

## Rubber Seed Shell Based Activated Carbon by Physical Activation for Phenol Removal

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This work was aimed at evaluating the characteristics of activated carbons derived from rubber seed shell through physical activation using CO<sub>2</sub> for phenol removal. Two activated carbons were obtained at different retention times of 30 min (AC1) and 90 min (AC2) at fixed temperature of 900 °C. Activated carbons were characterized for specific surface area, surface functional groups and morphology. The values of specific surface area were recorded as 852 m<sup>2</sup>/g and 606 m<sup>2</sup>/g for AC2 and AC1. AC2 shows a higher phenol removal capacity of 302 mg/g than AC1 (112 mg/g) that is directly related to the specific surface area of activated carbons. The equilibrium data fitted well to the Langmuir isotherm, suggesting monolayer coverage of phenol molecules on the homogeneous surface of activated carbons. The kinetics data obeyed pseudo-first-order model, indicating the external diffusion as the rate-limiting step in adsorption.

### 1. Introduction

The demand for phenol-related products has resulted in the manufacturing of phenol in large scale. One of the major products is phenolic resin that is produced through polymerization reaction of formaldehyde with phenol. The use of large amount of phenol in processing may eventually result in the chemical to find its ways to the environment (Dabrowski et al., 2005). Phenol is toxic and has high bio-accumulation rate due to its lipophilic character (Gad and Saad, 2008). The presence of phenol in water bodies, consequently renders serious pollution that may as well affects the aquatic creatures (Gad and Saad, 2008), food chain and public health (Lin et al., 2011). Hence, the effluent laden with phenol should be treated prior to its release to the environment. Malaysia is the leading country in the world that produces nearly 46 % of the world natural rubber (MREPC, 2016). As a result, large amount of rubber tree seed is produced over the season. The crop residue has trivial commercial value and is commonly left on the field to decompose or burnt together with dry leaves, which consequently, could lead to other environmental issues. Therefore, sustainable solutions are sought to utilize the material so as to minimize its related consequences to the environment. A promising approach is to convert the crop residue into activated carbon for environmental protection, especially in water and wastewater treatment.

Activated carbon has long been recognized as adsorbent that can remove various contaminants such as phenol (Kilic et al., 2011), lead (II) (Zaini et al., 2009), copper (II) (Zaini et al., 2010), reactive orange (Lin-Zhi and Zaini, 2017a), congo red (Shu-Hui and Zaini, 2017a), etc. from water. The process in which the solute molecules are attracted to the surface of activated carbon for the removal to take place is generally known as adsorption (Zaini et al., 2016a). Generally, activated carbon can be produced from carbonaceous materials such as palm kernel shell (Garcia et al., 2018), empty fruit bunch (Zaini and Shaid, 2016), textile sludge (Shu-Hui and Zaini, 2017b), castor seed (Lin-Zhi and Zaini, 2017b), etc. As such, rubber seed shell is also seen as a promising feedstock candidate that is cheap and abundantly available in the country to manufacture activated carbon. To date, there is still limited literature available to unlock the potential of rubber seed shell as activated carbon, hence worth to be further explored so as to enrich the body of present knowledge.

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This work was aimed to evaluate the characteristics of rubber seed shell-based activated carbons by physical activation using CO<sub>2</sub> for phenol removal. Physical activation was used owing to the fact that it is commonly used in the mass production of commercial activated carbon, that is in the absence of hazardous chemicals (Ming-Twang et al., 2015). The resultant activated carbons were characterized for textural and surface chemistry, and batch adsorption tests were performed for phenol removal at different phenol concentrations and contact times. The adsorption data were analyzed using isotherm and kinetics models, and the mechanisms governing the phenol adsorption were discussed.

## 2. Materials and methods

### 2.1 Materials

Rubber seed was collected at a local rubber cultivation field in Johor state of Malaysia. Carbon dioxide gas was supplied by Mega Mount Industrial Gases. Phenol (purity of > 99 %) was obtained from Sigma-Aldrich. The chemicals are of analytical grade and were used as received without further purification.

### 2.2 Physical activation

The inner seed was removed from the rubber seed shell. The empty shell was washed with water to remove dirt, followed by oven-dried at 105 °C for 24 h. Then, the shell was ground to a size of about 2 mm. The physical activation using carbon dioxide was performed in a tubular furnace at 900 °C for 30 min and 90 min. The flow rate of carbon dioxide was fixed at 100 mL/min. The resultant activated carbons were designated as AC1 and AC2, and were used for characterization and adsorption studies without further treatment.

### 2.3 Characterization of materials

The rubber seed shell was characterized for thermal decomposition profile using a Perkin-Elmer thermogravimetric analyzer (TGA 7) under a nitrogen flow of 10 mL/min and a heating rate of 10 °C/min. The specific surface area of activated carbons was obtained using a Micromeritics surface area analyzer (ASAP 2020) at a liquid nitrogen temperature of 77 K. The surface chemistry of rubber seed shell and its derived activated carbons was qualitatively determined using a Perkin Elmer FTIR spectrometer (Spectrum One). The surface morphology of activated carbons was characterized using a Hitachi scanning electron microscope (TM3000). The pH rubber seed shell-based activated carbons were determined in a 100 mL water bearing 10 g of the sample. The mixture was initially heated for 15 min and allowed to cool at room temperature prior to pH measurement using a portable pH meter (HI 9813-5, Hanna Instruments).

### 2.4 Adsorption studies

The adsorption properties of activated carbons were evaluated at different concentrations of phenol solution and contact times using a bottle-point technique. 50 mg of activated carbon was added into 50 mL of phenol solution of varying concentrations ranging between 2 mg/L to 1,000 mg/L. The mixture was allowed to equilibrate for 72 h. After that, the residual concentrations were measured using a Drawell UV-Vis spectrophotometer (DU-8200) at a wavelength of 269 nm. The calibration standard was determined as, a.u. = 0.013 × concentration, for 0 mg/L < phenol concentration < 20 mg/L with R<sup>2</sup> = 0.9989. The adsorption capacity and the removal performance were calculated from mass balance assumptions.

The rate of adsorption was performed at concentrations of 5 mg/L, 10 mg/L and 20 mg/L. Fifty milligrams of activated carbon was brought into intimate contact with 50 mL of phenol solution, and the concentration of phenol was measured at different time intervals until the constant reading was attained.

## 3. Results and discussion

### 3.1 Characteristics of materials

Figure 1 shows the thermogravimetric analysis of rubber seed shell. The profile represents the weight loss against temperature to assess the suitable temperature for activation. The first peak of derivative weight loss between 50 °C to 150 °C corresponds to the removal of physisorbed moisture. Active pyrolysis was observed between 355 °C and 385 °C, yields a peak centred at 340 °C. It indicates the decomposition of holocellulose and liberation of volatiles from the natural material. At this point, the material becomes rich in carbon content with rudimentary pores developed within the matrix. At 900 °C, the final weight loss is 17 %. From the viewpoint of physical activation, temperature of 900 °C would be needed for the oxidizing gas (CO<sub>2</sub>) to develop the pore pathways so as to increase the surface area of activated carbon (Zaini et al., 2010).

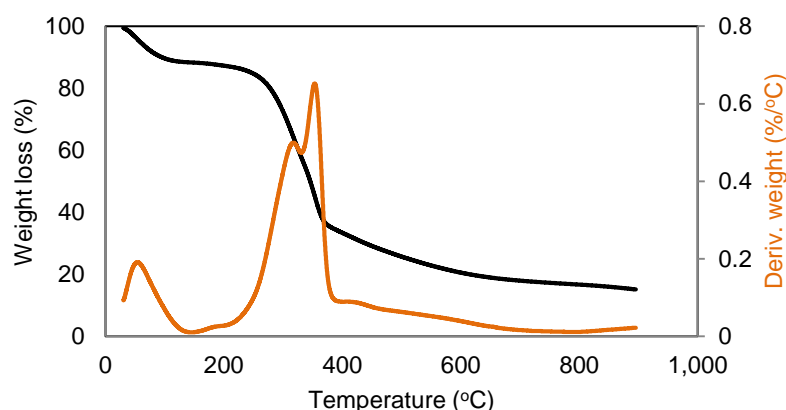


Figure 1: Thermal degradation of rubber seed shell

Table 1 shows the properties of activated carbon. Activation for 90 min produces activated carbon with a surface area of 852 m<sup>2</sup>/g, higher than the one activated for 30 min. It is suggested that the longer the activation time, the more porous channels can be developed within the material matrix. Both activated carbons are microporous in nature with average pore width of 1.5 nm which is nearly 2.7 times greater than the size of phenol molecule (0.56 nm). The yield of both activated carbons is about 17 % that is in accordance with the thermal gravimetric profile in Figure 1. Extending the activation time also results in a slight decrease of microporous texture due to pore collapse and enlargement to become mesopores.

Table 1: Characteristics of activated carbons

Sample	Activation time	Yield (%)	pH	BET surface area (m <sup>2</sup> /g)	Microporosity	Average pore width (nm)
AC1	30 min	16.5	6.2	606	0.934	1.51
AC2	90 min	17.4	6.0	852	0.911	1.53

Figure 2 displays the FTIR spectra of rubber seed shell and its derived activated carbons. All materials exhibit similar pattern of spectrum, but with decreasing intensity after activation at 900 °C. Although some of the temperature-sensitive functional groups are liberated, the CO<sub>2</sub> activation could in some way preserve the functional groups in the rubber seed shell from completely diminished, for which they may be useful in the activated carbon adsorption of water pollutants. The broad and medium intensity band ranging from 3600 cm<sup>-1</sup> to 3,000 cm<sup>-1</sup> corresponds to O–H, particularly moisture. The carbon backbone structure (alkenes) is associated with the peak at 2,920 cm<sup>-1</sup> (Zaini et al., 2016b). The peak at 1,420 cm<sup>-1</sup> is attributable to carboxylic acids, while the peak at 1,630 cm<sup>-1</sup> signifies the presence of C=O and C=C.

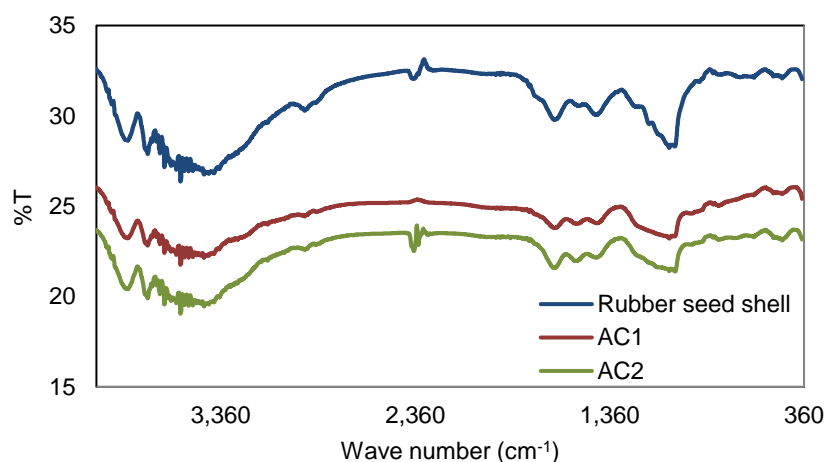


Figure 2: FTIR spectra of rubber seed shell and activated carbon derivatives

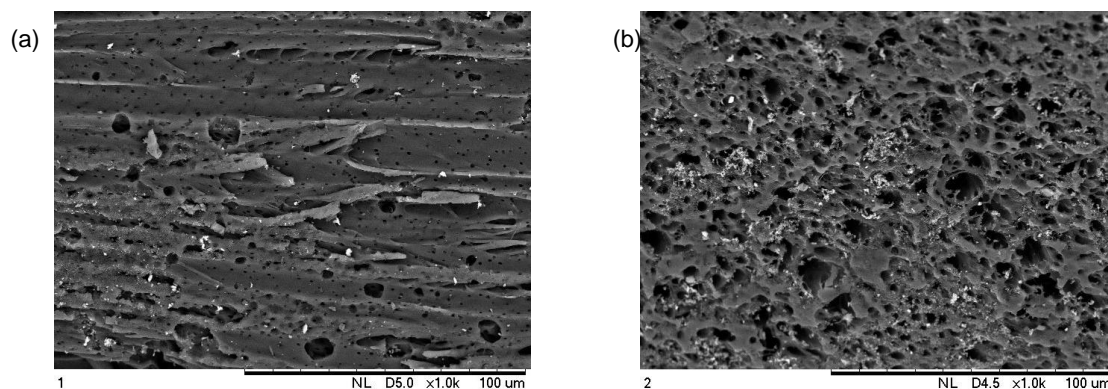


Figure 3: SEM images of activated carbons, (a) AC1 and (b) AC2

Figure 3 illustrates the SEM images of AC1 and AC2. Cracks and crevices can be seen on the surface of AC1, with some crater- and plate-like pores. AC2 demonstrates a well-developed porous surface with honeycomb-like pores. The images self-explained the values of surface area of activated carbons as presented in Table 1.

### 3.2 Phenol adsorption

Figure 4 shows the removal of phenol by AC1 and AC2. In general, the adsorption capacity increases with increasing phenol concentration to a point where the activated carbon surface is saturated for a maximum adsorption capacity. High concentration normally provides driving force for adsorption to counterbalance the solid mass transfer resistance. AC2 exhibits a higher phenol adsorption compared to AC1 for all concentrations studied. The maximum adsorption capacities were recorded as 262 mg/g and 108 mg/g for AC2 and AC1. The highest values of removal percentage are 79 % and 41 % which is at the same concentration of 200 mg/L. The removal percentage declines at concentration greater than 200 mg/L because of higher residual (equilibrium) concentration upon adsorption due to decreasing available active sites to accommodate phenol molecules although the saturation point has not been achieved.

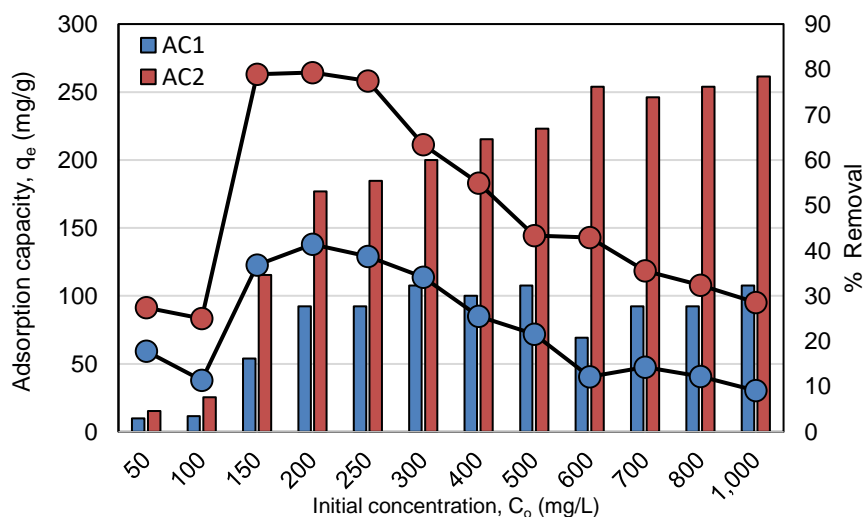


Figure 4: Removal of phenol by rubber seed shell-based activated carbons, adsorption capacity (bar) and removal percentage (line)

Figure 5 shows the equilibrium curves of AC1 and AC2 for phenol removal. The experimental data are well fitted with the Langmuir model with empirical equations of  $q_e = 1.19C_e / (1 + 0.011 C_e)$ ,  $R^2 = 0.805$  and  $q_e = 3.35C_e / (1 + 0.011C_e)$ ,  $R^2 = 0.823$  for AC1 and AC2. The predicted values of maximum phenol adsorption capacities by Langmuir model are 112 mg/g and 302 mg/g for AC1 and AC2. The underlying theory of Langmuir isotherm suggests that the removal of phenol is favourable through a localized monolayer adsorption onto a homogeneous adsorbent surface.

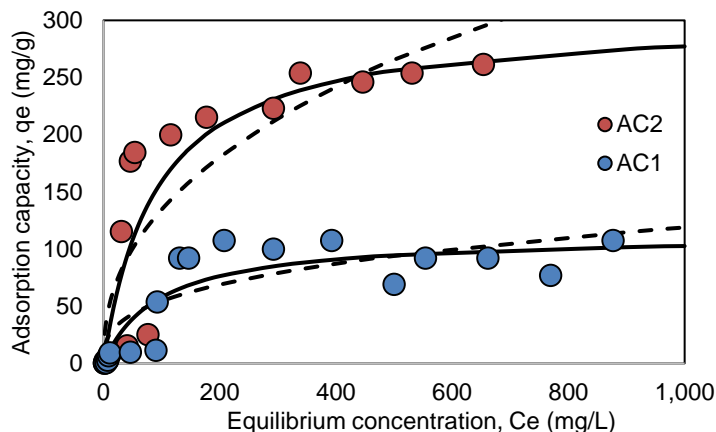


Figure 5: Adsorption equilibria of phenol on AC1 and AC2, model lines: solid (Langmuir model) and dashed (Freundlich model)

Figure 6 shows the curves of rate of phenol adsorption onto AC2. Generally, the phenol removal increases with increasing contact time to a point known as equilibrium (ca. 50 h), at which the rate of adsorption is equal to the rate of desorption. As such, the rate of adsorption (slope) increased with concentration because of the abundance of phenol molecules in the bulk solution at high concentration that enhances the transport (kinetics) towards the active sites. However, the rate of adsorption tends to slow down and subsides to zero as the contact time increases due to insufficient driving force and the repulsion among the phenol molecules on the active sites and in the bulk solution at equilibrium. The rate of adsorption could be interpreted by the pseudo-first-order kinetics model, which explains the external diffusion as the significant step in adsorption (Zaini et al., 2016b). The corresponding empirical equations are,  $q_t = 7.44 (1 - e^{-0.00046t})$ ,  $R^2 = 0.953$ ,  $q_t = 13.9 (1 - e^{-0.00048t})$ ,  $R^2 = 0.982$ ,  $q_t = 23.1 (1 - e^{-0.00050t})$ ,  $R^2 = 0.991$  for phenol concentrations of 5 mg/L, 10 mg/L and 20 mg/L.

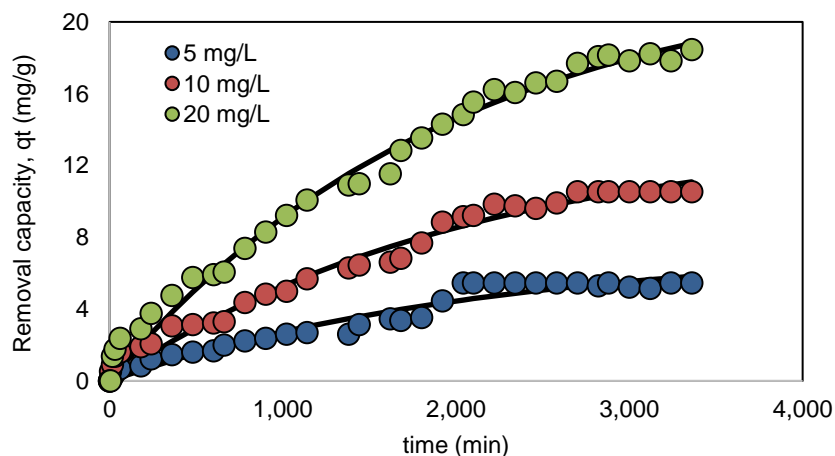


Figure 6: Adsorption kinetics of phenol on AC2, model lines (pseudo-first-order kinetics model)

Rubber seed shell-based activated carbons showed a promising phenol adsorption from water. The maximum removal capacity of 262 mg/g by AC2 is sufficiently higher than that of hydrophobic silica aerogel (surface area = 863 m<sup>2</sup>/g; 142 mg/g) (Qin et al., 2013), eggshell-based activated carbon (180 mg/g) (Giraldo and Moreno-Pirajan, 2014) and activated carbon cloth (surface area = 1,000 m<sup>2</sup>/g; 29.2 mg/g) (Arcibar-Orozco et al., 2015). Hence, converting rubber seed shell into activated carbon is a solution towards sustainable environment.

#### 4. Conclusion

Activated carbons were prepared from rubber seed shell by CO<sub>2</sub> activation at 900 °C. Activation for 90 min yields activated carbon with a higher surface area of 852 m<sup>2</sup>/g and maximum phenol adsorption capacity of 262 mg/g.

Phenol adsorption onto activated carbon at equilibrium could be described as monolayer coverage on the homogeneous surface active sites, while the rate-limiting step could be external diffusion. Rubber seed shell is a promising precursor of activated carbon for phenol-contaminated water, and possibly for other types of wastewater.

### Acknowledgments

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