

## Title: Preparation of Activated Carbon by Chemical Activation and Its *In Vitro* Adsorption Efficacy Tests for Paraquat

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### Abstract

The effects of different activation temperature on the pore size and surface morphology of activated carbon produced by H<sub>3</sub>PO<sub>4</sub> (30%) chemical activation were studied in this paper. Well developed pore size and highest surface area observed on activated carbon at 600<sup>0</sup>C were determined by Scanning Electron Microscope and Brunauer, Emmett and Teller (BET) method. The highest BET surface area was 1491 m<sup>2</sup>g<sup>-1</sup> observed with sample HEAC-2 (highly efficient activated carbon -2). The adsorption efficacy of activated carbon for paraquat was also investigated and compared with commercially available activated carbon. The study shows that the amount of paraquat adsorbed was 3.62 mgL<sup>-1</sup> for produced activated carbon and 3.42mg L<sup>-1</sup> for commercially available activated carbon. The adsorbing capacity of activated carbon (produced and commercially available) for paraquat increased when it was suspended in NaCl (0.9%) solution. In the presence of NaCl solution, the amount of paraquat adsorbed increased from 3.62mg L<sup>-1</sup> to 4.68mg L<sup>-1</sup> for produced activated carbon and 3.42 mg L<sup>-1</sup> to 4.18mg L<sup>-1</sup> for commercially available activated carbon

**Keywords:** Activated carbon, chemical activation, adsorption capacity, paraquat, NaCl (0.9%) solution

### 1. Introduction

The Ministry of Health, Malaysia, reported that from 1995 to 2000 there was an average of about 750 cases per year of pesticide and chemical poisoning<sup>1,2</sup>. The commonest poisons used was a weed killer containing paraquat compound and insecticides containing organophosphates. In 1997, the Ministry of Health Malaysia introduced a surveillance programme for occupational and work related diseases including poisonings for cases seen in government health facilities. The programme notified 95 cases of poisoning by chemicals and pesticides and reported the common causes of occupational poisonings were paraquat (19%), organophosphates (16%), agro-chemicals excluding pesticides (15%) and gases

(10%). The mortality from paraquat poisoning is higher than that from any other type of poisoning associated with agricultural chemicals<sup>3</sup>. Paraquat is a potent, non-selective herbicide and potentially lethal when ingested (accidentally or intentionally). Paraquat poisoning mainly affects the pulmonary system. The gastrointestinal tract prevention of paraquat absorption is critical due to the limited means to significantly increase its elimination from the body<sup>4</sup>. The fundamental treatment of paraquat poisoning is by means of gastrointestinal lavage and the selective excretion of toxic substances out of body following the administration of adsorbents. Clay minerals<sup>5</sup>, cation exchange resin<sup>6-8</sup>, fuller's earth and bentonite are used as adsorbents for the primary treatment of paraquat poisoning. Activated carbon, an adsorbent, is readily available and effective for the primary treatment of paraquat poisoning. Moreover, among the adsorbents, activated carbon has been evaluated as a reliable, safe and inexpensive antidote and is recommended for use in the treatment of acute poisoning<sup>9-11</sup>. *In vitro* studies have shown that paraquat adsorbs onto activated carbon more rapidly and effectively in normal saline (0.9% sodium chloride solution) than in distilled water<sup>12,13</sup>. Normal saline is the most suitable solvent for paraquat removal by activated carbon.

Activated carbon is usually derived from charcoal. It is made from wood, coal, peat, coconut shell, palm shell, etc. those are carbon rich materials. Activated carbon can adsorb poisonous substances before they can cause harm. Activated carbon (charcoal) works by adsorption which is an electrical phenomenon that attracts toxins to the surface of the fine carbon particles.

## 2. Materials and Methods

Paraquat dichloride 13% w/w class B was purchased from Kenso Corporation Sdn. Bhd., Malaysia and commercial activated carbon was obtained from Fisher Scientific Co., Malaysia. Activated carbon from palm shell was prepared through chemical activation using phosphoric acid ( $H_3PO_4$ ) as activating agent.

### 2.1.1 Preparation of activated carbon

Palm shell, a wastage from the oil palm industry, was used as the main raw material for the preparation of activated carbon because of its high carbon content and it is a cheap, solid waste. Palm shells were collected from the Felda Neram Mill, Neram, Terengganu, Malaysia. The dried palm shells were crushed and sieved. Materials of grain size 0.5 to 1.5 mm were selected for use. To treat the raw material, about 100g of crushed palm shell with particle size of 0.5-1.5 mm was taken and soaked with 5% sulphuric acid ( $H_2SO_4$ ) solution to loosen the cellulose and trace components. This step is very important to produce good quality activated carbon. It is known that some components of the untreated raw material can react with the surface of the raw material during carbonization and thus affecting the pore distribution in the activated carbon. The raw palm shells were sank into the 5%  $H_2SO_4$  solution for 24 hours. The dust particles floated on the surface of the acid solution and were decanted. Then the samples were washed with distilled water several times until acid was removed and then dried.

### Chemical activation

Approximately 50g of shell particles were taken. The particles were added into 100ml of freshly prepared 30% phosphoric acid ( $H_3PO_4$ ) solution and kept in the furnace (F47920-33/120C/2L/ Barnstead) at controlled temperatures for activation. The temperatures were set at 550°C, 600°C, and 650°C for 2 hours. The experiments were carried out from room temperature to the desired activation temperature. After cooling to ambient temperature, the sample was washed with distilled water to remove acid several times, until pH 5-7. Acidic pH can affect the surface area of activated carbon, which may decrease the pore volume. The surface of activated carbon can have some unwanted elements that interfere with the pore of activated carbon with acidic pH. The pH was determined by litmus paper test.

### Characterization

For characterization of activated carbon, Scanning Electron Microscope (SEM) and Brunauer, Emmett and Teller (BET) method were used to analyse the pore structures and surface area of the produced activated carbon. FT-IR was used to identify the functional groups. Before conducting scanning electron microscopy (SEM), the activated carbon produced which are not conductors need to be coated with a conducting medium (gold coating). The standard BET equation was applied within the relative pressure range from 0.05 to 0.3 to determine the BET surface area<sup>14-16</sup>.

#### 2.1.2 Determination of the *in vitro* adsorption efficacy of activated carbon (produced and commercial) for paraquat

To determine the adsorption efficacy of activated carbon, the adsorption isotherm of paraquat onto activated carbon need to be determined. Adsorption isotherm was measured as follows: Around 0.5g of activated carbon was shaken with 50ml of paraquat solution with different concentration for 24 hours at 25<sup>o</sup>C. After filtration, the paraquat concentration in the filtrate was measured at 600nm by a colorimetric method using UV light XT 2nm/SECOMAM. The amount of paraquat adsorbed was calculated from the difference between the initial total amount and the amount unadsorbed.

### 3. Results and Discussion

Scanning Electron Microscope (SEM) was used to study the surface morphology and pore size of the activated carbon. Figure 1(a, b, c) shows the surface of activated carbon treated with 30% phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), at retention time of 2 hours and pyrolysis temperatures of 550<sup>o</sup>C, 600<sup>o</sup>C and 650<sup>o</sup>C, respectively. Upon comparison Figure 1(b) shows the highest development of pore.

Table 1 shows the surface area, average pore diameter and total pore volume of produced activated carbon with different temperatures. Table 1 shows the BET surface area of activated carbon increased with increasing temperatures from 550<sup>o</sup>C to 600<sup>o</sup>C, however at 650<sup>o</sup>C the surface area decreased. In this study 600<sup>o</sup>C is the optimum temperature. Usually, the larger the specific surface area of the adsorbent, the greater is the adsorption<sup>17</sup>. In this study, the activated carbon has shown the optimum surface area 1491 m<sup>2</sup>g<sup>-1</sup>. The total pore volume of activated carbon increases with increasing number of pores thus controlling the pore diameter to less than 25Å. As a result, the adsorbing capacity of activated carbon automatically increases. From this study, the maximum surface area and total pore volume was obtained by HEAC-2 at 600<sup>o</sup>C. Under this condition, the lowest pore diameter was also obtained with HEAC-2, which is correlated with the surface area and pore volume.

The adsorption isotherms of paraquat in different solvents at 25<sup>o</sup>C both onto the commercial activated carbon and the produced activated carbon are shown in Figure 2(a, b). For both activated carbons, the amount of paraquat adsorbed was in the following order: In NaCl solution (0.9%) > distilled water. Table 2 shows that the amount of paraquat adsorbed is more in NaCl solution (0.9%) than in distilled water. Moreover, in both solvents, the produced activated carbon adsorbed larger amount of paraquat compared to the commercial activated carbon. In solution, the dissociation of paraquat was inhibited by sodium chloride, so the phenomenon of salting out occurred in solution and consequently paraquat was adsorbed more abundantly onto the activated carbon. A comparison of properties of activated carbon produced in this study and the activated carbon produced by other researchers are shown in Table 3.

It can be seen from Table 3, the surface area of activated carbon produced with H<sub>3</sub>PO<sub>4</sub> is higher than that reported by Devarly Prahast et. al who also used H<sub>3</sub>PO<sub>4</sub> as an activating agent to produce the activated carbon. Alwar et. al also shows a high surface area but he used ZnCl<sub>2</sub> as activating agent. It is an expensive method. However phosphoric acid is more preferred than zinc chloride due to the toxicological effects. It has also been reported that carbon activated with zinc chloride is not advisable for use in pharmaceutical and food industries to avoid contamination of the product.<sup>18</sup>

#### 4. Conclusion

**The possibility to prepare an activated carbon with high BET surface area from palm shell has been elucidated.** It was shown by the pyrolysis result of carbon preparation and the application of *in vitro* activated carbon as an adsorbent of toxin. **As a raw material, palm shells are suitable from the point of view of cost and environmental pollution control.** The quality of activated carbon mainly depends on the preparation condition. Here, **the optimum condition for preparing microporous activated carbon with high pore surface area and pore volume, were through pretreatment of the palm shells with 5% H<sub>2</sub>SO<sub>4</sub> solution for 24 hours before activation.** The high adsorbing capacity of activated carbon, both commercial and produced was evaluated by the *in vitro* test of carbon as an adsorbent of toxin (paraquat) in this study. So, it was concluded that, both commercial and produced activated carbon were effective to promote adsorption removal of paraquat and NaCl (0.9%) solution is the most effective solvent. **Paraquat was found to be adsorbed more by the produced activated carbon than the commercial activated carbon.**

#### Author Contributions

All authors contributed equally to this work

#### Conflicts of Interest

The authors declare no conflict of interest.

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**Table**

Table 1: Table 1 shows the surface area, average pore diameter and total pore volume of produced activated carbon with different temperatures.

Sample ID	Temperature (°C)	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (M <sup>3</sup> g <sup>-1</sup> )	Average pore diameter (Å)
HEAC-1	550	1153	0.711	25.3792
HEAC-2	600	1491	0.842	21.2575
HEAC-3	650	968	0.677	24.2643

Table 2 Amount of adsorbed paraquat (PQ) onto activated carbon

Name of carbon	Types of solvent	Amount adsorb (mg g <sup>-1</sup> )		
		At 10 mgL <sup>-1</sup>	At 25 mgL <sup>-1</sup>	At 50 mgL <sup>-1</sup>
Commercial Activated carbon	H <sub>2</sub> O	0.02	1.32	3.42
	NaCl (0.9%) solution	0.92	1.72	4.18
HEAC-2	H <sub>2</sub> O	0.62	1.72	3.62
	NaCl (0.9%) solution	0.92	1.92	4.68

Table 3 Comparison of surface area property between activated carbon produced in this study and activated carbon produced by other researchers

Author	Raw material	Activating agent	Temperature	Surface area	Pore volume
Mohosina b shahjahan et. al	Palm shell	H <sub>3</sub> PO <sub>4</sub>	600°C	1491m <sup>2</sup> /g	0.84
Allwar et. al	Palm shell	ZnCl <sub>2</sub>	600°C	1297m <sup>2</sup> /g	0.71
Devarly Prahas et.al	Jackfruit peel	H <sub>3</sub> PO <sub>4</sub>	550°C	1260m <sup>2</sup> /g	0.73
Hondu et. al	Coconut shell	NA	NA	849	NA
Miyoshi et. al	Petroleum pitch	NA	NA	1081	NA

NA: Not available

**Figures**

Figure 1: Figure 1 (a, b, c): SEM micrograph of produced activated carbon at 550<sup>0</sup>C, 600<sup>0</sup>C and 650<sup>0</sup>C, respectively

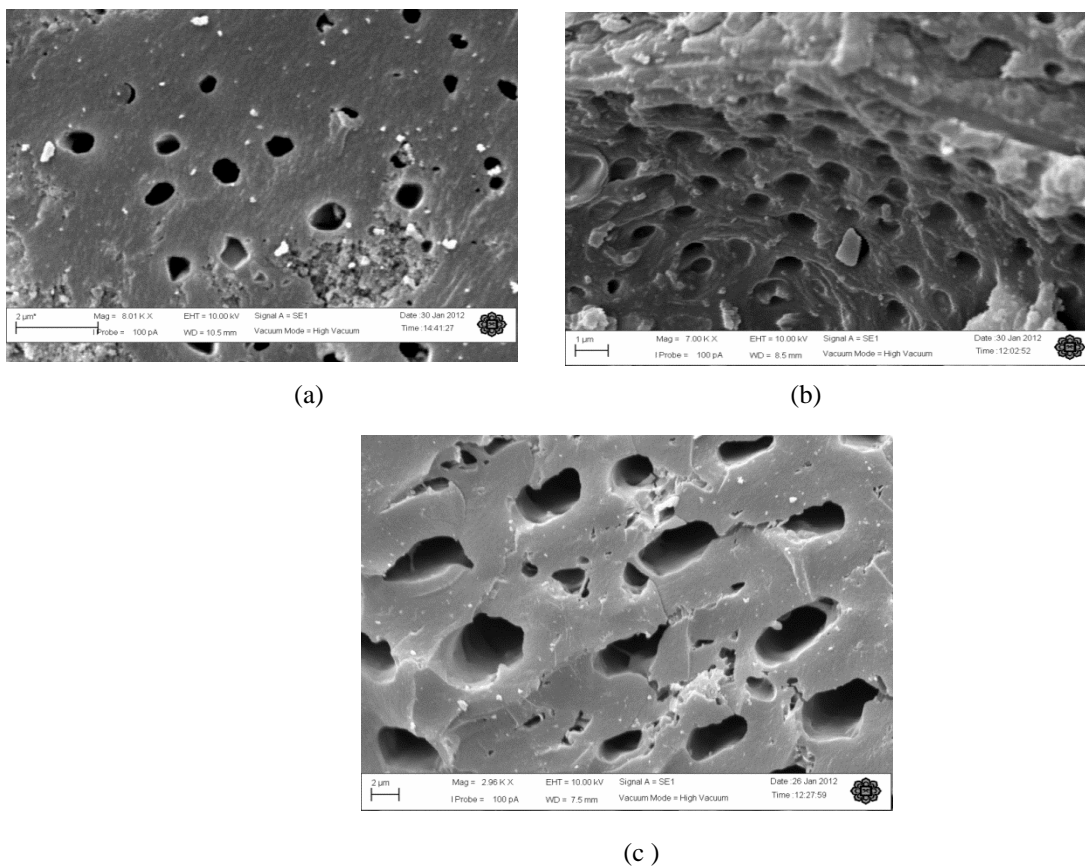


Figure 2: Figure 2 (a, b): Adsorption isotherm of paraquat at 25<sup>0</sup>C in NaCl (0.9%) solution and distilled water onto commercial activated carbon and produced activated carbon (HEAC-2), respectively

