

## Carbonization of Sulfuric-Acid-Impregnated Honeydew Rind for Metal Removal Application in Wastewater Treatment

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**Abstract:** In this study, honeydew rind a fruit waste was converted into activated carbon adsorbent as a potential metal removal from aqueous solution application. The waste was impregnated with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) 10% v/v prior to carbonization. The effects of carbonization temperature of 470, 490, 510 and 530°C on the development of pore surface were examined. The surface morphology and textural properties of produced ACs were characterized using surface analyzer and Field Emission Scanning Electron Microscope (FESEM). Percentage of yield (79.23%) and ash content (6.20%) were determined for each adsorbent produced adsorbent produced at optimal carbonization temperature of 510°C. Surface textural analysis demonstrated comparable surface area of 429.16 m<sup>2</sup>/g. FESEM micrograph showed the metal compound was infused into the pores after adsorption. This is evidently indicated by shiny and occupied pores compared to micrograph images before adsorption. This study has proven that honeydew rind, a non-value material can be transformed into an organic adsorbent with promising adsorbent characteristic and has a high potential to replace current commercial AC precursor.

**Key words:** Activated carbon, adsorption, honeydew rind, sulfuric acid, current commercial, surface textural

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### INTRODUCTION

With the affect of rapid growth in industrial sector felt worldwide, heavy metal pollution caused by the disposal of industrial effluent has become a significant issue of concerned. In this study, the researchers have discovered Zn(II) as an example of the heavy metal compound which contains a high concentration of effluent at (Gupta *et al.*, 2015). The metal is a form of production residue that is commonly found in effluent concentration with other production wastes. Metal production and fabrication industries are among major contributors to the accumulation of dangerous pollutant (Roney and Osier, 2005). Permittable recommended daily dose of Zn(II) for men, women, children and infant is 15, 12, 10 and 5 mg, respectively (Roney and Osier, 2005). The presence of heavy metals in the effluent is due to excess metal loads in the production.

The concentration of the pollutant life gradually accumulates in water sources. Consequently, this becomes a threat to nearby housing areas and aquatic area nearby and aquatic life. This sparks a health warning due to its harmful effects towards human internal organs

as well as to aquatic life. In addition, the behavior of polluted water bodies is difficult to control. Its mobility eventually drives the public interest on the treated metals. Therefore, the need for proper, efficient and cost effective method of heavy removal from industrial waste water is critical to reduce the level of metal ions concentration in water bodies and eventually reduce the harmful health effects toward human beings and aquatic lives.

The most common wastewater treatment employed in heavy metal removal are membrane separation, ion exchange, bioremediation, chemical treatment and adsorption (Ajemba, 2013). Although, these techniques have been applied in wastewater remediation for decades, the processes have also created large volume of dangerous chemical waste. Besides that they are time-consuming and involve tedious technical operations. A number of researchers on this topic have come to a conclusion that there is still a lack of efficient methods for metal ion removal in wastewater (Gupta *et al.*, 2016). Among the methods highlighted, it has been quoted that adsorption is the most practical and preferred technology in wastewater treatment due to its efficacy.

Currently, adsorption technology employs AC where its precursor originated from costly natural materials such as coconut shells and coal. A high demand for the current precursor material and depletion of the source of materials has caused a tremendous rise in its market value. This circumstance has caused total adsorption operational to become less cost effective. Therefore, the challenge in running adsorption in removing metal ions is to use an alternative adsorbent due to cut its cost of operational costs. Thus, numerous studies have been conducted to find other alternative activated carbon precursor apart from coconut kernel (Sun *et al.*, 2016; Abdullah and Sulaiman, 2013; Wankhade and Ganvir, 2013; Ahmed, 2016). Contemplating massive production of agricultural wastes from various agricultural industries initiated an investigation on new agricultural-waste-based activated carbon. The waste has been chosen in the production of activated carbon due to its abundance in availability. In addition, this characteristic can reduce cost of waste management indirectly. Agricultural waste possesses advantages in chemical property content as it is a form of lignocellulosic material which contains high carbon content, adsorptive functional groups. Hence, it is suitable for activated carbon production (Abdolali *et al.*, 2014). Apart from that by converting the waste into an upgraded adsorbent the cost waste disposal could be reduced.

The present study has investigated the potential of Honey Dew Rind (HDR), a form of waste from a fruit juice industry to serve as an organic adsorbent for metal removal from aqueous solution. The objectives of the study were to analyse its physicochemical properties and optimize the carbonization temperature in the production of its activated carbon. This is to fulfill its criteria as an adsorbent in metal removal application.

## MATERIALS AND METHODS

**Chemicals:** Nitric acid 5% v/v solution was prepared from nitric acid (QRec) 65%. Various concentrations  $H_2SO_4$  was prepared from sulfuric acid 95% (QRec). A stock solution of Zn(II) was prepared from  $ZnSO_4 \cdot 7H_2O$  (Sigma Aldrich). A series of desired concentration solutions was prepared by diluting the the stock solution. In order to control pH level of solutions a micro-pipette (pH meter, Thermo Fisher scientific-Singapore) was used to manually add 1.0M NaOH and 1.0M HCl accordingly for pH adjustment. All chemicals used in this research were of analytical grade. In this research, all glassware and containers used in the experiments were immersed in 5%  $HNO_3$  solution in order to ensure all glassware and containers were free from existing metals. The cleansing procedure was carried out to three days before these glassware were soaked in

distilled water and oven-dried. Experimental research was repeated to three samples of each observation in order to obtain a triplicate data. Average values are reported based on the triplicate data (Othman and Asharuddin, 2013).

**Raw materials:** Honeydew rind was collected from restaurants, fruit shop and stalls located in Parit Raja, Batu Pahat, Malaysia. The fruit waste was immediately cleaned up to get rid of dirt and other visible forms of contaminant in the laboratory. The rind was then soaked in the nitric acid (5%) for 6 h to remove existing metal content in the rind. Distilled water was used to rinse off any possible residue of acid by immersing the rind a container filled with distilled water. This step took place for about 24 h to minimize the remaining acid in the rind. Finally, the rind was oven-dried at 60°C for 8 h and kept in a dry storage. This sample will be used as precursor in honeydew rind activated carbon production.

### Experimental works

**Impregnation:** Dried honeydew rind HDR was impregnated with sulfuric acid (10%) v/v for 6 h. Then the chemical was drained off and the HDR was oven-dried at 110°C.

**Carbonization:** Muffle furnace was used to carbonize the impregnated HDR. Firstly, the carbonization temperature was programmed at the rate of 5°C/min. It began at room temperature up till 300°C. At this temperature, the heat was maintained for 15 min to allow water and organic compounds to evaporate from the sample. Secondly the temperature was raised to the final temperature, at the tested temperature of 470-530°C. The sample was soaked at the final temperature for 30 min to complete the carbonization process. The carbonized HDR was cooled until it reached room temperature and kept in a tight glass container for further uses. Later in this study, carbonized HDR will be denoted as ACS in subsequent study in this study (Yunus *et al.*, 2015).

**Determination of yield and ash content:** Determination of ACS yield was calculated by dividing the mass of sulfuric acid impregnated-HDR sample before carbonization with the mass of sample after the carbonization process. The calculation used Eq. 1 (Silgado *et al.*, 2014). All the samples must be in dried form:

$$\text{ACS yield percentage} = \frac{W_f}{W_i} \times 100\% \quad (1)$$

In this analysis approximately 1 g of dried sample was weighed in a dry and clean beaker. The sample was heated in a muffle furnace at 500°C until it was completely

burned. This procedure took for 4 h. After that it was allowed to cool down in a desiccator. The following Eq. 2 is used to find weight loss and ash content (Silgado *et al.*, 2014):

$$\text{Percentage of ash in ACS} = \frac{\text{Weight of sample after heating process} \times 100\%}{\text{Weight of sample before heating process}} \quad (2)$$

Where:

$W_i$  = The mass of the dried sample

$W_f$  = The final mass of sample when the sample has cooled down

**Surface textural analysis:** Surface analyzer was employed to determine pore characteristic of ACS. The specific surface area and pore distribution of the activated carbon was measured by nitrogen adsorption-desorption isotherm determination with a multiple-point gas adsorption measurement (SA 3100 Surface Analyser by Beckman Coulter)) at 77 K. Brunauer, Emmet and Teller (BET) method was employed to determine the specific surface area at a relative pressure of 33.5 ATM. The micropore volume was calculated by using t-Plot micropore volume. Barrett-Joyner-Halenda (BJH) model was used to determine the distribution of pore size. Prior to the measurement, approximately 0.05 g all the samples were crushed and powdered to shorten the time required for reaching equilibrium sample was put into sample tube holder followed by evacuation at 373 K for 1 h (Anisuzzaman *et al.*, 2014).

**Field Emission-Scanning Electron Microscopy (FESEM):**

A field scanning electron microscope (JEOL-JSM 7600F, USA) permits the observation and characterization of heterogeneous organic and inorganic on nanometer to micrometer (Cordero *et al.*, 2013). Prior to the analysis, the samples were prepared by depositing the samples onto specimen stubs with conductive double sticky copper tapes. Then the sample was put inside the sputter for the purpose of coating the sample surface with Au-Pd to avoid any electrical charging during examination (Yakout and Deen, 2011). Platinum sputtering of each sample was conducted for 120 sec at 30 mA in a high vacuum until all the samples were completely covered before they were ready to be analyzed.

**Metal adsorption:** A known concentration of adsorbent was put in 250 mL conical flasks and allowed to have contact with 100 mL of aqueous solutions of required concentrations of Zn(II) at room temperature (25±1 °C). The solution was agitated using orbital shaker at 125 rpm at a constant pH. The mixtures were filtered to separate the adsorbent and filtrate was collected and kept in glass

sample bottles. The FESEM analysis was conducted to obtain micrograph of unloaded and loaded ACS to investigate any changes on the surface morphology of the adsorbent. This investigation is a pre-observation work which has been carried out in batch adsorption study for metal removal. However, the discussion of the whole study will be highlighted elsewhere (Yunus *et al.*, 2015).

**RESULTS AND DISCUSSION**

**Effects of carbonization temperature on the yield and ash content of activated carbon:**

Result of yield and ash analyses of ACS is presented in Table 1. The importance of yield and ash content information is related to the aspect of longevity and strength of an adsorbent. The carbon yield is defined as the weight of dried carbon to the weight of precursor. This yield strongly dependent on variables such as temperature and impregnation ratio (Ahmed, 2016). In this study, ACS has resulted higher percentage of yield at high carbonization.

A high carbonization temperature most likely affirms the data obtained from other researchers. The ash content however showed lower values but follows similar trend. The highest ash content was obtained by ACS4 which was carbonized at 530°C. This analysis indicated that 510°C is a suitable carbonization temperature to produce high yield (79.23%) and moderate ash content (6.20%).

**Effect of carbonization temperature on the pore texture:**

The surface textural investigation which includes specific surface area and porosity properties is important as they influence the characteristic of an adsorbent and its adsorption efficiency eventually. Table 2 shows the surface area,  $S_{BET}$ , micropores, mesopore and total volume of pores of ACS produced at particular carbonization temperature.

Table 1: Yield and ash content of ACS produced at different carbonization temperature

Carbon	Yield (%)	Ash content (%)
ACS1	21.92	4.36
ACS2	46.94	4.12
<b>ACS3</b>	<b>79.23</b>	<b>6.20</b>
ACS4	36.02	7.59

ACS1 = Carbonized at 470°C, ACS2 = Carbonized at 490°C, ACS3 = Carbonized at 510°C, ACS4 = Carbonized at 530°C

Table 2: Textural properties of ACS

Carbon	$S_{BET}$	$V_{micro}$ (mL/g)	$V_{meso}$ (mL/g)	$V_{total}$ (mL/g)
ACS1	327.37	0.02	0.25	0.27
ACS2	411.63	0.05	0.34	0.39
<b>ACS3</b>	<b>429.16</b>	<b>0.04</b>	<b>0.28</b>	<b>0.32</b>
ACS4	401.58	0.06	0.33	0.39

ACS1 = Carbonized at 470°C, ACS2 = Carbonized at 490°C, ACS3 = Carbonized at 510°C, ACS4 = Carbonized at 530°C

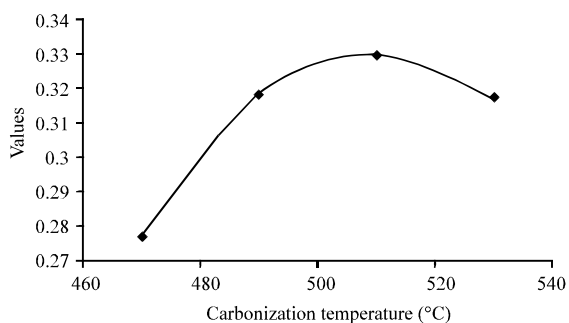


Fig. 1: The influence of total pore volume of ACS at different carbonization temperature

Pore evolution of ACS was obviously influenced by carbonization temperature. The carbon obtained at 470°C, ACS1 exhibited the lowest  $S_{BET}$ , microporous and mesoporous. However, the values increased for the carbon produced at higher temperature (490-530°C). Efficiency of an adsorbent is indicated by its surface area or active sites. The mesoporous and microporous volumes permit sufficient transportation of pollutants in aqueous condition. Thus, these characteristics are significantly important for wastewater treatment application. Based on the data, it is concluded that 10% v/v sulfuric-acid-impregnated HDR prepared at carbonization temperature of 510°C is more suitable to produce well-developed surface morphology and porosity compared to other studied temperatures. Figure 1 illustrates the trend of pore distribution of ACS at each carbonization temperature. It changes significantly from 470-530°C. This change consequently increased the formation of organic and volatile compound matters compared to the precursor. This investigation has clearly demonstrated that increasing carbonization temperature, pore development and new pore formation on the precursor's surface can be elevated. Apart from surface area, the information of pore development is undoubtedly essential in metal removal application due to its important role in both kinetic and equilibrium properties of porous material (Abbaszadeh *et al.*, 2016). Thus, the study of structural heterogeneity of porous materials particularly used in adsorption could be the most critical aspect in adsorbent characterization.

**Observation on surface morphology of acs before and after adsorption:** Surface morphology pattern and surface characteristics of the adsorbent can be observed using FESEM. It is a major analytical observation employed in examining pertinent changes and development of porosity on the adsorbent surface. The FESEM micrograph of unloaded adsorbent surface is shown in Fig. 2a and Zn-loaded adsorbent surface is portrayed in Fig. 2b. The surface of unloaded pore was rough, uneven and

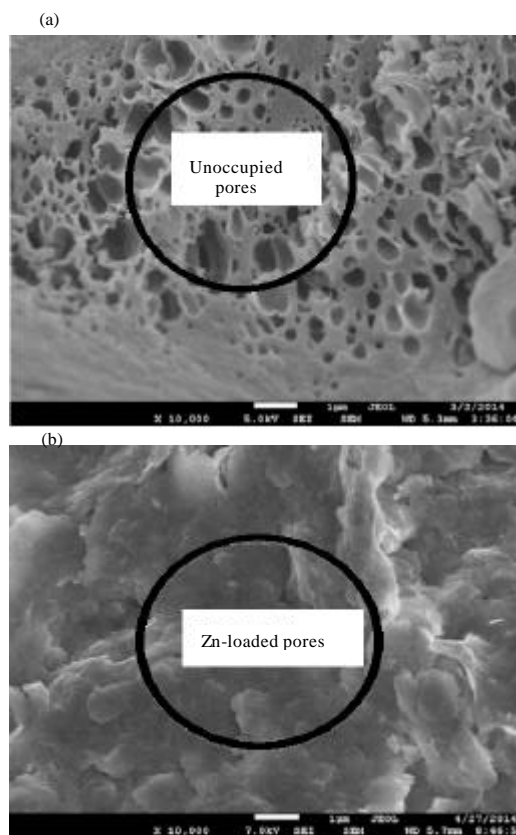


Fig. 2a): Surface morphology of ACS before metal adsorption and b) Surface morphology of ACS after metal adsorption

heterogeneous. The rough surface will increase the surface area's availability for metal adsorption. However, the adsorbent surface image as shown Fig. 2b was observed shiny and loaded. The possible reason for this observation can be attributed to the bounded pores caused by the presence of zinc that has occupied the vacant pores. The reaction that occurred during adsorption process can be explained as precipitation or complexation of metal ions onto the adsorbent surface (Kaur *et al.*, 2013).

### CONCLUSION

Based on the result of this study, it has been proven that a non-expensive fruit waste; honeydew rind is a promising precursor material for the production of AC used in adsorption. A high percentage yield 79.23% and ash content 6.20% produced by ACS shows that honeydew rind can be categorized as a good quality adsorbent. The optimization of carbonization temperature played a crucial role in determining the most sufficient pore development and textural properties of honeydew

rind activated carbon. The morphology studies indicated that the AC surface has clear pores with honeycomb-like structure. The FESEM micrograph showed that Zn has occupied most of the pores on the surface due to metal-surface interaction as a result of metal adsorption. This study has demonstrated that honeydew rind AC produced from 10% sulfuric acid impregnation process and carbonized at 510°C functions as a solid adsorbent with an optimal texture. Thus, there is a strong potential for honeydew rind to be one of the most promising options for the development of precursors for activated carbon production.

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