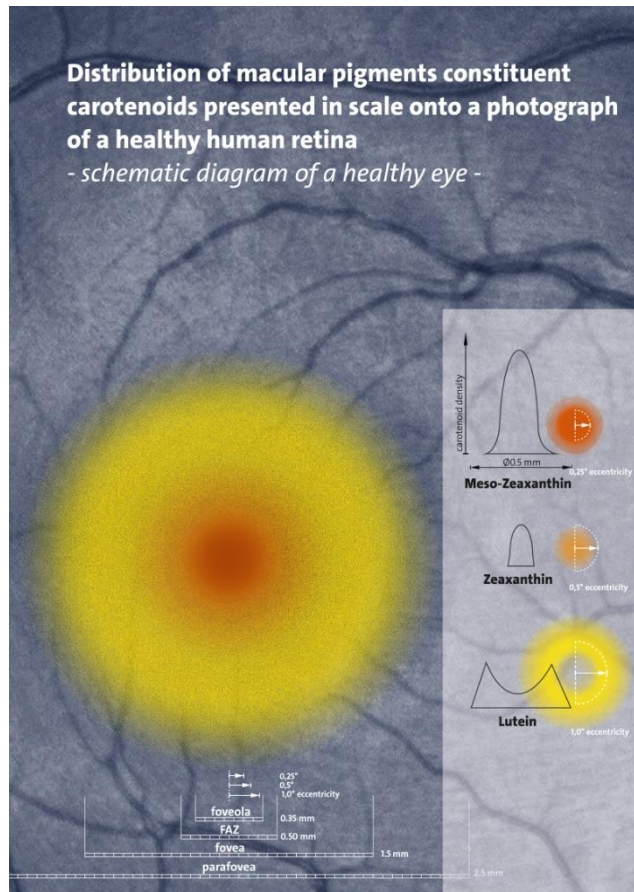


Figure 2-2: The pigment that forms in carotenoids (Chichibabin, 1957).

Besides, glycerin is organic compound arises by oxy-species groups consisted of chromophores. However, chromophores maybe chemical group that responsible for the color of the compound. Besides, the yellow color of in carotenoids, maybe due to the compound carotenoid may have quinone that providing the colour yellow. This proves that mostly the color of the glycerin compound is come from inside the carotenoid.

In some research, the quinone has a high color index and coloring power. It absorbs the blue region of the visible spectrum  $\Delta\lambda=4350-4800\text{\AA}$  and emits efficiently in the yellow region  $\Delta\lambda=5500-5850\text{\AA}$  (Chichibabin, 1957).



## **2.11 IODINE TEST**

Iodine test is a type of adsorption test. It is based upon a three-point adsorption isotherm (ASTM D 3860). Iodine solution is prepared and is treated with different kind of carbon material that had synthesized under specified conditions. The carbon material is then treated with iodine solutions. Next, carbon is filtered and iodine solution to separate the carbon from the treated iodine solution (filtrate).

Next, the iodine solution that left remaining during filtered in the filtrate is measured using titration method. The amount of iodine compound removed is calculated based on per gram of carbon. The calculation also is determined by the amount of carbon that is being treated. The amount of iodine adsorbed (in milligrams) by the carbon per gram during titration are the concentration that reported as the iodine number.

The initial iodine concentration needs to be standard solution. This is due to it might affect the capacity of an activated carbon for iodine adsorption. Therefore, the normality of the iodine solution must be standardized and maintained. In this experiment, few apparatus required, it consists of various types of laboratory glassware used to prepare solutions and contact carbon with the standard iodine solution. As for the filtration and titration equipment are needed in this experiment as well.

## **2.12 SOXHLET EXTRACTION**

Sample preparation for Soxhlet extraction is a necessity as it might be complex to use soxhlet extractor. Soxhlet extractor is mostly done for washing purposes. Therefore, soxhlet extraction is done to remove excess chemical in the carbon, to wash the chemical repeatedly. After each cycle of soxhlet extractor, some solvent of the non-volatile

compound such as acetone will than dissolves in the carbon. Soxhlet extraction will be done in multiple cycles, the desired compound to be removed is concentrated in the distillation flask. Soxhlet extraction having the advantage of using instead of huge amount of solvent being passed through the sample, just one batch of solvent is recycled and reused. Therefore, this extraction method is able to reduce large amount of solvent used. Figure 2-3 show soxhlet extraction method (Harwood and Moody, 1989).

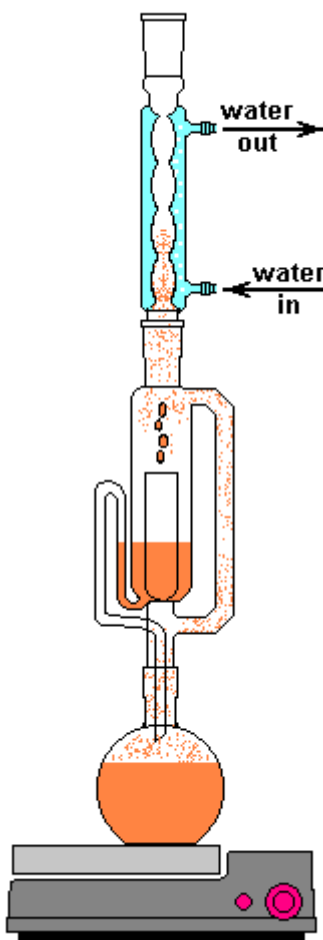


Figure 2-3: Soxhlet extraction (Harwood and Moody, 1989).

## **CHAPTER 3 METHODOLOGY**

### **3.1 REACTIVATION OF SPENT ACTIVATED CARBON**

The sample material is produced from fresh activated carbon that is spent in the industry. The spent activated carbon is then received from the industry (Acid Chem). SAC is then ground for 10 minutes using an agate mortar sieved to around 325 mesh size powder form. The spent carbon is used in multiple types of testing, such as SEM, FTIR, Iodine Test, XRD and TGA-DSC.

The collected SAC is then reactivated through CO<sub>2</sub> reactivation. It is first dried to remove excess moisture content and constant weight is obtained. Then the sample is weighted to obtain the weight before reactivation. After weighing, the sample is placed into the tube furnace for CO<sub>2</sub> reactivation. CO<sub>2</sub> reactivation is chosen due to is able to produce larger micropore. After reactivation, the sample is received and weighted to find the yield of the reactivation of carbon. Using different parameters such as temperature, soaking time and CO<sub>2</sub> flow rate. The best reactivation parameters are determined.

#### **3.1.1 CO<sub>2</sub> Reactivation Process**

Spent activated carbon (SAC) is weights using electric balance (Entris Sartorius) to obtain 16 g of samples. The samples are then transferred into tube furnace (MTI Corporation OTF-1200X). The cap of tube is then screwed until it is tightened. N<sub>2</sub> gas then flows pass the samples in the tube furnace for 2 minutes to ensure no other gas in the tube that will cause a reaction. CO<sub>2</sub> gas is purge on the soaking time, while N<sub>2</sub> purge in

the quartz tube furnace for heating and cooling time. The heating curve pattern was then computed on the furnace as shown in the Figure 3-1.

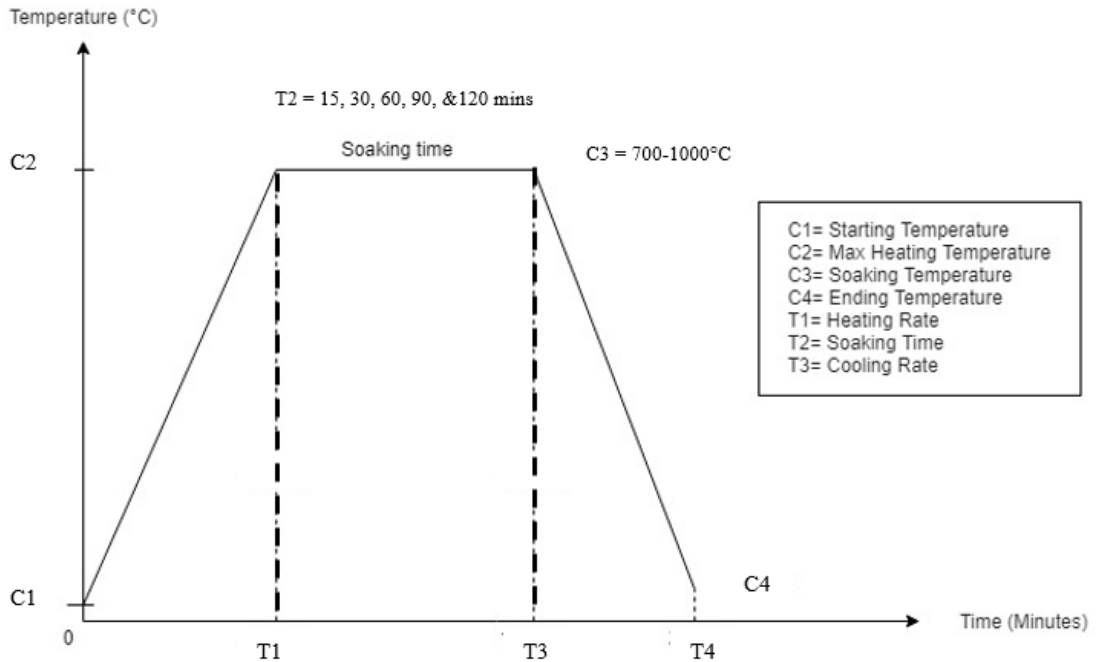


Figure 3-1: Heating rate and cooling rate of the furnace is set to 10°C per minute.

To obtain the best-reactivated carbon from carbon dioxide reactivation process, the parameter is optimized. Based on parameters such as time and temperature, the results will be summarizing into a table. Table 3-1 show the summarized table for reactivation process.

Table 3-1: Reactivation process summarize graph.

Sample	Soaking time with temperature (700°C/800°C/900°C /1000°C/1100°C)				
	15minutes	30minutes	60minutes	90minutes	120minutes
700°C	15 A	30 A	60 A	90 A	120 A
800°C	15 B	30 B	60 B	90 B	120 B
900°C	15 C	30 C	60 C	90 C	120 C

Starting with the first parameter, soaking time is fixed to 1hour and with different temperature variable of 700°C, 800°C, 900°C, 1000°C and 1100°C. All the samples measured is then treated with Iodine Test (Chapter 3.4.5) to obtain the best adsorption vs yield of the sample. The iodine number vs yield is then plotted into a graph. The optimum sample will be used as fix variable in the next parameter.

For example, 800°C is the optimum temperature, 800°C is set at a fixed temperature and soaking time varies from 15minutes to 2 hours. The parameter is set to 15, 30, 60, 90 and 120minutes. Then, the sample obtained is then treated with iodine test to obtain the best adsorption compared with yield carbon materials.

After the testing is done, the best parameter for both temperature and soaking time is then set as the best reactivation of SAC.

### 3.2 ACTIVATED CARBON OXIDATION

Oxidation of SAC & RAC is carried out to improve their adsorption characteristic and introduce of functional group. SAC and RAC surfaces were heated in the presence of concentrated  $\text{HNO}_3$  (16.9M) with the ratio of 1 g of carbon to 10ml of  $\text{HNO}_3$  at  $80^\circ\text{C}$ . The carbon was boiled until almost dry to produce oxidized spent carbon and oxidized reactivated carbon using water bath. The oxidized samples were washed thoroughly until no acidity using deionized water. the product is dried at  $100^\circ\text{C}$  until constant weight is achieved. Figure 3-2 illustrates the changes of the functional group to the carbons.

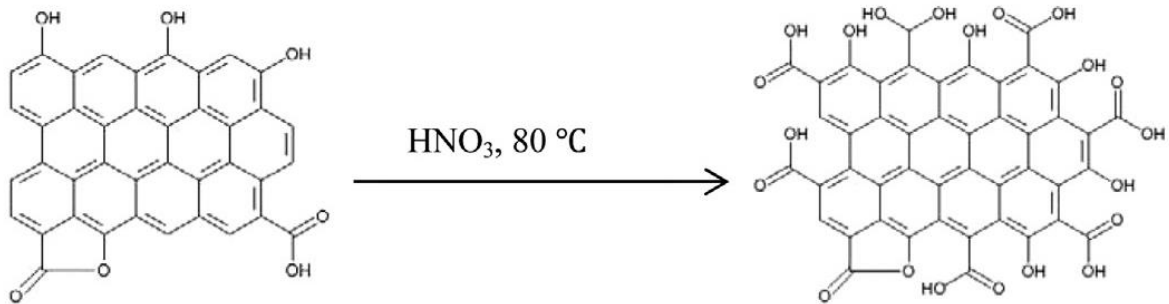


Figure 3-2: oxidation of carbon that changes the functional group to the carbons(El-Shafey et al., 2016).

5g of RAC and SAC is weighed using an electronic balance (Entris Sartorius). The sample is then placed in a small beaker. The beaker was then placed in a water bath. When the temperature reached  $80^\circ\text{C}$ , 50ml of concentrated  $\text{HNO}_3$  is poured into the beaker with carbon sample. The heating continued for around 3hours until the almost dry to produce OSAC and ORAC in slurry form. The setup is shown in Figure 3-3.